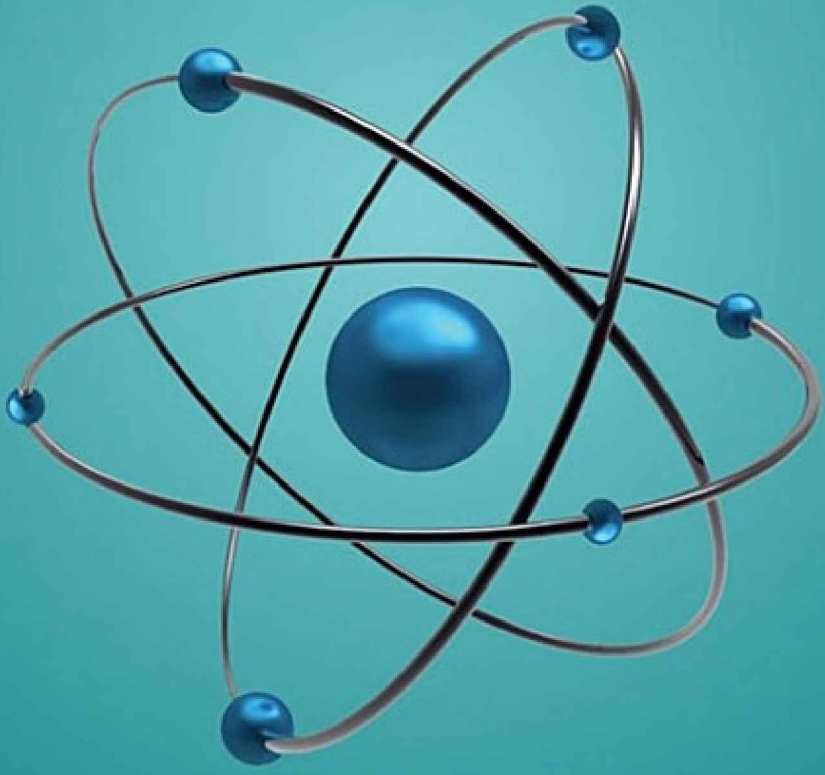
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R L Madan

Mc Graw Hill Education

Physical Chemistry

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Government Post Graduate College
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Dedicated to the Memory of

My Loving Mother
Late Mrs janki Devi
Who made me what I am and to whom I owe a lot

Foreword

Chemistry has made a significant impact on society and is intimately linked to the well-being of humankind. The rate of advancement of basic sciences is so high that academicians look forward for strategies to cope with those advancements. Physical chemistry provides a decent bridge between mathematical sciences and experimental sciences. The present textbook is a sincere effort in this direction. This book provides a unified approach to the study of chemistry for undergraduate (Pass and Honours) students. The text is well illustrated with examples from surrounding environments which will help students grasp the concepts easily.

There are several highlights of this book. The chapter dealing with mathematical concepts and computers will provide a powerful tool to students in understanding the basic concepts and solve numerical problems in shorter time. Partial differentiation and integration needs special mention in this regard. Incorporation of computers and introducing analog and digital devices will provide a good basic platform to understanding physical chemistry Biographical sketches of some scientists relevant to particular topics will surely enthuse students. Liquid state, colloidal state chemical kinetics and thermodynamics have been written especially in a systematic, lucid and comprehensible style. Learning objectives have been given exhaustively in each chapter of the book. Sufficient examples have been given at the end of each chapter, along with summary for quick revision, key relations, question bank including multiple-choice questions and general questions so that students can evaluate their learning potential themselves.

The level of text material in each chapter is sufficient to escalate this book to international standard. I am sure this book will procure the author and publishers a good name in the market. The hard work done by the author is commendable and deserves to be congratulated. I wish huge success to this book.

N K Sandle

Prof. Department of Chemistry, Indian Institute of Technology (IIT), Delhi

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Preface

I feel immensely pleased to present *Physical Chemistry* to the teaching fraternity and the students. Physical chemistry is the study of macroscopic, atomic, sub-atomic and particulate phenomena in chemical systems. It applies the principles, practices and concepts of motion, energy, force, time, thermodynamics, quantum chemistry, statistical mechanics and equilibrium.

Physical chemistry, a branch of chemistry, is a core subject at undergraduate science and technology course curricula of different universities and autonomous institutes in the country. In the study of this subject for the above courses, a number of books by foreign authors are widely used as reference books. The teaching fraternity in India was feeling the need of a textbook written in a simple language and an interesting manner which could be grasped even by an average student. The present book has been written in response to the aspirations of the teaching community and the students.

Target Audience

This book covers the syllabus of Physical Chemistry for the students of BSc I, II and III (Pass and Honours or Major and Minor) of different Indian Universities. Students of other undergraduate professional courses having physical chemistry as a major subject may also use this book. The only prerequisite is that the students must possess a basic knowledge of chemistry of 11^{th} and 12^{th} standard to utilize this book. A basic knowledge of mathematics is also expected.

Salient Features

- Covers all important topics—Gaseous State, Liquid State, Solid State, Colloidal State, Chemical Kinetics, Catalysis, Thermodynamics, Chemical Equilibrium, Phase Equilibria, Distribution Law, Electrochemistry, Atomic Structure and Wave Mechanics, Chemical Bonding and Wave Mechanics, Spectroscopy, Photochemistry, Physical Properties and Molecular Structure, Liquid Solutions, Dilute Solutions, Adsorption, Polymers and Nuclear Chemistry
- Latest IUPAC notations and SI units used
- Principles and laws explained in the simplest possible way

- Analogies from daily life used to clarify difficult points
- Concept explanation through more than 1200 step-wise solved problems
- Numerical problems for practice
- Applications and case studies like applications of equilibrium constant, cases to understand structure of liquid crystals and how they flow
- More than 500 line, phase, and real-time illustrations

- Prologue on mathematical concepts
- Key words and Key relations provided in the summary
- Concept boxes to highlight important facts that are asked in examinations
- Special features such as interesting facts, common pitfalls, key terms interspersed
- Subject index provided for quick location of terms, laws, theories, etc.
- Over 450 solved examples covering all types of problems in different chapters
- More than 800 review questions
- Over 400 objective-type questions

About the Book

The style of the book is such that it encourages students to understand physical chemistry rather than learn it by rote memorization. Simple and comprehensible language has been used to explain the principles involved in different topics. The opening chapter, Basic Concepts, acquaints the students with different systems and units of physical quantities. As recommended by IUPAC and CGPM, SI system of measurement and units of physical quantities have been followed by and large, although CGS system has been retained in some problems. This is because questions in some university papers still appear in CGS units. IUPAC has recommended changes in the names of certain terms, for example, *conductivity* in place of *specific conductance*, and *Gibbs energy* in place of *Gibbs free energy*. This has been highlighted in the chapters on electrochemistry and thermodynamics. Readers can refer to the Table of Content to know more about the topics covered in this book.

Biographical sketches of scientists are given to inspire and stimulate the minds of students towards the subject. Analogies from daily life have been chosen to explain intricate points. Historical developments leading to the establishment of different theories and laws have found due place in the book. How the different principles of physical chemistry come to the rescue of people in difficult situations has been explained with the help of interesting pictures. Although this part is non-evaluative, it makes the subject exciting and easily understandable. The text is supported by a large number of solved examples and problems for practice.

Learning Objectives given at the beginning of each chapter give the detailed contents of the chapter. *Summary* provided at the end of a chapter lists the important information in brief for last-minute revision before the examination. Also given in the summary are Key Points and Key Relations, which are required in solving numerical problems. *Exercises* consist of two parts, objective evaluation and subjective evaluation. As per the latest recommendation on the setting of question papers, multiple-choice questions, fill-in-the-blanks questions, short-answer questions and general (long-

answer) questions have been provided to prepare the students to face examinations boldly.

Online Learning Center

The text is accompanied by an Online Learning Center, which can be accessed at https://www.mhhe.com/madan/pc1. This includes objective-type questions, concept boxes, and answers to unsolved problems.

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Basic Concepts

1

LEARNING OBJECTIVES

- Acquaint with different systems of measurement of different quantities
- Understand how we gradually shifted from the British system to the metric system
- Know the seven basic physical quantities and their units
- Learn in detail about the units of the seven physical quantities
- Differentiate between mass and weight
- Write very large or very small numbers in scientific notation
- Carry out arithmetical calculations using exponential notation
- Differentiate between precision and accuracy
- Define significant figures and learn the rules for deciding significant figures in different kinds of numbers
- Learn addition, subtraction, multiplication and division ofsignificantfigures
- Learn conversion of units from one system to another through dimensional analysis

1.1 INTRODUCTION

A substance is associated with physical properties and chemical properties. Some examples of physical properties are colour, odour, smell, density, melting point and boiling point. These properties can be measured without the substance undergoing decomposition or association. Observation of a chemical property requires a chemical change to occur. Chemical properties of a substance include acidic or basic nature, combustibility, etc.

We require some parameters to assess certain properties. For example, properties like length, width, area, volume, etc., are quantitative in nature. That is, they are associated with definite values. Any quantitative measurement is represented by a number followed by units in which it is measured. It is absurd to say that a particular substance measures 6—in length we need to specify whether it is 6 cm or 6 m. When we say it is 6 m long, we mean it measures 6 units on the scale of metre.

1.2 SYSTEMS OF MEASUREMENT

In scientific studies and research, two different systems of measurement have been in use. These are the ***English System*** and the ***Metric System.*** The metric system originated in France in the late eighteenth century and is more convenient to use because it is based on the decimal system

of numbers. Before 1960, both the systems of measurement were being used by the scientific community. Some parts of the globe preferred the English system because they were used to it. Greater proportion of the scientific population advocated a switch to the metric system because it was more convenient and hence more scientific.

The metric system is called the ***International System of Units*** (called ***Le Systems International d' Unites*** in French and abbreviated as SI units). Historically, this system was established by the 11th General Conference on Weights and Measures (Conference General des Poides at Measures in French and abbreviated as CGPM). The CGPM is an intergovernmental treaty organization created by a diplomatic treaty known as ***Meter Convention*** which was signed in Paris in 1875.

As a consequence of serial meetings of the international scientific community, it was agreed in 1960 to adopt SI units for scientific experimentation and studies, although both the units continue to be used in textbooks. We have been rather slow in adopting SI units in our works. The SI system has seven base units pertaining to seven fundamental quantities as listed in Table 1.1.

Table 1.1 *Seven basic physical quantities and their units*

Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	t	kelvin	K
Amount ofthe substance	n	mole	mol
Luminous intensity	I_v	candela	cd

SI base units are separately defined as under:

1. **Metre** The metre is the length of the path travelled by light in vacuum during a time interval of 1/299792458 of a second.
2. **Kilogram** The kilogram is equal to the mass of the international prototype of the kilogram.
3. **Second** The second is the duration of 9192631770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
4. **Ampere** The ampere is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross section,

and placed 1 metre apart in vacuum would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.

5. **Kelvin** The Kelvin is the 1/273.16 fraction of the thermodynamic temperature of the triple point of water.
6. **Mole** The mole is the amount of substance which contains as many elementary entities are there are atoms in 0.012 kilogram of carbon-12. Its symbol is **mol.** The elementary entities must be specified and may be one of atoms, molecules, ions, electrons or other specified particles.
7. **Candela** The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiations of 540×10^{12} hertz frequency and that has a radiant intensity in that direction of 1/683 watt per steradian.

The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit as given below in Table 1.2. In fact, this is the strength of the SI system because it is based on decimal system (multiples or submultiples of 10)

Table 1.2 *Prefixes in SI system*

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-24}	yocto	*y*	10	deca	*da*
10^{-21}	zepto	*z*	10^{2}	hecto	*h*
10^{-18}	atto	*a*	10^{3}	kilo	*k*
10^{-15}	femto	*f*	10^{6}	mega	*M*
10^{-12}	pico	*p*	10^{9}	giga	*G*
10^{-9}	nano	*n*	10^{12}	tera	*T*
10^{-6}	micro	*μ*	10^{15}	peta	*P*
10^{-3}	milli	*m*	10^{18}	exa	*E*
10^{-2}	centi	*c*	10^{21}	zeta	*Z*
10^{-3}	deci	*d*	10^{24}	yotta	*Y*

The other physical quantities such as speed, acceleration, volume, density, pressure, force, etc., can be derived from the basic seven units.

1.3 MASS AND WEIGHT

Mass of a substance is the amount of matter present in it while **weight** is the force exerted by gravity on an object. The mass of a substance is constant whereas the weight may vary from place to place due to change in gravitational force. The mass of a substance can be determined accurately in the laboratory by using an analytical balance. Presently, we have the electronic top-weighing balance which directly gives the mass of the substance correct up to three or four decimal places depending upon the precision of the balance used. The SI unit of mass is one kg. However, its 10^{-3} multiple (1 kg = 1000 g), that is gram, is used more frequently for weighing small amounts of chemicals that are used in chemical reactions.

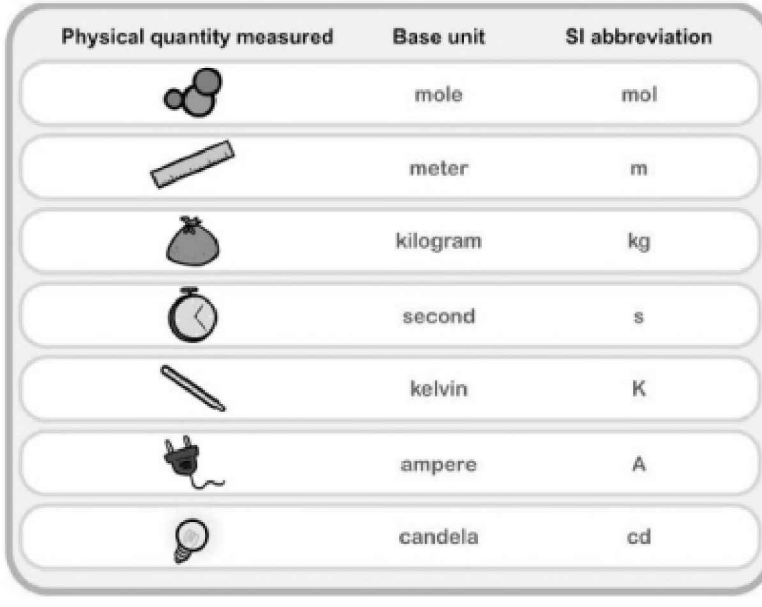


Fig 1.1 *Seven base units*

1.4 VOLUME

The unit of volume is (length)^3. As the SI unit of length is metre, the SI unit of volume is (metre)^3 or m^3. In chemical laboratories, we use smaller volumes for experimentation. Hence, volumes are often denoted in cm^3 or dm^3 units.
Litre (L) which is not an SI unit is used for the measurement of volumes of liquids.

$$1\ L = 1000\ mL \text{ and } 1000\ cm^3 = 1\ dm^3$$

Thus, $$1\ L = 1\ dm^3 = 1000\ mL = 1000\ cm^3$$

Volumes of liquids or solutions are measured with the help or graduated cylinders, burettes, pipettes, etc.

Derived SI Units		
Quantity	Unit	Symbol
Volume	liter	L
Force	newton	N
Pressure	pascal	Pa
Energy	joule	J

Fig 1.2 *Derived SI units*

1. Density The density of a substance is its amount per unit mass. The SI unit of density can be computed as under:

$$\text{Density (in SI units)} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}}$$

$$= \frac{\text{kg}}{\text{m}^3} \text{ or } \text{kg m}^{-3}$$

A chemist often expresses the density as g cm^{-3} because the SI unit gives large values.



Fig 1.3 *Anders Celsius (1701-1744) was a Swedish astronomer. The scale of temperature named after him was devised by him.*

2. Temperature Three scales have been in use for the measurement of temperature—degree Celsius (°C), degree Fahrenheit (°F) and Kelvin (K). *Kelvin* is the SI unit of temperature. However, thermometers are manufactured based on Celsius and Fahrenheit degrees. Generally, Celsius scale thermometers are calibrated from 0° to 100°C based on the freezing and boiling points of water. However, thermometers from 0°C to about 250°C are available when higher temperatures are required to be measured. The Celsius scale of temperature was earlier known as centigrade scale. The Fahrenheit scale is represented between 32°F to 212°F. The temperatures on Fahrenheit and Celsius scales are related to each other by the following relationship.

$$°F = \frac{9}{5}(°C) + 32 \tag{1.1}$$

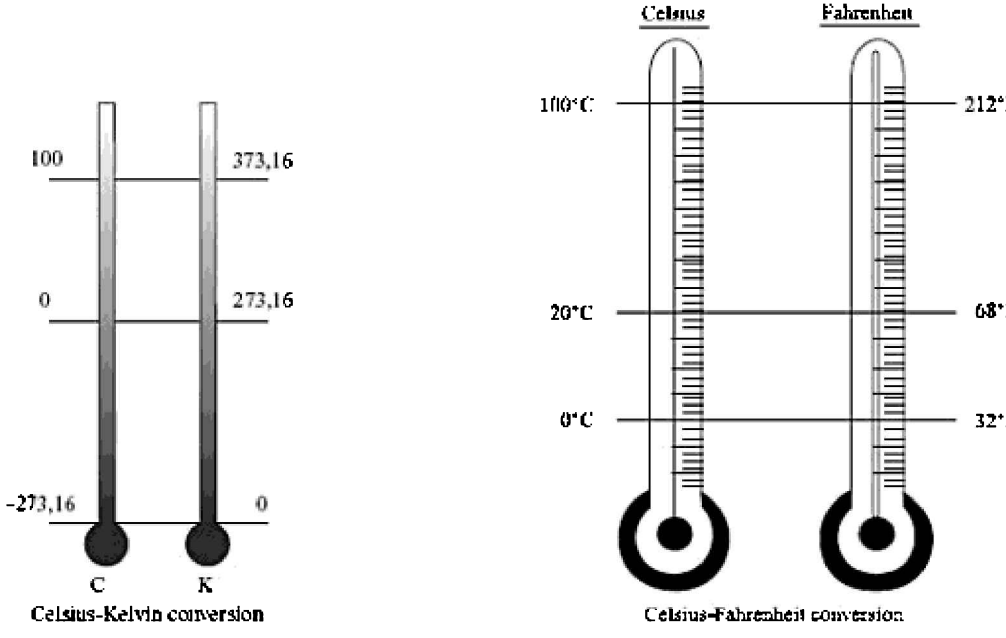


Fig. 1.4 *Temperature conversion*

The relation between the Kelvin scale and Celsius scale is as under:

$$K = °C + 273.16 \tag{1.2}$$

It may be of interest to note that negative values of temperature on the Celsius scale is possible while this is not so on the Kelvin scale.

Revamping Reference Standards

The mass standard has been the kilogram since 1889. It has been defined as the mass of platinum-iridium cylinder that is stored in an airtight jar at the International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and atmospheric action and its mass is not likely to change for an extremely long time. Scientists are in search of a new standard for mass. This is being done though accurate determination of Avogadro constant. Work on this new standard follows methods to measure accurately the number of atoms in a well-defined mass of the sample. This will provide a precise value of the Avogadro number and a new reference standard for mass.

3. Velocity Velocity is expressed as m/s in SI units. In the CGS system it is expressed as cm/s.

4. Acceleration Acceleration is expressed as m/s^2 in SI units. In the CGS system, it is expressed as cm/s^2.

5. Force Force is obtained by multiplying mass with acceleration. The unit of force is ***newton.*** A mass of 1 kg moving with an acceleration of 1 m/s^2 has a force of one newton. In the CGS system, the unit of force is dyne. ***Dyne*** is the force exerted by a mass of 1 g moving with an acceleration of 1 cm/ s^2, 1 Newton = 1 kg ms^{-2}

6. Work Work is obtained by multiplying force with displacement. The SI unit of work is ***joule.*** When a force of one newton makes a displacement of one metre, a work of one joule is said to be done. In the CGS system, the unit of work is ***erg.*** An erg of work is done when a force of one dyne makes a displacement of 1 cm. 1 Joule = 1 kg m^2 s^{-2}

1.5 SCIENTIFIC NOTATION

We come across terms like Avogadro number, Planck's constant, speed of light, charge on particles, etc., which are associated with very large numbers or very small numbers. If we write the values for these quantities, it involves a large number of zeros. It becomes extremely difficult to use these values in calculations like addition, subtraction, multiplication or division. It offers a real challenge in chemical arithmetic. This problem is solved by using ***scientific notation*** for such numbers. We also call it **exponential notation** in which any large or small quantity can be represented as

$$N \times 10^n$$

where n is the exponent having positive or negative value and N varies from 1 to 9. This is illustrated as under:

The number 4297.32 can be written as 4.29732×10^3 in scientific notation.

How did we do that?

We want the decimal point to be placed after 4 (remember N varies between 1 to 9). Thus, we have to move three places to the left. The exponent n is equal to the number of places we have moved the decimal point. When we move the decimal point to the left, the exponent n is positive (+ 2 or simply 2).

Let us take an example of a small quantity, say 0.0000029. This can be written as 2.9×10^{-6} in scientific notation. Remember we have to convert it into the form $N \times 10^n$, where N lies between 1 and 9. To obtain the number in this form, we need to shift the decimal point six places to the right. The exponent will again be equal to the number of places we are shifting the decimal point, i.e. 6, but with a negative sign, i.e –6. Hence, the scientific notation for this number will be 2.9×10^{-6}.

1.5.1 Addition and Subtraction

For the purpose of addition or subtraction of numbers in scientific notation, the numbers are written in such a way that they have the same exponent. After that the coefficients are added or subtracted as the case may be.

Example 1 *Add 5.34×10^5 and 7.97×10^4*

Solution: Make the exponent 5 in both numbers (equal to higher of the two exponents). We obtain the numbers as

$$5.34 \times 10^5 \text{ and } 0.797 \times 10^5$$

And now we shall add the coefficient and represent the sum as

$$(5.34 + 0.797) \times 10^5 = 6.137 \times 10^5$$

Now consider a case of subtraction.

Example 2 *Subtract* 8.2×10^{-4} *from* 7.8×10^{-3}

Solution: Make the exponent –3 in both cases to proceed further; thus, the numbers can be written as 0.82×10^{-3} and 7.8×10^{-3}. Therefore,

$$(7.8 \times 10^{-3}) - (0.82 \times 10^{-3})$$

Subtract the coefficients of two numbers and write the answer as

$$(7.8 - 0.82) \times 10^{-3} = 6.98 \times 10^{-3}$$

1.5.2 MultiplicationandDivision

In these two operations, the rules as applicable to exponential numbers are followed. Let the two numbers that are multiplied be $N_1 \times 10^x$ and $N_2 \times 10^y$. The multiplication result would be $N_1 \times N_2 \times 10^{x+y}$. In the division of the above numbers, the result would be $\frac{N_1}{N_2} \times 10^{x-y}$ This is illustrated with the help of the following examples:

Example 3 *Multiply* 6.7×10^3 *and* 8.9×10^5

Solution:
$$(6.7 \times 10^3) \times (8.9 \times 10^5)$$
$$= 6.7 \times 8.9 \times 10^{3+5}$$
$$= 59.63 \times 10^8$$

Example 4 *Divide* 1.5×10^{-2} *by* 3.7×10^{-4}

Solution:
$$= \frac{1.5 \times 10^{-2}}{3.7 \times 10^{-4}}$$
$$= \frac{1.5}{3.7}$$
$$= 0.41 \times 10^2$$

1.6 UNCERTAINTY

There is some element of uncertainty in any experimental measurement. However, it is our endeavour to have precise and accurate results.

1. Precision Precision refers to the closeness of various measurements for the same quantity.

2. Accuracy Accuracy is the agreement of a particular value to the true value of the result.

We illustrate this with the help of the following table which records the measurements in metre by three students *X*, *Y*and *Z*. The true value of the result is 3.00 m.

	Measurements/m		
	1	2	Average Value (m)
Student X	2.97	2.98	2.975
Student Y	2.98	3.10	3.04
Student Z	2.99	3.01	3.00

Every student takes two measurements indicated under 1 and 2.

Student *X* reports the measurements as 2.97 m and 2.98 m. These measurements are precise (because they are close to each other) but these are not accurate because they are far away from the true result which is 3.0 m.

Student *Y* reports the measurements as 2.98 m and 3.10. These results are neither precise nor accurate.

Student *Z* reports the measurements as 2.99 and 3.01. These results are both precise and accurate.

1.6.1 Significant Figures

The uncertainty in the measurements or calculated values is indicated by mentioning the number of ***significant figures.*** Significant figures are meaningful digits which are known with certainty. The last digit in the number is taken as uncertain while other digits are certain. If we write the result as 20.6 cm, we say that 20 is certain and 6 is uncertain. The uncertainty in the measurement is ±1 in the last digit. An uncertainty of ±1 is assumed in the last digit, unless otherwise stated.

1. Rules for Number of Significant Figures

(a) All non-zero digits are significant. For example, in 375 mL, there are three significant figures and in 0.65 mL, there are two significant figures.

(b) Zeros preceding the first non-zero digit are not significant. Such a zero indicates the position of decimal point. Thus, 0.07 has one significant figure and 0.0075 has two significant figures. Zeros between two non-zero digits are significant. Thus, 7.035 has four significant figures.

(c) Zeros at the end or right of a number are significant provided they are on the right side of the decimal point. For example, 0.440 has three significant figures. If the above condition is not satisfied then the zeros are not significant figures. For example, 100 has only one significant figure.

(d) Exact numbers have an infinite number of significant figures. For example, in 4 tables or 10 chairs, there are infinite significant figures as these can be represented by writing infinite number of zeros after placing the decimal point. Thus, 2 = 2.00000… and 10 = 10.00000…

In case a number is written in scientific notation ($N \times 10^n$), the number of digits in the N part of the number are significant figures.

2. Addition and Subtraction of Significant Figures *The result of addition or subtraction of numbers cannot have more digits to the right of the decimal point than any of the numbers.* For example,

8.0
11.12
15.214
34.334

The number 8.0 has only one digit after the decimal. Therefore, the result cannot have more than one digit after the decimal point. Hence, the result would be 34.3.

3. Multiplication and Division of Significant Figures In the multiplication and division of numbers, the *result must be reported with significant figures which are no more than in the number with least significant figures*. For example,

$$1.8 \times 2.29 = 4.122$$

As 1.8 contains only two significant figures, the result of multiplication should also contain two significant figures. Hence, the result is 4.1.

Consider an example of division:

$$18.5 \times 3.43 = 5.3935$$

As both the original numbers contain three significant figures, the result should also contain three significant figures. Hence the result should be expressed as 5.39.

4. Rounding Off The following points have to be kept in mind for rounding off the numbers after the significant figures have been decided.

(a) It the digit on the extreme right to be removed is more than 5, the preceding digit is increased by one. For example, in the number 4.678, if the last digit is to be removed then it is rounded to 4.68.

(b) If the digit on the extreme right to be removed is less than 5, the preceding digit is not changed. Thus, if in the number 7.884, the last digit 4 is to be removed then it will be rounded to 7.88.

(c) It the digit on the extreme right to be removed is 5 then the preceding digit is not changed if it is an even number but it is increased by one if it is an odd number. For example, if 8.75 is to be rounded off by removing 5, we need to increase the preceding digit by 1, that is, the result would be 8.8. However, if the number is 8.45 and we need to round it by removing 5 then the preceding digit 4 will remain unchanged and the number will the rounded to 8.4.

Example 5 *What would be the SI unit for the quantity* $\frac{pv^2T^2}{n}$ *?*

Solution: The SI unit would be $\frac{\text{k pa } (\text{dm}^3)^2(\text{K}^2)}{\text{mol}}$

or $\frac{\text{N m}^{-2}(\text{m}^3)^2(\text{K})^2}{\text{mol}} = \text{Nm}^4\text{K}^2\,\text{mol}^{-1}$

Example 6 *Express the following in SI base units using power of 10 notation.*

(a) 1.35 mm (b) 1 day (c) 6.45 mL
(d) 48 μg (e) 0.0426 inch

Solution:

(a) $1.35\ \text{mm} = 1.35 \times 10^{-3}\ \text{m}$

(b) $1\ \text{day} = 1 \times 24 \times 60 \times 60 = 86{,}400\ \text{s} = 8.64 \times 10^{4}\ \text{s}$

(c) $6.45\ \text{mL} = 6.45 \times 10^{-3}\ \text{L}$

(d) $48\ \mu\text{g} = 48 \times 10^{-6}\ \text{g} = 4.8 \times 10^{-8}\ \text{kg}$

(e) $0.0426\ \text{inch} = 0.0426\ \text{inch} \times \dfrac{2.54 \times 10^{-2}\ \text{m}}{1\ \text{inch}} = 1.08 \times 10^{-3}\ \text{m}$

Example 7 *Convert into metre:*

(a) *7 nm (diameter of a small virus)*

(b) *40 Em (thickness of milky Way galaxy)*

(c) *1.4 Gm (diameter of the sun)*

(d) *41 Pm (distance of the nearest star)*

Solution:

(a) $7\ \text{nm} = 7 \times 10^{-9}\ \text{m}$

(b) $40\ \text{Em} = 40 \times 10^{18}\ \text{m} = 4.0 \times 10^{19}\ \text{m}$

(c) $1.4\ \text{Gm} = 1.4 \times 10^{9}\ \text{m}$

(d) $41\ \text{Pm} = 41 \times 10^{15}\ \text{m} = 4.1 \times 10^{16}\ \text{m}$

Example 8 *Convert the following in kilograms:*

(a) 0.91×10^{-27} g (mass of electron)

(b) 1 fg (mass of human DNA)

(c) 500 Mg = (Mass of jumbo jet, loaded)

(d) 3.34×10^{-24} g (mass of hydrogen molecule)

Solution:

(a) $0.91 \times 10^{-27}\ \text{g} = 0.91 \times 10^{-30}\ \text{kg} = 9.1 \times 10^{-31}\ \text{kg}$

(b) $1\ \text{fg} = 1 \times 10^{-15}\ \text{g} = 1 \times 10^{-18}\ \text{kg}$

(c) $500\ \text{Mg} = 500 \times 10^{6}\ \text{g} = 500 \times 10^{3}\ \text{kg} = 5.0 \times 10^{5}\ \text{kg}$

(d) $3.34 \times 10^{-24}\ \text{g} = 3.34 \times 10^{-27}\ \text{kg}$

PROBLEMS FOR PRACTICE

1. Express the following in scientific notation:

(i) 0.0048

(ii) 234,000

(iii) 8008

(iv) 500.0

(v) 6.0012

[**Ans.** (i) 4.8×10^{-3} (ii) 2.34×10^{5} (iii) 8.008×10^{3} (iv) 5.000×10^{2} (v) 6.0012×10^{0}]

2. Match the following prefixes with their multiples:

Prefixes	*Multiples*
(i) *micro*	10^{6}
(ii) deca	10^{9}
(iii) mega	10^{-6}
(iv) giga	10^{-15}
(v) femto	10

[**Ans.** Micro → 10^{-6}, deca → 10, mega → 10^{6}, giga → 10^{9}, femto → 10^{-15}]

3. How many significant figures are present in the following?

(i) 0.0025

(ii) 208

(iii) 5005

(iv) 500.0

(v) 2.0034

[**Ans.** (i) 2 (ii) 3 (iii) 4 (iv) 4 (v) 5)]

4. Round up the following up to three significant figures:

(i) 34.216

(ii) 10.4107

(iii) 0.04597

(iv) 2808

[Ans. (i) 34.2 (ii) 10.4 (iii) 0.046 (iv) 2810]

1.7 | DIMENSIONAL ANALYSIS

We often need to convert units from one system to another during calculations. The method that is used to carry out the conversion is known as ***unit factor*** method. This is also called ***dimensional analysis.*** This is illustrated as under:

Let us say we want to convert 5 inches into centimetres. This will be achieved as under.

We know that 1 inch = 2.54 cm

It can be written as

$$\frac{1 \text{ inch}}{2.54 \text{ cm}} = 1 = \frac{2.54 \text{ cm}}{1 \text{ inch}}$$

Thus,

$$\frac{1 \text{ inch}}{2.54 \text{ cm}} = 1 \tag{1.3}$$

$$\frac{2.54 \text{ cm}}{1 \text{ inch}} = 1 \tag{1.4}$$

Both of these are called unit factors. If some number is multiplied by these unit factors, it will not be affected. Thus, we can multiply Eq. (1.4) by 5 inches on both sides

$$5 \text{ inches} = 5 \text{ inches} \times \frac{2.54 \text{ cm}}{1 \text{ inch}}$$

$$= 5 \times 2.54 \text{ cm} = 12.7 \text{ cm}$$

It may be noted that the unit factor which is to be used for multiplication is that one which gives the desired units.

It may be noted that units can be treated just like other numerical part. They can be cancelled, multiplied on divided.

Example 9 *How many seconds are there in 3 days?*

Solution: We know 1 day = 24 hours

The unit factors will be

$$\frac{1 \text{ day}}{24 \text{ hours}} = 1 = \frac{24 \text{ hours}}{1 \text{ day}}$$

Also

$$1 \text{ hour} = 60 \text{ min}$$

$$\frac{1 \text{ hour}}{60 \text{ min}} = 1 = \frac{60 \text{ min}}{1 \text{ hour}}$$

Also

$$1 \text{ min} = 60 \text{ seconds}$$

$$\frac{1 \text{ min}}{60 \text{ s}} = 1 = \frac{60 \text{ s}}{1 \text{ min}}$$

For converting 3 days into seconds, the unit factors can be multiplied.

$$3 \text{ day} = 3 \text{ day} \times \frac{24 \text{ hour}}{1 \text{ day}} \times \frac{60 \text{ min}}{1 \text{ hour}} \times \frac{60 \text{ s}}{1 \text{ min}}$$

$$= 3 \times 24 \times 60 \times 60 \text{ seconds}$$

$$= 259\,200 \text{ seconds}$$

Example 10 *Pressure is defined as force per unit area of the surface. The SI unit of pressure, pascal is shown as below*

$$1 \, Pa = 1 \, NMm^{-2}$$

If the mass of air at sea level is 1034 gcm^{-2}, calculate the pressure in pascals.

Solution: Pressure is the force per unit area and the force here is the weight

$$\text{Weight} = mg$$

$$\text{Pressure} = \frac{1034\,g \times 9.8\ ms^{-2}}{cm^2}$$

$$= \frac{1034\,g \times 9.8\ m\,s^{-2}}{cm^2} \times \frac{1\,kg}{1000\,g} \times \frac{100\,cm \times 100\,cm}{1\,m \times 1\,m} \times \frac{1\,N}{kg\,ms^{-2}} \times \frac{1\,Pa}{1\,N\,m^{-2}}$$

$$= 1.01332 \times 10^5\ Pa$$

Example 11 *Fill in the blanks in the following conversions:*

(*a*) *1 km* = _____ *mm* = _____ *pm*

(*b*) *1 mg* = _____ *kg* = _____ *ng*

(*c*) *1 mL* = _____ *L* = _____ dm^3

Solution:

(a) $1\ km = 1\ km \times \frac{1000\ m}{1\ km} \times \frac{100\,cm}{1\ m} \times \frac{10\,mm}{1\ cm} = 10^6\ mm$

$1\ km = 1\ km \times \frac{1000\ m}{1\ km} \times \frac{1\ pm}{10^{-12}\ m} = 10^{15}\ pm$

(b) $1\ mg = 1\ mg \times \frac{1\ g}{1000\ mg} \times \frac{1\ kg}{1000\ g} = 10^{-6}\ kg$

$1\ mg = 1\ mg \times \frac{1\ g}{1000\ mg} \times \frac{1\ ng}{10^{-9}\ g} = 10^6\ ng$

(c) $1\ mL = 1\ mL\ \frac{1\ L}{1000\ mL} = 10^{-3}\ L$

$1\ mL = 1\ cm^3 = 1\ cm^3 \times \frac{1\,dm \times 1\,dm \times 1\,dm}{10\ cm \times 10\ cm \times 10\ cm} = 10^{-3}\ dm^3$

PROBLEMS FOR PRACTICE

1. If the speed of light is $3.0 \times 10^8\ ms^{-1}$, calculate the distance covered by light in 2.00 ns.

[**Ans.** 0.6 m]

2. Convert the following into basic units.

(i) 28.7 pm (ii) 15.15 pm (iii) 25365 mg

[**Ans.** (i) 2.87×10^{-11} m (ii) 1.515×10^{-5} s (iii) 2.5365×10^{-2} kg]

3. How many significant figures should be present in the answer of the following?

(i) $\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$

(ii) 5×5.364
(iii) $0.0125 + 0.7864 + 0.0215$

[**Ans.** (i) 3 (ii) 4 (iii) 4]

SUMMARY

1. Any quantitative measurement is represented by a number followed by units in which it is measured.
2. In scientific studies, two different systems of measurement have been in use. These are the *English System* and the *Metric System*.
3. The metric system is called the International System of Units (SI units).
4. The SI system has seven base units pertaining to *seven* fundamental quantities, viz. length, mass, time, electric current, thermodynamic temperature, amount of the substance and luminous intensity.
5. The SI system allows the use of *prefixes* to indicate the multiples or submultiples of a unit.
6. *Mass* of a substance is the amount of matter present in it while *weight* is the force exerted by gravity on an object.
7. *Density* of a substance is its amount per unit volume.
8. A very large or very small number (or quantity) can be represented using *scientifc notation* ($N \times 10^n$) where n is the exponent having positive or negative value and N varies between 1 and 9.
9. Precision refers to the closeness of various measurements for the same quantity.
10. Accuracy is the agreement of a particular value to the true value of the result.
11. The uncertainty in the measurements or calculated values is indicated by mentioning the number of *significant figures*.
12. Significant figures are meaningful digits which are known with certainty.
13. The result of addition or subtraction of numbers cannot have more digits to the right of the decimal point than any of the numbers.
14. In the multiplication and division of numbers, the result must be reported with significant figures which are no more than in the number with least significant figures.
15. For conversion of units form one system to another, unit factor method or dimensional analysis is carried out.

EXERCISES

Based on Different University Papers Objective Questions

Multiple-Choice Questions

1. Which of the following is not a base unit?

(a) Length

(b) Area

(c) Mass

(d) Time

2. The SI unit of time is

(a) second

(b) minute

(c) hour

(d) day

3. 10^2 multiple of a quantity is represented as

(a) centi

(b) deci

(c) hecto

(d) deca

4. Density of a substance in SI units is

(a) mol L^{-1}

(b) kg m^{-3}

(b) gL^{-1}

(d) g cm^{-3}

5. Conversion between Fahrenheit and Celsius degrees can be achieved through the relation

(a) $°F = \frac{9}{5}\ (°C) + 32$

(b) $°F = \frac{5}{9}\ (°C) + 32$

(c) $°C = \frac{9}{5}(°F) + 32$

(d) $°C = \frac{5}{9}\ (°F) + 32$

6. Tick the correct relation

(a) 1 J = 1 kg m s^{-2}

(b) 1 J = 1 kg m^2 s^{-2}

(c) 1 J = 1 kg m^2 s^{-1}

(d) 1 J = 1 kg m^3 s^{-1}

7. The measurements of length taken by a student are 15.5 cm and 15.6 cm whereas the true value is 16 cm. The measurement taken by the student are

(a) precise

(b) accurate

(c) not precise

(d) neither precise not accurate

8. The number of significant figures in 1.20×10^2 is

(a) 3

(b) 2

(c) 5

(d) 4

9. Which of the prefix–multiple combinations is wrong?

(a) micro–10^{-6}

(b) Mega–10^6

(c) deca–10^2

(d) Giga–10^9

10. How many significant figures should be present in the answer of the following?

$$\frac{0.03781 \times 275.12 \times 0.224}{0.7654}$$

(a) 4

(b) 3

(c) 5

(d) None of these

Answers

1. (b) 2. (a) 3. (c) 4. (b) 5. (a) 6. (b) 7. (a) 8. (a) 9. (c) 10. (b)

SHORT-ANSWER QUESTIONS

1. What is the SI unit of mass? How is it defined?
2. Give the prefixes for the multiples: 10^{-3}, 10^{-1}, 10^{+1}, 10^{+3}
3. What do you mean by significant figures? Explain with an example.
4. Explain the following in scientific notation:

(i) 0.000123 (ii) 5670000 (iii) 74932

5. Round off the following to four significant figures:

(i) 1.3785 (ii) 11.175 (iii) 0.069327

6. Fill in the blanks with the following conversion:
   1 m = _____ mm = _____ nm
7. Vanadium metal is added to steel to impart strength. The density of vanadium is 5.96 g cm^{-3}. Express this in SI unit kg m^{-3}.
8. Express the following numbers to four significant numbers:

(i) 5.607892 (ii) 1.78986×10^3 (iii) 5.608

9. What is the significant figure in (i) Avogadroa number (6.0×10^{23}), and (ii) Planck's constant

(6.62×10^{-34} Js)?

GENERAL QUESTIONS

1. Give the sequence of events that led to the adoption of SI system of units.
2. Write the names and symbols for basic physical quantities in the SI system.
3. Define the following SI quantities: ampere, mole, candela
4. Define density of a substance. A substance has a density of 13.5 g cm^{-3}. Convert it into SI units.
5. A jug contains 1.5 litres of milk. Calculate the volume of the milk in m^3.

[**Ans.** 1.5×10^{-3} m^3]

6. Convert 0.74 Å into pm units by unit factor method

[**Ans.** 74 pm]

7. Calculate the mass of one litre of mercury in grams and in kilograms if the density of liquid mercury is 13.6 g cm^{-3}.

[**Ans.** mass in g = 1.36×10^4 g, Mass in kg = 13.6 kg]

8. Explain the following:

(a) Precision and accuracy (b) Dimensional analysis

9. State the number of significant figures in the following:

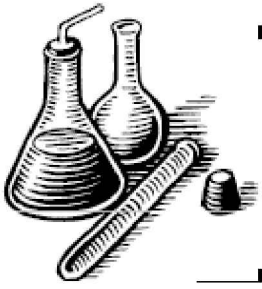
(a) 2.653×10^4 (b) 0.00368

[**Ans.** (a) 4 (b) 3]

10. Convert litre-atmosphere to joule (SI unit of energy).

[**Ans.** 101.325 J]

11. Discuss rules for arriving at the number of significant figures.



Mathematical Concepts and Computers

2

LEARNING OBJECTIVES

- Know different logarithmic relations and learn how to do calculations using logarithmic relations
- Learn curve sketching for different functions
- Draw linear graphs and determine the slopes
- Learn the method of finding the derivative of a function
- Know important trigonometric relations
- Learn how to determine the maxima and minima for a function
- Find partial derivatives of first and higher order
- Know the significance of integration and learn important integration formulae
- Understand and calculate definite integrals
- Learn permutations and combinations of different arrangements
- Determine the probability of occurrence of an event
- Realise the importance of computers
- Know different components of a computer
- Classify software into different types
- Learn about binary system of numbers
- Learn about operating systems and their different types

2.1 INTRODUCTION TO MATHEMATICAL CONCEPTS

The study of physical chemistry requires a strong background in mathematics. For complex calculations, we use logarithms and antilogarithms. For the study of linear relations between two physical quantities, we need to determine the slope and intercept on the axes in order to arrive at certain quantities and constants used in the equation. Similarly, we need to carry out differentiation and integration to arrive at certain results. If we have an equation between two variables, we can do curve sketching. A knowledge of definite integrals helps us obtain the total change in a quantity for a definite change in the other quantity. In statistical studies, we require formulas to arrive at the probability of an event. The maximum and minimum values of a physical quantity can be determined if its relation with the other quantity is known.

Use of computers in calculations and mathematical modelling has changed the face of all the disciplines of knowledge. The purpose of this chapter in the book is to acquaint the students with these mathematical procedures and give some insight into the working of computers.

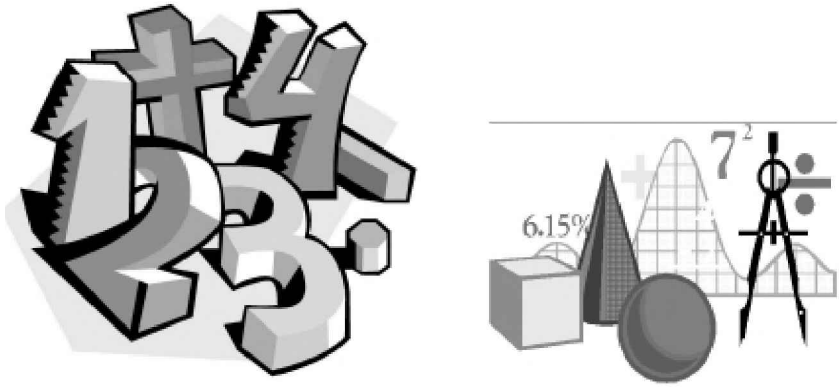


Fig. 2.1 *Illustrations on mathematics*

2.2 LOGARITHMIC RELATIONS

1. Definition of Logarithm The logarithm of a number with respect to a given base is the power to which the base must be raised to represent the number.

For example, $1000 = 10^3$

$\log_{10} 1000 = 3$

In general, $N = a^x$

Then $\log_a N = x$

As $a^\circ = 1$, it follows that $\log_a 1 = 0$

$a^1 = a$, it follows that $\log_a a = 1$.

2. Four Standard Formulae of Logarithms These four formulae are commonly used. We are mentioning them without proof.

$\log_a mn = \log_a m + \log_a n$ (Product formula)

$\log a \frac{m}{n} = \log_a m - \log_a n$ (Quotient formula)

$\log_a m^n = n \log_a m$ (Power formula)

$\log_a m = log_b m \times \log_a b$ (Base-changing formula)



Fig. 2.2 *John Napiers (1550-1617) was a Scottish mathematician, physicist and astronomer. He discovered logarithms.*

Example 1 *If a, b, c, d are four positive numbers, prove that* $\log_b a \times \log_c b \times \log_d c = \log_d a$

Solution:

$$\begin{aligned}
\text{LHS} &= \log_b a \times \log_c b \times \log_d c \\
&= \frac{\log_m a}{\log_m b} \times \frac{\log_m b}{\log_m c} \times \frac{\log_m c}{\log_m d} \left(\begin{array}{c} \text{By base} \\ \text{changing} \\ \text{formula} \end{array} \right) \\
&= \frac{\log_m a}{\log_m d} \\
&= \log_d a \\
&= \text{RHS}
\end{aligned}$$

Example 2 *Express* $\log \dfrac{x^3 \sqrt[5]{y^2}}{\sqrt{z^3}}$ *in terms of* $\log_a x$, $\log_a y$ *and* $\log_a z$.

Solution:

$$\begin{aligned}
\log_a \frac{x^3 \sqrt[5]{y^2}}{\sqrt{z^3}} &= \log_a \frac{x^3 y^{2/3}}{z^{3/2}} \\
&= \log(x^3 y^{2/3}) - \log_a z^{3/2} \text{ (Quotient formula)} \\
&= \log_a x^3 + \log_a y^{2/3} - \log_a z^{3/2} \quad \text{(Product formula)} \\
&= 3\log_a x + \frac{2}{5}\log_a y - \frac{3}{2}\log_a z \quad \text{(Power formula)}
\end{aligned}$$

which is the result.

PROBLEMS FOR PRACTICE

1. Prove that $\log \frac{a^2}{bc} + \log \frac{b^2}{ca} + \log \frac{c^2}{ab} = 0$

2. $\log \frac{42}{55} = \log 2 + \log 3 + \log 7 - \log 11 - \log 5$. Prove it.

3. Express in terms of log x, log y and log z:

(i) $\log_a \frac{x^3}{y^2 z^4}$ (ii) $\log_a \frac{\sqrt[n]{x^m y^r}}{\sqrt[3]{z}}$

4. Prove that $\log_a mnp = \log_a^m + \log_a^n + \log_a^p$

Answers

3. (i) $3 \log_a x - 2 \log_a y - 4 \log_a z$ (ii) $\frac{m}{n} \log_a x + r \log_a y - \frac{1}{3} \log_a z$

3. Two Systems of Logarithms The two systems of logarithms in common use are the following:

(a) Neparian Log or Natural Log Here, the base is e, where $e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \ldots$ In all theoretical calculations, we use natural logarithms.

(b) Common Logarithm Here, the base of log is 10. In all numerical calculations, we use common log. We can convert natural log into common log as follows.

$$\log_e m = \log_{10} m \times \log_e 10$$

and $$\log_e 10 = 2.3026 \times \log_{10} 10$$
$$= 2.3026 \times 1 = 2.3026 \quad [\because \log_{10} 10 = 1$$

$\therefore$ $$\log_e m = 2.3026 \log_{10} m$$

4. Log Tables Log tables are the standard common log tables which are available to us for calculations. These are usually four-digit tables and are given at the end of the book. The logarithm of any given number can be read from these tables. The logarithm of a number consists of two parts:

(a) Integral part called ***characteristic***

(b) Decimal part called ***mantissa***

(a) Characteristic It can be zero, positive or negative. We use the following two rules for finding the characteristic.

Rule I If the given number > 1, its characteristic is +ve. Count the number of digits to the left of the decimal point. Subtract 1 from this number. This is the characteristic of the log of a given number.

For example,

Characteristic of log 1798.3 is 4 – 1 = 3

Characteristic of log of 28.78 is 2 – 1 = 1

Characteristic of log of 1.923 is 1 – 1 = 0

Rule II If the given number is less than one, its characteristic is negative. It is put under a bar. Count the number of zeros immediately after the decimal point. Add 1 to this number. If gives

us the characteristic of the log of the given number.

For example,

Characteristic of log 0.5828 = $-(0 + 1) = \bar{1}$

Characteristic of log 0.0628 = $-(1 + 1) = \bar{2}$

Characteristic of log 0.0008 = $-(3 + 1) = \bar{4}$

(b) Mantissa As mentioned above, it is the decimal part of the log of a given number. It is always positive, and can be read from the log tables as follows.

(i) In the given number, omit the decimal point and zeros in the beginning and at the end. For example, in log of 0.001175, we have to look up the mantissa of 1175

(ii) Take the first two digits, i.e. 11, and locate then in the first vertical column of the four-figure log table.

(iii) Go through the horizontal row beginning with 11 and look up the value under the column headed by the third digit, i.e. 7. From the log tables, we find this number as 0.682.

(iv) Continue moving in the same horizontal line and note the number in the small differences column headed by the fourth digit, i.e. 5. This number is 18.

(v) Add 18 to 0682, we got 0700.

$\therefore$ the mantissa is 0.0700.

Note: If the number consists of a single digit, put zeros at the end of the number to complete four digits. Read the mantissa as explained above.

For example, log 7 = log 7.000 = 0.8451

Mantissa for 7, 70, 700, 0.7, etc. is the same.

5. Antilogarithm Antilogarithm is the reverse process of logarithm. Thus, antilogarithm to logarithm is as division to multiplication.

For example, if log 7 = 0.8451 then antilog 0.8451 = 7. Standard antilog tables are also given at the end of the book for calculations. We follow the rules given below for reading antilog tables.

(a) Read the antilog of mantissa only (i.e. of decimal part). Locate the four digits the way we did in reading the mantissa from log tables.

(b) If the characteristic is positive, say n, the decimal is placed after $(n + 1)$ digits in the value read.

(c) If the characteristic is –ve, say $\bar{n}$ then $(n - 1)$ zeros are placed before the left side of the number read; then the decimal point is placed.

For example, antilog of $\bar{2}.3478 = 0.02227$

antilog of $1.7192 = 52.38$

antilog of $0 = 1.000$

6. Use of Logarithms Logarithms are practically very useful in simplifying complicated calculations. Logarithm means a rule to shorten arithmetic. It was invented by John Napier in 1614. the following examples will enable students to use log tables for such purposes.

Example 3 *Simplify* $\dfrac{1.7927 \times 77.4}{(129.7)^{2/3}}$.

Solution: Let $x = \dfrac{1.792 \times 77.4}{(129.7)^{2/3}}$

Taking log on both sides, we get

$$\log x = \log 1.792 + \log 77.4 - \frac{2}{3}\log (129.7)$$
$$= 0.2534 + 1.8887 - \frac{2}{3}(2.1130)$$
$$= 0.2534 + 1.887 - 1.4087$$
$$= 2.1421 - 1.4087$$
$$= 0.7334$$
$$x = \text{antilog } 0.7334$$
$$= 1.5413 \text{ which is the result.}$$

Example 4 *Find the fifth root of0.0076.*

Solution : Let $x = (0.0076)^{1/5}$

Taking log on both sides, we get

$$\log x = \frac{1}{5}\log (0.0076)$$
$$= \frac{1}{5}(\bar{3}.8808) \text{ (From the tables)}$$
$$= \frac{1}{5}(\bar{3}.8808 + 2 - 2)$$
$$= \frac{1}{5}(\bar{5}.8808 + 2)$$
$$= \frac{1}{5}(\bar{5} + 2.8808)$$
$$\log x = \bar{1}.5762$$

Taking antilog on both sides, we get

$$x = 0.3769$$

PROBLEMS FOR PRACTICE

1. Simplify the following:

   (a) $(0.05246)^{1/8} - 2.6055$

   (b) $\dfrac{3.142 \times (80.2)^{1/2}}{(9.8)^{1/2}}$

2. Find the antilog of

   (a) —2.6674 [*Hint.* $(-2.6674 = \bar{3}.3326)$]

   (b) –3.01

3. Simplify the following:

   (a) $(0.0036)^{1/5}$

   (b) $(0.056)^{2/3}$

   (c) $10^{-1/5}$

Answers

1. (a) –1.9137
   (b) 8.989
2. (a) 0.002151
   (b) 0.0009772
3. (a) 0.3245
   (b) 0.1464
   (c) 0.6310

2.3 CURVE SKETCHING

When a variable point $P(x, y)$ moves under a given set of conditions then the path traced by P is called the graph or locus of P. The equation which relates the variables x and y is called the equation of the graph of P.

Every point which is on the graph satisfies the given set of conditions and any point satisfying the given set of conditions lies on the graph.

To draw the graph or to sketch the curve, we take y as the dependent variable and x is the independent variable. To draw the graph, the following points are followed:

1. Write the given equation equal to y.
2. Now give three, four values of x and find the corresponding values of y.
3. Plot these points in the graph by taking two perpendicular lines; horizontal line as x-axis and vertical line as y-axis, we get the required curve.

Example 5 *Sketch the curve* $y = x^2 - 9$.

Solution : First of all, we get a table of values for $y = x^2 - 9$ by taking x as independent and y as dependent variables. We get the table of values as under.

x	–3	–2	–1	0	1	2	3
y	0	–5	–8	9	–8	–5	0

Plot these points in the graph and join it with a free hand as shown in Fig. 2.3.

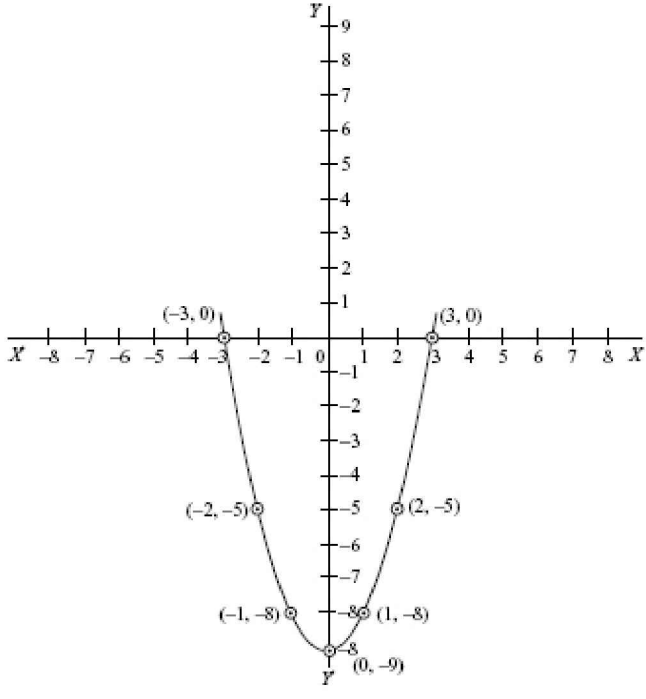


Fig. 2.3

Example 6 *Sketch the curve* $y = x^3 + 1$

Solution : First of all, we get the table of values for $y = x^3 + 1$ by taking x as independent variable and y as dependent variable. We get the table of values as under.

x	–2	–1	0	1	2
y	–7	0	1	2	9

Plot these points in the graph and join it with a free hand as shown in Fig. 2.4.

Example 7 *Sketch the curve* $y = x^2 + 2x - 3$

Solution : First of all, we get the table of values for $y = x^2 + 2x - 3$ as under.

x	–2	–1	0	2	–4
y	–3	–4	–3	5	5

Plot these points in the graph and join it with a free hand as illustrated below in Fig. 2.5.

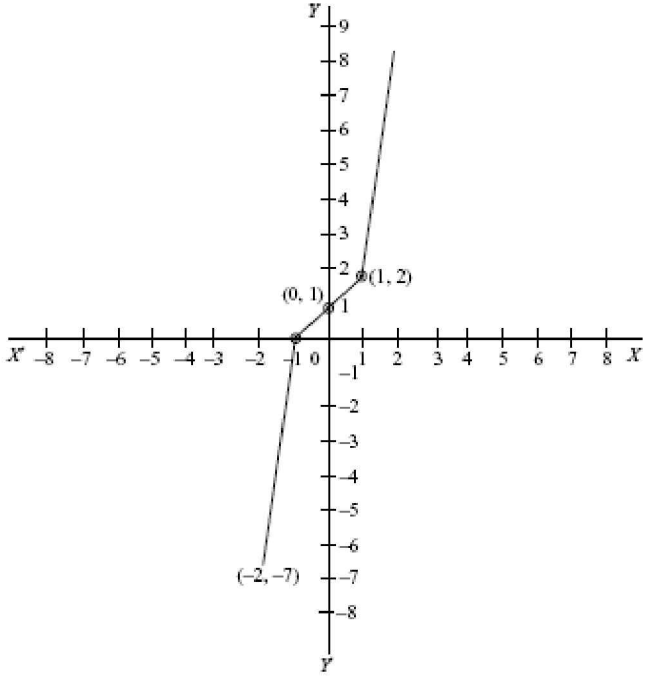


Fig. 2.4

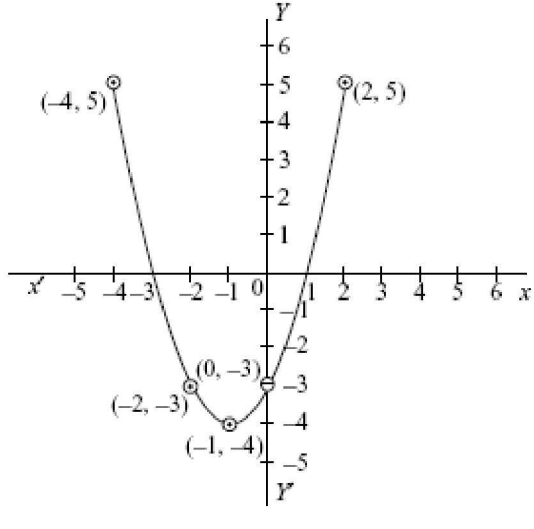


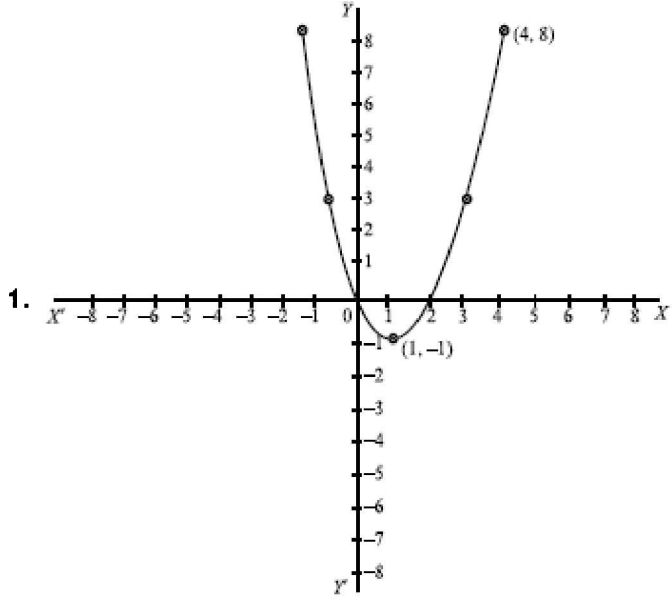
Fig. 2.5

PROBLEMS FOR PRACTICE

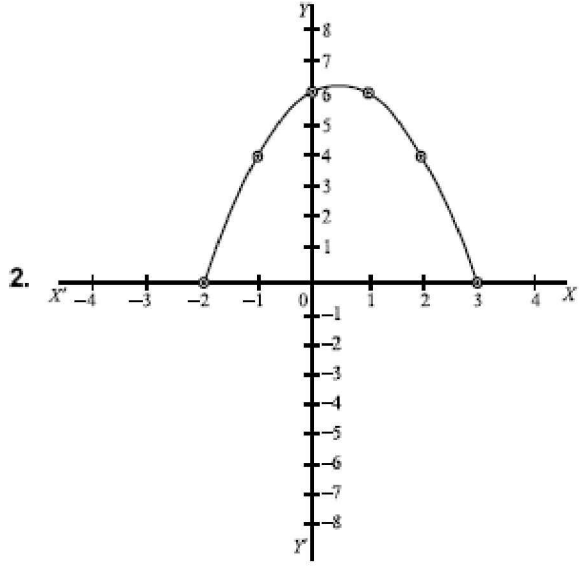
1. Sketch the curve $y = x^2 - 2x$
2. Sketch the curve $y = x^2 + x + 6$
3. Sketch the graph $y = x^4 - 1$.

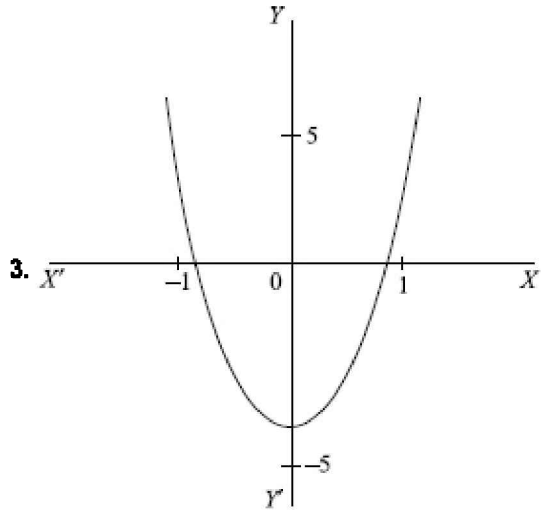
Answers

1.



2.





2.4 LINEAR GRAPHS AND CALCULATION OF SLOPES

1. Linear Graph The graph of a linear equation is called the linear graph.

2. Linear Equation *An equation of the form ax + by + c = 0, where a, b, c are constants and x and y are two variables, is called a linear equation of two variables.* Every linear equation in x and y represents a straight line. The various cases are discussed below one by one.

(a) The equation $x = a$ represents a straight line parallel to the y-axis and at a distance a from it.
If the line is to the right of the y-axis, a is +ve
If the line is to the left of the y-axis, a is –ve.
If the line coincides with the y-axis, $a = 0$, the equation of y-axis is $a = 0$.
The graphs of $x = 5$, $x = 0$, and $x = -4$ are shown in Fig. 2.6.

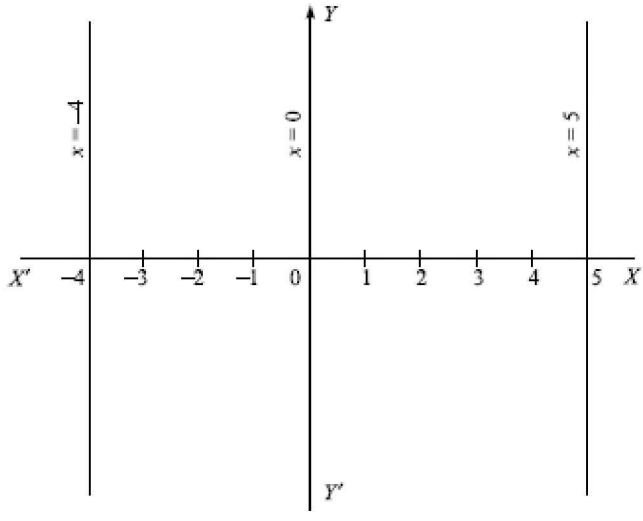


Fig. 2.6 *The line x = a*

(b) The equation $y = b$ represents a straight line parallel to the x-axis and at a distance b from it.
If the line is above the x-axis, b is +ve. If the line is below x-axis, b is –ve.
If the line coincides with the x-axis, $b = 0$.
The equation of the x-axis, $y = 0$.
The graphs of $y = 2$, $y = 0$ and $y = -3$ are shown Fig. 2.7.

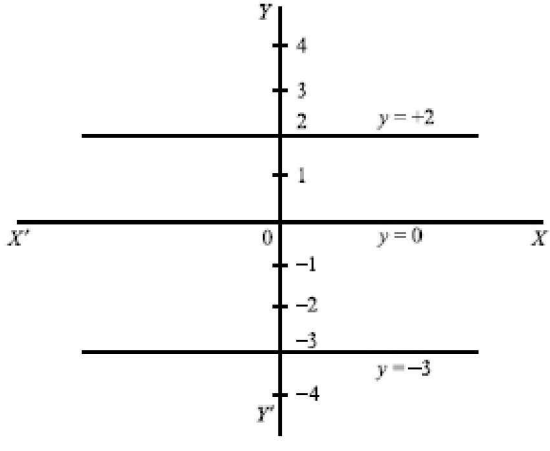


Fig. 2.7 *The line y = b*

General Method to Draw the Graph of a Linear Equation ax + bx + c = O and to Find the Slope of the Line

(a) Write the given equation in the form showing one variable in terms of the other variable (generally, in the form $y = mx + c$)

(b) Now give three, four values to x and find the corresponding values of y.

(c) Plot these points named by ordered pairs.

(d) Draw the straight line joining these points.

To Find the Slope of the Line

(a) Calculate the change in y over the corresponding change in x. It is the slope of the line, i.e. change in y.

$$\frac{\text{change in } y}{\text{change in } x}.$$

(b) If the equation is in the form $y = mx + c$ then m is called the slope of the line.

(c) If the equation is of the form $ax + by + c = 0$ then slope is given by $-\dfrac{\text{coeff. of } x}{\text{coeff. of } y} = \dfrac{-a}{b}$

(d) Differentiate the given equation to find $\dfrac{dy}{dx}$. Then $\dfrac{dy}{dx}$ is also the slope of the line.

Example 8 *Draw the graph of a function $y = 3x + 8$ and find the slope of the line.*

Solution : The equation of the line is

$$y = 3x + 8$$

Putting $x = 0$, we get $y = 8$
Putting $x = 1$, we get, $y = 11$
Putting $x = 2$, we get, $y = 14$

$A(0, 8)$, $B(1, 11)$, $C(2, 14)$ are three points on the line. Plot these points and join them by a foot ruler.

To find the slope, draw BK, CM perpendicular to the x-axis and BN perpendicular to CM.

The slope is given by

$$\frac{CN}{BN} = \frac{\text{Change in } y}{\text{Change in } x}$$

Now,

$$CN = CM - NM = 14 - 11 = 3$$
$$BN = KM = OM - OK = 2 - 1 = 1$$

Slope $= \dfrac{3}{1} = 3$. Hence, the result.

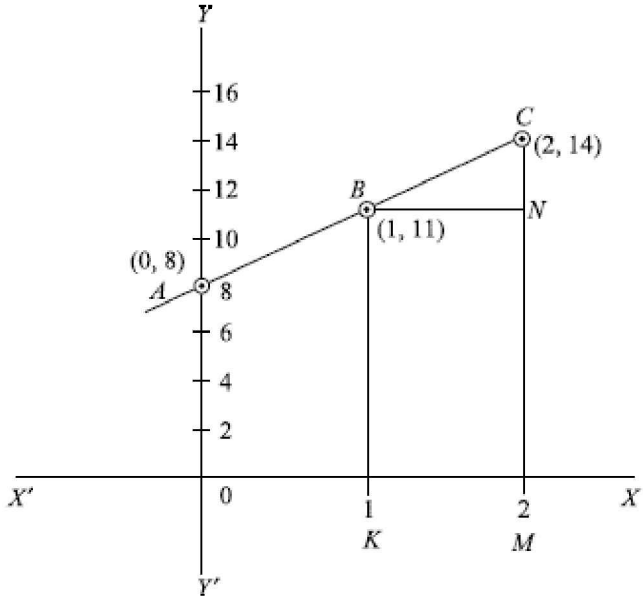


Fig. 2.8

PROBLEMS FOR PRACTICE

1. Draw the graphs and find the slopes:

(a) $2x - y = 3$

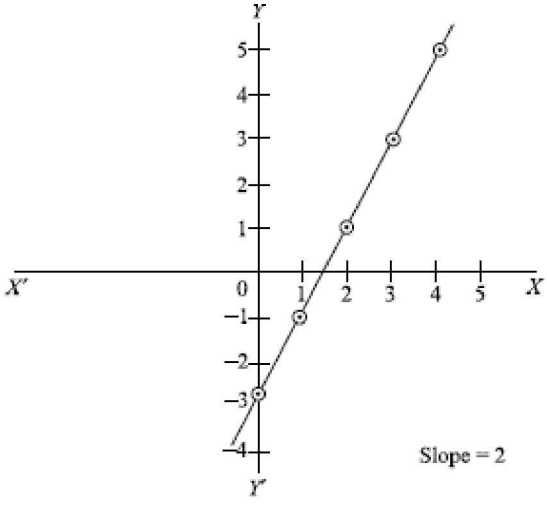
(b) $4x + y = 3$

(c) $x + y = 0$

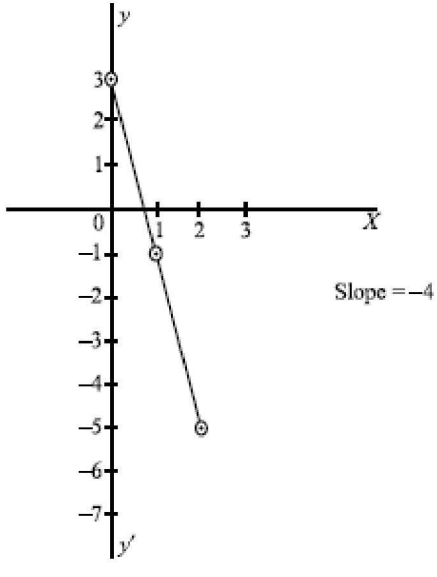
(d) $x - y = 2$

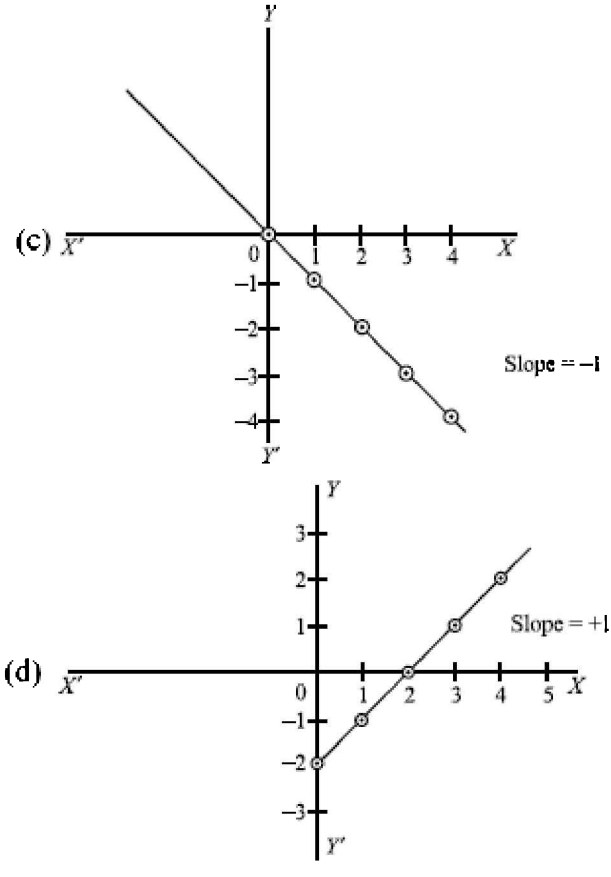
Answers

(a)



(b)





2.5 DIFFERENTIATION

1. Function *When the value of a quantity y depends on another quantity x then y is said to be a function of x.* We represent it as $y = f(x)$
Note that $f(x)$ is a symbol. It is not f multiplied by x.

2. Differential Coefficient The derivative or differential coefficient of y w.r.t. x is denoted by

$$\frac{d}{dx}(y) = \frac{dy}{dx} = \underset{\delta x \to 0}{\text{Lt}} \frac{\delta y}{\delta x}$$

where δx is the small change in the value of x and δy is the corresponding small change in the value of y.

3. Method of Finding Derivative of a Function Let $y = f(x)$ be a derivable function of x. Let x represent any arbitrary but fixed point in the domain of the function. Let δx be the small increment of x and let δy, the corresponding increment of the value of y.

$$\therefore \quad y + \delta y = f(x + \delta x)$$

$$\text{or} \quad \delta y = f(x + \delta x) - f(x)$$

$$\text{or} \quad \frac{\delta y}{\delta x} = \frac{f(x + \delta x) - f(x)}{\delta x}$$

By definition,

$$f'(x) = \underset{\delta x \to 0}{\text{Lt}} \frac{\delta y}{\delta x} = \underset{\delta x \to 0}{\text{Lt}} \frac{f(x\delta x)\ f(x)}{\delta x}$$

It is worthwhile to note that $\frac{\delta y}{\delta x}$ is the quotient of δy and δx but $\frac{dy}{dx}$ is not the quotient of δy and dx.

Instead, $\frac{dy}{dx}$ is to be interpreted as $\frac{d}{dx}(y)$, i.e. differentiation of y w.r.t. x.

(a) Derivative of kx w.r.t. x

Let $y = kx$ …(2.1) where k is any constant.

Let δx be an increment of x and δy, the corresponding increment of y.

$$\therefore \quad y + \delta y = k(x + \delta x) \qquad \ldots(2.2)$$

(2.2) – (2.1) or $y + \delta y - y = k(x + \delta x) - kx$

$$\delta y = k\delta x$$

$$\text{or} \quad \frac{\delta y}{\delta x} = k$$

Taking limits $\delta x \to 0$

$$\underset{\delta x \to 0}{\text{Lt}} \frac{\delta y}{\delta x} = \underset{\delta x \to 0}{\text{Lt}}\ k$$

$$\frac{dy}{dx} = k$$

$$\frac{d}{dx}(kx) = k$$

(b) Derivative of x^n w.r.t. x

Let $y = x^n$ …(2.3) where n is any natural number

Let δx be an increment of x and δy, the corresponding increment of y.

$$y + \delta y = (x + \delta x)^n \qquad \ldots(2.4)$$

(2.4) – (2.3) or $\delta y = (x + \delta x)^n - x^n$

$$\text{or} \quad \delta y = x^n + n_{c_1} x^{n-1}\,\delta x + n_{c_2} x^{n-2}(\delta x)^2 + \ldots + n_{c_n}(\delta x)^n - x^n$$

$$\text{or} \quad \delta y = n x^{n-1}\,\delta x + \frac{n(n-1)}{\lfloor 2} x^{n-2}(\delta x)^2 + \ldots + (\delta x)^n$$

or $$\delta y = \delta x \left[n x^{n-1} + \frac{n(n-1)}{\lfloor 2} x^{n-2}\, \delta x + \ldots + (\delta x)^{n-1} \right]$$

Dividing both sides by δx,

or $$\frac{\delta y}{\delta x} = \frac{\delta x \left[n x^{n-1} + \frac{n(n-1)}{\lfloor 2} x^{n-2}\, \delta x + \ldots + (\delta x)^{n-1} \right]}{\delta x}$$

or $$\frac{\delta y}{\delta x} = n x^{n-1} + \frac{n(n-1)}{\lfloor 2} x^{n-2}\, \delta x + \ldots + (\delta x)^{n-1}$$

or $$\underset{\delta x \to 0}{\text{Lt}} \frac{\delta y}{\delta x} = \underset{\delta x \to 0}{\text{Lt}} \; n x^{n-1} + \frac{n(n-1)}{\lfloor 2} x^{n-2}\, \delta x + \ldots + (\delta x)^{n-1}$$

$$\frac{\delta y}{\delta x}(x^n) = n x^{n-1}$$

$\therefore$ $$\frac{d}{dx}(x^n) = n x^{n-1}$$

(c) Derivative of log x w.r.t. x

Let $y = \log x$ … (2.5)

Let δx be the small increment in x and the corresponding increment in y be δy.

Then $y + \delta y = \log (x + \delta x)$ … (2.6)

(2.6) – (2.5) or $$\delta y = \log (x + \delta x) - \log x$$

or $$\delta y = \log \frac{(x + \delta x)}{x}$$

or $$\frac{\delta y}{\delta x} = \frac{1}{\delta x} \log \left(1 + \frac{\delta x}{x} \right)$$

or $$\frac{\delta y}{\delta x} = \frac{1}{x} \cdot \frac{x}{\delta x} \log \left(1 + \frac{\delta x}{x} \right)$$

or $$\frac{\delta y}{\delta x} = \frac{1}{x} \cdot \log \left(1 + \frac{\delta x}{x} \right)^{\frac{x}{\delta x}}$$

Taking limits,

$$\underset{\delta x \to 0}{\text{Lt}} \frac{\delta y}{\delta x} = \underset{\delta x \to 0}{\text{Lt}} \frac{1}{x} \log \left(1 + \frac{\delta x}{x}\right)^{\frac{x}{\delta x}}$$

$$\frac{dy}{dx} = \frac{1}{x} \underset{\delta x \to 0}{\text{Lt}} \log \left[1 + \frac{\delta x}{x}\right]^{\frac{x}{\delta x}}$$

when $\delta x \to 0$ then $\frac{\delta x}{x} \to 0$

or $$\underset{\frac{\delta x}{x} \to 0}{\text{Lt}} \left(1 + \frac{\delta x}{x}\right)^{\frac{x}{\delta x}} = e$$

or $$\frac{dy}{dx} = \frac{1}{x} \log e$$

$$= \frac{1}{x} \qquad [\because \log e = 1]$$

or $$\frac{d}{dx}(\log x) = \frac{1}{x}$$

(d) Derivative of e^x w.r.t. x

Let $y = e^x$ ... (2.7)

Let δx be an increment of x and δy be the corresponding increment of y.

$$y + \delta y = e^{x+\delta x} \qquad \ldots(2.8)$$

(2.8) − (2.7) or $$\delta y = e^{x+\delta x} - e^x$$

or $$\delta y = e^x \cdot e^{\delta x} - e^x$$

or $$\frac{\delta y}{\delta x} = \frac{e^x \cdot e^{\delta x} - e^x}{\delta x}$$

$$= \frac{e^x (e^{\delta x} - 1)}{\delta x}$$

Taking limits, $\delta x \to 0$

$$\lim_{\delta x \to 0} \frac{\delta y}{\delta x} = \lim_{\delta x \to 0} \frac{e^x (e^{\delta x} - 1)}{\delta x}$$

$$\frac{dy}{dx} = e^x \log e$$

$$\because \lim_{\delta x \to 0} \frac{e^{\delta x} - 1}{\delta x} = \log e$$

$$\frac{dy}{dx} = e^x \qquad [\because \log e = 1]$$

$$\frac{dy}{dx}(e^x) = e^x$$

(e) Derivative of sin x w.r.t. x

Let $y = \sin x$ ... (2.9)

Let δx be an increment of x and δy, the corresponding increment of y.

$\therefore$ $y + \delta y = \sin(x + \delta x)$ ...(2.10)

(2.10) – (2.9) or $\delta y = \sin(x + \delta x) - \sin x$

$$= 2 \cos\left(x + \frac{1}{2}\delta x\right) \sin \frac{\delta x}{2}$$

$$\frac{\delta y}{\delta x} = \frac{2 \cos\left(x + \frac{\delta x}{2}\right) \sin \frac{\delta x}{2}}{\delta x}$$

$$\because \sin C - \sin D = 2 \cos \frac{C + D}{2} \sin \frac{C - D}{2}$$

or

$$\frac{\delta y}{\delta x} = \frac{\cos\left(x + \frac{\delta x}{2}\right) \sin \frac{\delta x}{2}}{\frac{\delta x}{2}}$$

Taking limits,

$$\lim_{\delta x \to 0} \frac{\delta y}{\delta x} = \lim_{\delta x \to 0} \cos\left(x + \frac{\delta x}{2}\right) \lim_{\delta x \to 0} \frac{\sin\frac{\delta x}{2}}{\frac{\delta x}{2}}$$

$$= \cos x \cdot 1 \qquad \because \lim_{\delta x \to 0} \frac{\sin x}{x} = 1$$

$$\therefore \quad \frac{dy}{dx} = \cos x$$

i.e. $$\frac{d}{dx}(\sin x) = \cos x$$

On the lines of sin x, we can find the following derivatives:

$$\frac{d}{dx}(\cos x) = -\sin x \qquad \frac{d}{dx}(\tan x) = \sec^2 x$$

$$\frac{d}{dx}(\cot x) = -\operatorname{cosec}^2 x \qquad \frac{d}{dx}(\sec x) = \sec x \tan x$$

$$\frac{d}{dx}(\operatorname{cosec} x) = -\operatorname{cosec} x \cot x \qquad \frac{d}{dx}(a^x) = a^x \log a \qquad \text{(on the lines of } e^x\text{)}$$

(i) $\frac{d}{dx}(x^7) = 7x^6$ $\quad \left| \because \frac{d}{dx} x^n = nx^{n-1} \right.$

(ii) $\frac{d}{dx}\left(\sqrt{x}\right) = \frac{d}{dx}\left(x^{1/2}\right) = \frac{1}{2}x^{1/2-1} = \frac{1}{2}x^{-1/2} = \frac{1}{2\sqrt{x}}$

(iii) $\frac{d}{dx}(x^2 + 3) = \frac{d}{dx}(x^2) + \frac{d}{dx}(3) = 2x + 0 = 2x$ $\quad \left[\left| \because \frac{d}{dx}(C) = 0 \right. \right]$

(iv) $\frac{d}{dx}(c \cdot v) = c \cdot \frac{d}{dx}(v) = c \cdot \frac{dv}{dx} = c$ $\quad |\because v$ is the function of x

(v) $\frac{d}{dx}(5x^2) = 5\frac{d}{dx}x^2 = 5.2x = 10x$

(vi) $\frac{d}{dx}(\sin 7x) = \cos 7x \frac{d}{dx}(7x) = 7\cos 7x$

(vii) $\frac{d}{dx}[(2x+3)^5] = 5(2x+3)^4 \frac{d}{dx}(2x+3) = 5(2x+3)^4 \cdot 2 = 10(2x+3)^4$

(viii) $\frac{d}{dx}(\log x^2) = \frac{d}{dx}(2\log x) = 2\frac{d}{dx}\log x = \frac{2}{x}$

(ix) $\frac{d}{dx}(e^{5x}) = e^{5x}\frac{d}{dx}5x = 5e^{5x}$

PROBLEMS FOR PRACTICE

1. Find the derivative of the following functions

(a) (i) $\frac{1}{x^2}$

(ii) $x + \frac{1}{x}$

(iii) $x^2 + 2$

(b) (i) $x^{-2} - \frac{x^3}{x^4}$

(ii) $(ax + b)^n$

(iii) $x^{3/2}$

(c) (i) $e^{x^2 + 5}$

(ii) $5x^{2/3}$

(iii) $a^{\sin x}$

(d) (i) $\sin 5x$

(ii) $\cos 5x$

(iii) $\tan 5x$

(e) If $x = a(\theta + \sin\theta)$, $y = a(1 - \cos\theta)$ Find $\frac{dy}{dx}$

$$\left(\text{Hint. } \frac{dx}{d\theta} = (1 + \cos\theta),\ \frac{dy}{d\theta} = a\sin\theta,\ \frac{dy}{dx} = \frac{dy/d\theta}{dx/d\theta} \right)$$

Answers

(a) (i) $\frac{-2}{x^3}$

(ii) $1 - \frac{1}{x^2}$

(iii) $2x$

(b) (i) $\frac{-2}{x^3} + \frac{1}{x^2}$

(ii) $an(ax + b)^{n-1}$

(iii) $\frac{3}{2}x^{1/2}$

(c) (i) $2xe^{x^2 + 5}$

(ii) $5 \times \frac{2}{3}x^{-1/3}$

(iii) $a^{\sin x}\log a\cos x$

(d) (i) $5 \cos 5x$

(ii) $-5 \sin 5x$

(iii) $5\sec^2 5x$

(e) $\tan \dfrac{\theta}{2}$

Some Important Rules of Trigonometry Used in Differentiation and Integration

1. $\sin^2 \theta + \cos^2 \theta = 1$
2. $\sec^2 \theta = 1 + \tan^2 \theta$
3. $\text{cosec}^2 \theta = 1 + \cot^2 \theta$
4. $\sin(A \pm B) = \sin A \cdot \cos B \pm \cos A \sin B$ and $\sin 2A = 2\sin A \cos A$
5. $\cos (A \pm B) = \cos A \cos B \pm \sin A \sin B$ and $\cos 2A = \cos^2 A - \sin^2 A$ or $1 - 2 \sin^2 A$ or $2 \cos^2 A - 1$
6. $\sin C + \sin D = 2\sin \dfrac{C + D}{2} \cos \dfrac{C - D}{2}$
7. $\sin C - \sin D = 2\cos \dfrac{C + D}{2} \sin \dfrac{C - D}{2}$
8. $\cos C + \cos D = 2\cos \dfrac{C + D}{2} \cos \dfrac{C - D}{2}$
9. $\cos C - \cos D = 2\sin \dfrac{C + D}{2} \sin \dfrac{D - C}{2}$
10. $1 + \cos A = 2\cos^2 \dfrac{A}{2}$
11. $1 - \cos A = 2\sin^2 \dfrac{A}{2}$
12. $\tan (A + B) = \dfrac{\tan A + \tan B}{1 - \tan A \tan B}$ and $\tan 2A = \dfrac{2 \tan A}{1 - \tan^2 A}$

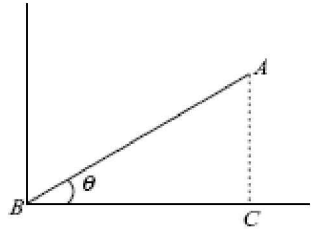


Fig. 2.9 *Right-angled triangle*

$$\sin \theta = \frac{AC}{AB} = \frac{\text{Perpendicular}}{\text{Hypotenuse}}$$

$$\cos \theta = \frac{BC}{AB} \frac{\text{Base}}{\text{Hypotenuse}}$$

Table 2.1 *Trigonometric Values*

θ	0	$\pi/6$	$\pi/4$	$\pi/3$	$\pi/2$
$\sin\theta$	$\sqrt{\frac{0}{4}}$	$\sqrt{\frac{1}{4}}=\frac{1}{2}$	$\sqrt{\frac{2}{4}}=\frac{1}{\sqrt{2}}$	$\sqrt{\frac{3}{4}}=\frac{\sqrt{3}}{2}$	$\sqrt{\frac{4}{4}}=1$
$\cos\theta$	$\sqrt{\frac{4}{4}}=1$	$\sqrt{\frac{3}{4}}=\frac{\sqrt{3}}{2}$	$\sqrt{\frac{2}{4}}=\frac{1}{\sqrt{2}}$	$\sqrt{\frac{1}{4}}=\frac{1}{2}$	$\sqrt{\frac{0}{4}}=0$
$\sin(-\theta)=-\sin\theta$	$\cos(-\theta)=\cos\theta$	$\tan(-\theta)=-\tan\theta$			
$\sin(90°+\theta)=\cos\theta$	$\cos(90°+\theta)=-\sin\theta$	$\tan(90°+\theta)=-\cot\theta$			
$\sin(90°-\theta)=\cos\theta$	$\cos(90°-\theta)=\sin\theta$	$\tan(90°-\theta)=\cot\theta$			
$\sin(180°+\theta)=-\sin\theta$	$\cos(180°+\theta)=-\cos\theta$	$\tan(180°+\theta)=\tan\theta$			
$\sin(180°-\theta)=\sin\theta$	$\cos(180°-\theta)=-\cos\theta$	$\tan(180°-\theta)=-\tan\theta$			
$\sin(270°+\theta)=-\cos\theta$	$\cos(270°+\theta)=\sin\theta$	$\tan(270°+\theta)=-\cot\theta$			
$\sin(270°-\theta)=-\cos\theta$	$\cos(270°+\theta)=-\sin\theta$	$\tan(270°-\theta)=\cot\theta$			
$\sin(360°+\theta)=\sin\theta$	$\cos(360°+\theta)=\cos\theta$	$\tan(360°+\theta)=\tan\theta$			
$\sin(360°-\theta)=-\sin\theta$	$\cos(360°+\theta)=\cos\theta$	$\tan(360°-\theta)=-\tan\theta$			

2.6 MAXIMA AND MINIMA

Maxima is the plural word for maximum values and ***minima*** is the plural word for minimum values. If we draw the graphs of functions, we observe the following maximum and minimum values. (See Fig. 2.10). It represents an arbitrary function, whose graph has been drawn. y_3 is the maximum value of the function corresponding to x_1, and y_4 is the maximum value corresponding to x_3 on the x-axis. Thus, y_3 and y_4 are maxima of the function.

Similarly, $y1$ represents the minimum value of the function corresponding to x_2, and y_2 represents the minimum value corresponding to x_4 on the x-axis. Thus, y_1 and y_2 are the minima of the function.

The following steps are performed to find the maximum and minimum values of a function $f(x)$.

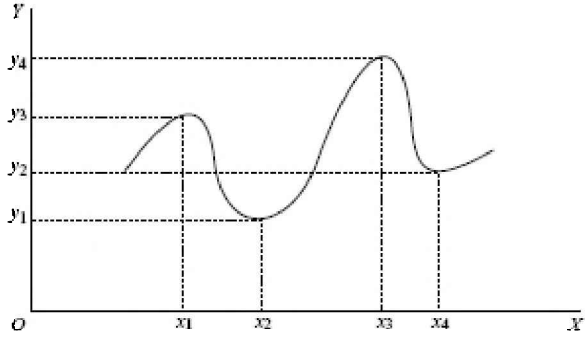


Fig. 2.10 *Maxima and minima*

Step 1 Put the given function = y

Step 2 Calculate $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ for the function.

Step 3 Put $\frac{dy}{dx}$ = 0 and solve the equation, i.e. determine the possible values of x. These are known as ***critical values.***

Step 4 Let one of the values of x be a. Substitute this value for x in the result of $\frac{d^2y}{dx^2}$

If the result is negative, the function has maximum value at $x = a$. Calculate the value of y by putting $x = a$ in the function $f(x)$.

If by putting $x = a$ in the result of $\frac{d^2y}{dx^2}$, we get a positive result, the function has a minimum value at $x = a$. Determine the value of y by putting $x = a$ in $f(x)$.

Step 5 Repeat the above steps for the values b, c, d, … etc. obtained in step 4 (other than a) This is illustrated with the help of the following examples.

Example 9 *Find the maximum and minimum values of the following functions:* $y = x^3 - 6x^2 + 9x + 15$

Solution :

$$y = x^3 - 6x^2 + 9x + 15$$

$$\frac{dy}{dx} = 3x^2 - 12x + 9 \quad \text{or } 3(x^2 - 4x + 3)$$

$$\frac{d^2y}{dx^2} = 6x - 12$$

$$3(x^2 - 4x + 3) = 0 \quad \text{or} \quad 3(x - 1)(x - 3) = 0$$

or $$x = 1 \quad \text{and} \quad x = 3$$

First, take up $x = 1$. Substitute this value in the result of $\frac{d^2y}{dx^2}$, i.e. $(6 \times 1) - 12 = -6$ which is negative.

Therefore, the function has a maximum value at $x = -6$. To find out the maxima, put this value in y, i.e.

$$(1)^3 - 6(1)^2 + 9(1) + 15 = 19$$

Thus, the maximum value of the function is 19.

Now consider the second value of x, i.e. 3 or $x = 3$. Substitute this value in the result of $\frac{d^2y}{dx^2}$

$$6x - 12 \text{ or } (6 \times 3) - 12 = 6$$

This is positive. Therefore, the function has a minimum value at $x = 3$.

Substitute the value in y.

$$(3)^3 - 6(3)^2 + 9(3) + 15$$
$$= 27 - 54 + 27 + 15$$

= 15

Thus, the minimum value of the functions is 15 at $x = 3$

Example 10 *Show that the following functions do not have maxima or minima:*

(a) 2x + 7 (b) log x

Solution:

(a) $y = 2x + 7$

$$\frac{dy}{dx} = 2$$

$$\frac{d^2y}{dx^2} = 0$$

or 2 = 0 which is not possible

(we need to put the result of *dy/dx* equal to zero)

Thus, the given function has no maxima or minima.

(b) $y = \log x$

$$\frac{dy}{dx} = \frac{1}{x} \quad \text{and} \quad \frac{d^2y}{dx^2} = -x^{-2}$$

$\frac{1}{x} = 0$, This is not possible for a finite value of x.

Therefore, the function has no maxima or minima.

Example 11 *Find the maximum and minimum value of the following functions:*

(a) $2x^2 - 3x + 5$

(b) $-5x^2 + 20x + 9$

Solution:

(a) $y = 2x^2 - 3x + 5$

$$\frac{dy}{dx} = 4x - 3 \quad \text{or} \quad x = \frac{3}{4}$$

$$\frac{d^2y}{dx^2} = 4$$

We don't need to substitute the value of x in the result of d^2y/dx^2 as it is already a definite numerical value, i.e. 4. As the value is positive, the function has a minimum value at $x = 3/4$. The value of minima is obtained by substituting $x = 3/4$ in y, i.e.

$$2x^2 - 3x + 5$$

or $$2\left(\frac{3}{4}\right)^2 - 3\left(\frac{3}{4}\right) + 5$$

or $$\left(2 \times \frac{9}{16}\right) - \frac{9}{4} + 5$$

or $$\frac{9}{8} - \frac{9}{4} + 5$$

$$= \frac{31}{8}$$

Thus, the minimum value of the function is $\frac{31}{8}$ at $x = \frac{3}{4}$

(b) $y = -5x^2 + 20x + 9$

$$\frac{dy}{dx} = -10x + 20$$

$$-10x + 20 = 0 \text{ or } x = 2$$

$\frac{d^2y}{dx^2} = -10$ which is negative

(We don't need to substitute the value of x in the result of d^2y/dx^2 *as* it is already a definite numerical.)

Thus, the function has a maximum value at $x = 2$.

The maximum value of the function is obtained as

$$-5(2)^2 + (20 \times 2) + 9$$

$$= -20 + 40 + 9 = 29$$

Thus, the function has a maxima equal to 29 at $x = 2$

PROBLEMS FOR PRACTICE

1. Show that the following functions do not have maxima or minima. (a) $x + 5$ (b) $\log (x + 4)$
2. Find the points of maxima and minima and also find the maximum and local minimum values of the following functions.

   (a) x^2

   (b) $2x^3 - 21x^2 + 36x - 20$
3. Find the critical values for the following functions:

   (a) $x^2 - 2x + 4$

   (b) $x^3 - 1$

Answers

2 (a) Local minimum value = 0 at $x = 0$

(b) Local maximum value = –3 at $x = 1$
Local minimum value = –128 at $x = 6$

3 (a) $x = 1$

(b) $x = 0$

2.7 PARTIAL DIFFERENTIATION

2.7.1 Partial Derivatives of First Order

Let $z = f(x, y)$ be a real-valued function of two independent variables x and y; then $\underset{\delta x \to 0}{\text{Lt}} \frac{f(x+\delta x, y) - f(x, y)}{\delta x}$, if it exists, is called partial derivative of z (or f) w.r.t. x and it is generally denoted by $\frac{\partial f}{\partial x}$ or $\frac{\partial z}{\partial x}$ or $fx(x, y)$ or $f(x)$ or zx- $\frac{\partial f}{\partial x}$ and read as curly f by curly x.

Similarly, $\underset{\delta x \to 0}{\text{Lt}} \frac{f(x, y+\delta y) - f(x, y)}{\delta y}$ if it exists is called partial derivative of z (or f) w.r.t. y and is generally denoted by $\frac{\partial f}{\partial y}$ or $\frac{\partial z}{\partial y}$ or $fy(x, y)$ or fy or zy.

From the above definition, we conclude that if $\mu = f(x, y)$ is a function of two variables x and y then the partial derivative of μ w.r.t. x is the differentiation of μ w.r.t. x taking y as constant.

Example 12 *If $f(x, y) = \log(x^2 + y^2)$, find fx and fy*

Solution: $f(x, y) = \log(x^2 + y^2)$

Differentiating partially w.r.t x, we get

$$f(x) = \frac{\partial f}{\partial x} = \frac{1}{x^2 + y^2} 2x = \frac{2x}{x^2 + y^2}$$

Differentiating partially w.r.t. y we get

$$\frac{\partial f}{\partial y} = \frac{1}{x^2 + y^2} \times 2y = \frac{2y}{x^2 + y^2}$$

Example 13 *Find fx and fy for the function $f(x, y) = y$*

Solution : $f(x, y) = y^x$

Differentiating partially w.r.t. x, we get

$$fx = \frac{\partial f}{\partial x} = y^x \log y \qquad \left[\because \frac{d}{dx}(a^x) = a^x \log a \right]$$

Now differentiating partially w.r.t. y, we get

$$fy = \frac{\partial f}{\partial y} = xy^{x-1} \qquad \left[\because \frac{d}{dx}(x^n) = nx^{n-1} \right]$$

PROBLEMS FOR PRACTICE

1. Find $\frac{\partial \mu}{\partial x}, \frac{\partial \mu}{\partial y}, \frac{\partial \mu}{\partial z}$ if it is given that $\mu = x^2y + y^2z + z^2x$.
2. Find the first-order derivatives of the following functions
   (a) $\frac{1}{\sqrt{x^2 + y^2}}$
   (b) $ax^2 + 2hxy + by^2$

Answers

1. $\frac{\partial \mu}{\partial x} = 2xy + z^2 \quad \frac{\partial \mu}{\partial y} = x^2 + 2yz \quad \frac{\partial \mu}{\partial z} = y^2 + 2zx$
2. (a) $\frac{-x}{(x^2 + y^2)^{3/2}}; \frac{-y}{(x^2 + y^2)^{3/2}}$
   (b) $2(ax + hy); 2(hx + by)$

2.7.2 Partial Derivatives of Higher Order

Since each of the partial derivatives $\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}$, in general, is a function of x and y, so each of them possesses partial derivatives w.r.t. the independent variables x and y.

1. The partial derivative of $\frac{\partial f}{\partial x}$ w.r.t. x is given by $\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial x^2}$ or fxx
2. The partial derivative of $\frac{\partial f}{\partial y}$ w.r.t. y is given by $\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial y^2} = fyy$
3. The partial derivative of $\frac{\partial f}{\partial x}$ w.r.t. y is given by $\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial y \cdot \partial x}$ or fxy
4. The partial derivative of $\frac{\partial f}{\partial y}$ w.r.t. x is given by $\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial x \partial y}$ or fxy

$\therefore \frac{\partial^2 f}{dx^2}, \frac{\partial^2 f}{\partial y^2}, \frac{\partial^2 f}{\partial x \cdot \partial y}, \frac{\partial^2 f}{\partial y \partial x}$ are all called second order partial derivatives.

Example 14 *If* $f = \tan^{-1}\left(\frac{y}{x}\right)$, *verify that* $\frac{\partial^2 f}{\partial y \cdot \partial x} = \frac{\partial^2 f}{\partial x \partial y}$.

Solution : Given

$$f = \tan^{-1}\left(\frac{y}{x}\right) \qquad \ldots(i)$$

Differentiating (i) partially w.r.t. x, we get

$$\frac{\partial f}{\partial x} = \frac{1}{1+(y/x)^2} \cdot \left(\frac{-y}{x^2}\right) = \frac{-y}{x^2+y^2} \quad \ldots(ii)$$

Differentiating (i) partially w.r.t. *y*, we get

$$\frac{\partial f}{\partial x} = \frac{1}{1+\left(\frac{y}{x}\right)^2} \cdot \frac{1}{x} = \frac{x}{x^2+y^2} \quad \ldots(iii)$$

Differentiating (ii) partially w.r.t. *y*. we get

$$\frac{\partial^2 f}{\partial y \cdot \partial x} = \frac{\partial}{\partial y}\left(\frac{-y}{x^2+y^2}\right)$$

$$= \frac{(x^2+y^2)(-1)-(-y)(2y)}{(x^2+y^2)^2}$$

$$= \frac{y^2-x^2}{(x^2+y^2)^2} \quad \ldots(iv)$$

Differentiating (iii) partially w.r.t. *x*, we get

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{x}{x^2+y^2}\right) = \frac{(x^2+y^2)(1)-x(2x)}{(x^2+y^2)^2}$$

$$= \frac{y^2-x^2}{(x^2+y^2)^2} \quad \ldots(v)$$

From (iv) and (v), we get

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}. \text{ Hence the result}$$

PROBLEMS FOR PRACTICE

1. Verify that $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$ when $z = ax^2 + 2bxy + by^2$

1. Verify that $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$ when $z = \log \frac{x^2+y^2}{xy}$

2.8 INTEGRATION

Integration is just the reverse process of differentiation. The purpose of integration is to find out the function whose differential coefficient is given.

The symbol $\int dx$ represents the operation of finding the integral of the function w.r.t. *x*.

Thus, $\int \cos x\, dx = \sin x + C$

$\therefore \dfrac{d}{dx}(\sin x) = \cos x$

where C is called the ***constant of integration***.

Important Integration Formulae

1. $\int x^n\, dx = \dfrac{x^{n+1}}{n+1} + C$ provided $n \neq -1$ as $\dfrac{d}{dx}\left(\dfrac{x^{n+1}}{n+1}\right) = x^n$
2. $\int 1\, dx = x + C$ as $\dfrac{d}{dx}(x) = 1$
3. $\int (\mu + v)\, dx = \int \mu\, dx + \int v\, dx$
4. $\int \dfrac{1}{x}\, dx = \log x + C$ as $\dfrac{d}{dx}(\log x) = \dfrac{1}{x}$
5. $\int a^x\, dx = \dfrac{a^x}{\log_e a} + C$ as $\dfrac{d}{dx}(a^x) = a^x \log a$
6. $\int e^x\, dx = e^x + C$ as $\dfrac{d}{dx}(e^x) = e^x$
7. $\int \cos x\, dx = \sin x + C$ as $\dfrac{d}{dx}(\sin x) = \cos x$
8. $\int \sin x\, dx = -\cos x + C$ as $\dfrac{d}{dx}(\cos x) = -\sin x$
9. $\int \sec^2 x\, dx = \tan x + C$ as $\dfrac{d}{dx}(\tan x) = \sec^2 x$
10. $\int \operatorname{cosec}^2 x\, dx = -\cot x + C$ as $\dfrac{d}{dx}(\cot x) = -\operatorname{cosec}^2 x$
11. $\int \sec x \tan x\, dx = \sec x + C$ as $\dfrac{d}{dx}(\sec x) = \sec x \tan x$
12. $\int \operatorname{cosec} x \cot x\, dx = -\operatorname{cosec} x + C$ as $\dfrac{d}{dx}(\operatorname{cosec} x) = -\operatorname{cosec} x \cdot \cot x$

2.9 DEFINITE INTEGRAL

A definite integral is one whose lower and upper limits are given.

It is denoted by $\int_a^b f(x)\, dx$ and is read the as integral of $f(x)$ w.r.t. x between $x = a$ and $x = b$

If

$$\int f(x)\, dx = g(x)$$

then,

$$\int_a^b f(x)\,dx = [g(x)]_a^b = g(b) - g(a)$$

Example15 *Evaluate* $\int_1^2 x^2\,dx$

Solution: $\int_1^2 x^2\,dx = \left[\frac{x^3}{3}\right] = \frac{2^3}{3} - \frac{(1)^3}{3} = \frac{8}{3} - \frac{1}{3} = \frac{7}{3}$

Example 16 $\int_0^{\pi/4} \sin x \cos x\,dx$

Solution:

$$\int_0^{\pi/4} \sin x \cdot \cos x\,dx = \int_0^{\pi/4} \frac{1}{2}(2\sin x \cdot \cos x)dx$$

$$= \frac{1}{2}\int_0^{\pi/4} \sin 2x\,dx = \frac{1}{2}\left[\frac{-\cos 2x}{2}\right]_0^{\pi/4}$$

$$= \frac{-1}{4}[\cos 2x]_0^{\pi/4}$$

$$= \frac{-1}{4}\left[\cos 2\frac{\pi}{4} - \cos 0\right]$$

$$= \frac{-1}{4}[0-1] = -\frac{-1}{4}\left[\cos\frac{\pi}{2} - \cos 0\right]$$

$$= \frac{1}{4}$$

PROBLEMS FOR PRACTICE

1. Evaluate the following integrals

   (a) $\int_0^{30^\circ} \sin 7x\,dx$ (b) $\int_{15^\circ}^{30^\circ} \cos(4x-3)\,dx$

2. Evaluate $\int (1+\cos x)^{1/2}\,dx$ Hint $\int (1+\cos x) = 2\cos^2\frac{x}{2}$

3. Integrate the following functions w.r.t. x and find within the limits $x = 2$ to $x = 4$.

4. Evaluate the following integrals:

(a) $\int_0^5 \frac{dx}{5^x}$ (b) $\int \sqrt{1+x}\, dx$

Answers

1. (a) 0.2666

   (b) $\frac{1}{4}[\sin 117^\circ - \sin 57^\circ]$

2. $2\sqrt{2}\cos\frac{x}{2}$

3. (a) 60

   (b) 3.448

4. (a) $\frac{1}{5}\log\frac{5}{2}$

   (b) $\frac{2}{3}(1+x)^{3/2} + C$

2.10 FACTORIALS

1. Factorial Notation The continued product of the first n natural numbers, i.e. product of all natural numbers beginning with 1 and ending with n is written as $\underline{|n}$ or $n!$ and read as factorial n.

Thus, $n! = 1.2.3. \ldots n$

or writing the factors in reverse order,

$$n! = n(n-1)(n-2)\ldots 3.2.1$$

For example, $4! = 4.3.2.1 = 24$

$3! = 3.2.1 = 6$

and $0!$ is always equal to 1 (i.e., $0! = 1$)

2. Property of Factorials

$$\begin{aligned} 6! &= 6.5.4.3.2.1 = 6.5! \\ &= 6.5.4! = 6.5.4.3! \\ &= 6.5.4.3.2! \end{aligned}$$

Also, we know that

$$n! = n(n-1)(n-2)\ldots 3.2.1$$

which can be written as $n = n(n-1)!$

or $n = n(n-1)(n-2)!$

or $n = n(n-1)(n-2)(n-3)!$ and so on.

Example 17 *Prove that* $(2n)! = 2^n n! [1.3.5 \ldots (2n-1)]$.

Solution :

$$\begin{aligned}(2n)! &= 1.2.3.4 \ldots (2n-1)\,2n \\ &= (2.4.6 \ldots 2n)\,[1.3.5 \ldots (2n-1)] \\ &= 2n(1.2.3 \ldots n)\,[1.3.5 \ldots (2n-1)] \\ &= 2^n\, n!\,[1.3.5 \ldots (2n-1)]\end{aligned}$$

Hence, the result.

Example 18 *Find the value of* $\frac{11!}{7!\,4!}$.

Solution:

$$\begin{aligned}\frac{11!}{7!\,4!} &= \frac{11.10.9.8.7!}{7!\,4!} \\ &= \frac{11.10.9.8}{4.3.2.1} = 330\end{aligned}$$

PROBLEMS FOR PRACTICE

1. Prove that $12! = 2^6.\ 6!\ (1.\ 3.\ 5.\ 7.\ 9.\ 11)$
2. $(2n)!\ (n-1)! = 2(n!)\ (2n-1)!$ Prove it.
3. Find the value of
   (a) $\frac{8!}{6!}$
   (b) $\frac{10!-9!}{9!}$
4. $\frac{(n+2)!}{n!} = n^2 + 3n + 2$. Prove it.

Answers

3. (a) 56
   (b) 9

2.11 PERMUTATIONS AND COMBINATIONS

2.11.1 Permutation

The different arrangements that can be made with a given number of things taking some or all of them at a time are called permutations.

The symbol ${}^nP_r$ is used to denote the number of permutations of n things taken r at a time.

To Find the Value of ${}^nP_r$ The number of permutations of n things taken r at a time is the same as the number of ways in which r places in a row can be filled with n different things.

Suppose that we have n things. The first place can be filled up by any one of these n things. Thus, there are n ways of filling up the first place.

When the first place has been filled up by any one of the n ways, we are left with $(n-1)$ things and any one of them can be put in the second place. Therefore, the second place can be filled up in $(n-1)$ ways. So by the principle of association, the number of ways of filling up the first two places is $n(n-1)$.

When the first two places have been filled up in any one of the $n(n-1)$ ways then we are left with $(n-2)$ things. So the third place can be filled up in $(n-2)$ ways.

By the principle of association, the number of ways of filling up the first three places is $n(n-1)(n-2)$.

Proceeding in this way, the number of ways in which r places can be filled up is

$$\begin{aligned} {}^nP_r &= n(n-1)(n-2)\ldots \text{ up to } r \text{ factors} \\ &= n(n-1)(n-2)\ldots(n-(r-1)) \\ &= n(n-1)(n-2)\ldots(n-r+1) \end{aligned}$$

Therefore, $${}^nP_r = n(n-1)\ldots(n-r+1)$$

For example, $${}^7P_4 = 7\times 6\times 5\times 4 = 840$$

$${}^5P_4 = 5\times 4\times 3\times 2 = 120$$

when $r = n$ $\quad {}^nP_r = {}^nP_n = n(n-1)(n-2)\ldots$ to n factors

$$\begin{aligned} &= n(n-1)(n-2)\ldots(n-(n-1)) \\ &= n(n-1)(n-2)\ldots 1 \\ &= n! \end{aligned}$$

So, $${}^nP_n = n!$$

Now to prove that

$${}^nP_r = n\times {}^{n-1}P_{r-1} = \frac{n!}{(n-r)!}$$

$$\text{LHS} = {}^nP_r = n(n-1)(n-2)\ldots(n-r+1)$$

$$= \frac{\{n(n-1)(n-2)\ldots(n-r+1)\}\{(n-r)(n-r-1)\ldots 3.2.1\}}{(n-r)(n-r-1)\ldots 3.2.1}$$

$$= \frac{n!}{(n-r)!}$$

$$\text{R.HS} = n\times {}^{n-1}P_{r-1}$$

$$= n\times \frac{(n-1)!}{((n-r)\cdot(r-1))!}$$

$$= \frac{n\cdot(n-1)!}{(n-r)!}$$

$$\therefore {}^nP_r = n\times {}^{n-1}P_{r-1} = \frac{n!}{(n-r)!}$$

$\left[\because \text{We have proved above } {}^nP_r = \frac{n!}{(n-r)!}\right]$

Example 19 *If* ${}^{n-1}P_3 = {}^{n+1}P_3 = 5:12$, *Find the value of n.*

Solution:

$$\frac{{}^{n-1}P_3}{{}^{n+1}P_3} = \frac{5}{12}$$

or $$\frac{(n-1)(n-2)(n-3)}{(n+1)n(n-1)} = \frac{5}{12}$$

Simplifying $$\frac{(n-2)(n-3)}{(n+1)n} = \frac{5}{12}$$

Cross-multiplying, $$12(n^2 - 5n + 6) = 5n(n+1)$$

or $$12n^2 - 60n + 72 = 5n^2 + 5n$$

or $$7n^2 - 65n + 72 = 0$$

or $$n = \frac{65 \pm \sqrt{(-65)^2 - 4(7)(72)}}{2 \times 7}$$

$$= \frac{65 \pm 47}{14} = 8 \quad \text{or} \quad \frac{9}{7}$$

Rejecting $\frac{9}{7}$ as n is a +ve integer.

Hence, $n = 8$

Example 20 *How many words can be formed from the letters of the word DAUGHTER so that the vowels are never together?*

Solution: Total number of letters in the word DAUGHTER is 8. These 8 letters are all different. First of all, let us find those arrangements in which vowels are always together.

When the vowels *A, E, U* are always together, they can be supposed to be put in a bracket and treated as one letter (*A, E, U*). So the number of letters become 6,

i.e. (8 – 3 + 1) (*D, G, H, T, R, (A, E, U)*)

These 6 letters can be arranged in ${}^6P_6$ ways = 6! ways.

Now the three letters in the group (*A, E, U*) can be arranged among themselves in ${}^3P_3$ = 3! ways.

∴ required numbers of such words = 6! 3!

$$= 720 \times 6 = 4320$$

Now total numbers of arrangements of letters of the word DAUGHTER is 8!

∴ Number of words in which vowels are never together

= Total number of words – Numbers of words in which vowels are always together.

= 8! – 4320

= 40320 – 4320 = 36000

Example 21 *Find the value of* ${}^{12}P_4$

Solution :

$$^{12}P_4 = 12 \times 11 \times 10 \times 9$$
$$= 11880$$

Example 22 *In how many ways can the letters of 'Lahore' be arranged?*

Solution: Total number of letters in the word
Lahore = 6
These are all different letters.
∴number of arrangements of these letters taken all at a time, $^6P_6 = 6! = 720$

PROBLEMS FOR PRACTICE

1. Prove that $^{2n}P_n = 1.3.5 \ldots (2n - 1).\ 2^n$
2. In how many ways can 5 English books and 4 Hindi books can be placed on a shelf so that the books in the same language always remain together?
3. How many words can be formed out of the letters of the word 'ORIENTAL' so that no two of the vowels are together?
4. How many different words can be formed with the letters of the word 'LUCKNOW'?
5. Find n if $^{n-3}P_6 : {}^{n-2}P_4 = 14 : 1$

Answers

2. 5! 4! 2!
3. 4! $^5P_4 = 2880$
4. 7! = 5040
5. 4

2.11.2 Combinations

The different selections or groups that can be made out of a given number of things taking some or all of them at a time are called combinations.

The symbol ^nC_r is used to denote the number of combinations of n things taken r at a time.

To Find the Value of ^nC_r The number of combinations of n things taken r at a time is denoted by ^nC_r. Let these combinations be x. Because each combination contains r things and these r things in any one of the combinations can be arranged among themselves in $r!$ ways (as we know by permutations), hence, one combination will give rise to r! permutations. So x combinations will give rise to $x \cdot r!$ permutations.

But the number of permutations of things taken r at a time is ^nP_r.

$$^nP_r = x \cdot r! = {}^nC_r \cdot r!$$

$$^nC_r = \frac{^nP_r}{r!} = \frac{n!}{(n-r)!\,r!}$$

$\therefore$ $$^nC_r = \frac{n!}{r!\,(n-r)!}$$

To prove that $^nC_r = {}^nC_{n-r}$

We know that $^nC_r = \frac{n!}{r!\,(n-r)!}$

Changing r to $n - r$ we get

$$^nC_{n-r} = \frac{n!}{(n-r)!\,(n-(n-r))}$$

$$= \frac{n!}{(n-r)!\,r!}$$

$$^nC_r = {}^nC_{n-r}$$ Hence the result.

Example 23 *Evaluate $^{50}C_{47}$.*

Solution:

$$^{50}C_{47} = {}^{50}C_{50-47} = {}^{50}C_3 = \frac{\lfloor 50}{\lfloor 3 \lfloor 47} = \frac{50 \cdot 49 \cdot 48 \cdot \lfloor 47}{\lfloor 3 \cdot \lfloor 47}$$

$$= \frac{50 \cdot 49 \cdot 48}{3 \cdot 2 \cdot 1} = 19600$$

Example 24 *If $^nC_{10} = {}^nC_{15}$ find the value of $^{27}C_n$*

Solution: Given

$$^nC_{10} = {}^nC_{15}$$

Either $10 = 15$ or $10 + 15 = n$ $\quad \because {}^nC_r = {}^nC_{n-r}$

But $10 = 15$ is impossible.

So $n = 10 + 15$

$\therefore$ $n = 25$

Now we have to calculate $^{27}C_n$, i.e. $^{27}C_{25}$ $\quad \because n = 25$

$$^{27}C_{25} = \frac{27!}{25!\,2!} = \frac{27 \cdot 26 \cdot 25!}{25!\,2!}$$

$$= \frac{27 \cdot 26}{2 \cdot 1} = 351$$

So, $$^{27}C_{25} = 351$$

Example 25 *If $^{n+1}C_{r+1} : {}^nC_r = 11 : 6$ and $^nC_r : {}^{n-1}C_{r-1} = 6:3$; find the values of n and r.*

Solution: $\dfrac{{}^{n+1}C_{r+1}}{{}^{n}C_{r}} = \dfrac{11}{6}$ and $\dfrac{{}^{n}C_{r}}{{}^{n-1}C_{r-1}} = \dfrac{6}{3}$

or $\dfrac{\dfrac{(n+1)!}{(r+1)!\{(n+1)-(r+1)\}!}}{\dfrac{n!}{r!(n-r)!}} = \dfrac{11}{6}$

and $\dfrac{\dfrac{\lfloor n}{\lfloor r \lfloor n-r}}{\dfrac{(n-1)!}{(r-1)!\{(n-1)-(r-1)\}!}} = \dfrac{6}{3} = 2$

or $\dfrac{(n+1)!}{(r+1)!(n-r)!} \times \dfrac{r!(n-r)!}{n!} = \dfrac{11}{6}$ and $\dfrac{\lfloor n}{\lfloor r \lfloor n-r} \times \dfrac{(r-1)!(n-r)!}{(n-1)!} = 2$

or $\dfrac{(n+1)!\,r!}{(r+1)!\,n!} = \dfrac{11}{6}$ and $\dfrac{n!(r-1)!}{r!(n+1)!} = 2$

or $\dfrac{(n+1)n!\,r!}{(r+1)\,r!\,n!} = \dfrac{11}{6}$ and $\dfrac{n(n-1)!(r-1)!}{r(r-1)!(n-1)!} = 2$

or $\dfrac{n+1}{r+1} = \dfrac{11}{6}$ and $\dfrac{n}{r} = 2$

or $6n + 6 = 11r + 11$ and $n = 2r$

or $6(2r) + 6 = 11r + 11$

or $12r + 6 = 11r + 11$

$r = 5$ and $n = 2r = 2 \times 5 = 10$

Hence, $n = 10, r = 5$

PROBLEMS FOR PRACTICE

1. If ${}^{n}P_{r} = {}^{n}P_{r-1}$ and ${}^{n}C_{r} = {}^{n}C_{r-1}$; find n and r
2. If ${}^{18}C_{r} = {}^{18}C_{r-2}$ evaluate ${}^{r}C_{5}$ and ${}^{11}C_{r}$
3. Evaluate (a) ${}^{51}C_{49}$ (b) ${}^{100}C_{96}$
4. Prove that ${}^{2n}C_{n} = \dfrac{2^{n}\,1 \cdot 3 \cdot 5 \ldots (2n-1)}{n!}$

Answers

2. 56, 165
3. (a) 1275
   (b) 3921225

2.12 PROBABILITY

Probability means chance or possibility of occurrence of some event.

1. Experiment An experiment is defined as a process of well-defined outcomes.

2. Random Experiment A random experiment is defined as an experiment in which all possible outcomes are known in advance.

For example, If we toss a coin, we will either get head or tail. or, in throwing of a dice, there are 6 possibilities 1 or 2 or 3 or 4 or 5 or 6.

3. Sample Space The sample space of a random experiment is the set of all possible outcomes.

Table 2.2 *Sample space*

	Random Experiment	Sample Experiment
1.	Throwing of a fair dice	S = {1, 2, 3, 4, 5, 6}
2.	Tossing of a coin	S = {H, T}
3.	Tossing of two coins	S = {HH, HT, TH, TT}
4.	A family of two children	S = {BB, BG, GB, GG}

4. Event An event is a subset of sample space. An event is called a simple event, if it contains only one sample point. In the experiment of throwing a dice, the event A of getting 3 is a simple event.

5. Equalles Likely Outcomes The outcomes of a random experiment are called equally likely, if all of these have equal preferences. In the experiment of tossing of a coin, the outcomes head and tail are equally likely.

6. Exhaustive Outcomes The outcomes of a random experiment are called exhaustive if they cover all the possible outcomes of the experiment. In throwing of a dice, the outcomes 1, 2, 3, 4, 5, 6 are exhaustive.

7. Probability Suppose in a random experiment, there are n equally likely, exhaustive outcomes. Let A be an event and there are m outcomes favourable to the happening of it.

Then the probability $P(A)$ of the happening of the event A is defined as

$$P(A) = \frac{m}{n}$$

or $P(A) = \dfrac{\text{Total no. of favourable cases in the happening of } A}{\text{Total no. of equally likely exhaustive cases}}$

It is clear from the definition that

$$0 \le m \le n \quad \text{or} \quad 0 \le \frac{m}{n} \le 1$$

or $$0 \le P(A) \le 1$$

The number of cases favourable to the non-happening of the event A is $n - m$.

$\therefore$ $$P(\text{not } A) = \frac{n-m}{n}$$

$$= \frac{n}{n} - \frac{m}{n} = 1 - \frac{m}{n}$$

$$= 1 - P(A)$$

$$P(\bar{A}) = 1 - P(A) \qquad (\bar{A} = \text{not } A)$$

or $$P(\bar{A}) + P(A) = 1$$



Fig. 2.11 *Probability in the throwing of dice*

Example 26 *What is the probability of getting an even number in the throw of an unbiased dice?*

Solution: In this experiment, there are 6 equally likely possible outcomes, i.e. {1, 2, 3, 4, 5, 6}. Let A be the event of getting an even number.

$$A = \{2, 4, 6\}$$

$$\text{Favourable cases} = 3$$

$$\text{Total no. of cases} = 6$$

$$P(A) = \frac{3}{6} = \frac{1}{2}$$

Example 27 *Find the probability of getting a 'King' or a 'Queen ' in a single draw from a well-shuffled pack of playing cards.*

Solution : Let A be the event of getting a 'King' or a 'Queen' in the draw.

Number of favourable cases for happing of the event A is

$$4 + 4 = 8$$

Total number of cases = 52

$$P(A) = \frac{8}{52} = \frac{2}{13}$$

Example 28 *Find the probability of getting the sum 10 in a single throw of two dice.*

Solution : Here, S = {(1,1), (1,2), (1,3) … (6,5), (6,6)}

Number of possible outcomes are $6 \times 6 = 36$

Let A be the event of getting the sum 10.

$$A = \{(4,6), (5,5), (6,4)\}$$

Favourable cases = 3

$$P(A) = \frac{3}{36} = \frac{1}{12}$$

PROBLEMS FOR PRACTICE

1. Find the probability of getting a number less than 2 in a single throw of a fair dice.
2. Find the probability of getting no head in a single toss of three coins.
3. A ball is drawn at random from a box containing 4 white, 7 red and 12 black balls. Determine the probability that the ball drawn is red.
4. Find the probability of getting an odd number in a single throw of a fair dice.
5. In a simultaneous toss of two coins, find the probability of getting exactly two heads.

Answers

1. $\frac{1}{6}$
2. $\frac{1}{8}$
3. $\frac{7}{23}$
4. $\frac{1}{2}$
5. $\frac{1}{4}$

2.13 MUTUALLY EXCLUSIVE EVENTS

Two events are said to be mutually exclusive events if both cannot occur together with in the same trial. In the experiment of rolling a dice, the events A = {1, 3} and B = {2, 4, 6} are mutually exclusive events. In the same experiment, the events A = {1, 3} and C = {1, 3, 5, 6} are not mutually exclusive events because if 3 appears on the die it is favourable to both A and C.

1. Addition Theorem (For Mutually Exclusive Events) If A and B are mutually exclusive events associated with a random experiment, then

$$P(A \text{ or } B) = P(A) + P(B)$$

Proof

Let n be the total number of exhaustive, equally likely cases of the experiment.

Let m_1 and m_2 be the number of cases favourable to the happening of the events A and B respectively.

$$P(A) = \frac{m_1}{n}$$

and

$$P(B) = \frac{m_2}{n}$$

As the events are given to be mutually exclusive, so there will be no sample point common to both events A and B.

$\therefore$ the events A or B can happen in exactly $m_1 + m_2$ ways.

$$P(A \text{ or } B) = \frac{m_1 + m_2}{n} = \frac{m_1}{n} + \frac{m_2}{n} \; P(A) + P(B)$$

Hence,

$$P(A \text{ or } B) = P(A) + P(B)$$

2. Addition Theorem (For Non-mutually Exclusive Events) If A and B are two non-mutually exclusive events associated with a random experiment then

$$P(A \text{ or } B) = P(A) + P(B) - P(AB)$$

Proof Let n be the total number of exhaustive and equally likely cases of the experiment.

Let m_1 and m_2 be the number of cases favourable to the happening of the events A and B respectively.

$\therefore$

$$P(A) = \frac{m_1}{n}$$

$$P(B) = \frac{m_2}{n}$$

As the events are given to be non-mutually exclusive, there will be some sample points common to both events A and B.

Let m_3 be the number of common sample points.

$$P(AB) = \frac{m_3}{n}$$

These m_3 sample points are also included in the events A and B separately.

$\therefore$ total number of sample points in A or B

$$= m_1 + m_2 - m_3$$

$$P(A \text{ or } B) = \frac{m_1 + m_2 - m_3}{n} = \frac{m_1}{n} + \frac{m_2}{n} - \frac{m_3}{n}$$

$$= P(A) + P(B) - P(AB)$$

Example 29 *The probability that a company executive will travel by bus is 2/3 and that he will travel by train is 1/5. Find the probability of his travelling by bus or train.*

Solution : Let A = the event that the company executive travels by bus

$$P(A) = 2/3$$

Let B = the event that the company executive travels by train

$$P(B) = \frac{1}{5}$$

Events in this question are mutually exclusive because either the person can travel by bus or by train.

∴ the probability of his travelling by bus or by train.

$$P(A \text{ or } B) = P(A) + P(B) = \frac{2}{3} + \frac{1}{5} = \frac{13}{15}$$

Example 30 *One number is drawn from numbers 1 to 150. Find the probability that it is either divisible by 3 or 5.*

Solution:

Here,

$$S = \{1, 2, 3\ldots, 149, 150\}$$

A = the event that the number is divisible by 3

$$A = \{3, 6, 9, \ldots, 147, 150\}$$

$$P(A) = \frac{50}{150}$$

B = The events that the number is divisible by 5.

$$B = \{5, 10, 15, \ldots, 145, 150\}$$

$$P(B) = \frac{30}{150}$$

The events are not mutually exclusive because some points are common to both A and B.

The common points are 15, 30, 45, …, 150.

So,

$$AB = \{15, 30, 45, \ldots, 135, 150\}$$

$$P(AB) = \frac{10}{150}$$

So by the addition theorem,

$$P(A \text{ or } B) = P(A) + P(B) - P(AB)$$

$$= \frac{50}{150} + \frac{30}{150} - \frac{10}{150} = \frac{70}{150} = \frac{7}{15}$$

Hence, the result.

PROBLEMS FOR PRACTICE

1. A bag contains 30 balls numbered from 1 to 30. One ball is drawn at random. Find the probability that the number of the ball is a multiple of 5 or 6.

2. Find the probability that a card drawn from a pack of playing cards is either a king or spade.
3. A box contains 4 red balls, 4 green balls and 7 white balls. What is the probability that a ball drawn is either red or white?

Answers

1. $\frac{1}{3}$
2. $\frac{4}{52}+\frac{13}{52}-\frac{1}{52}$
3. $\frac{11}{15}$

2.14 INTRODUCTION TO COMPUTERS

1. Definition A computer is an electronic device which is able to process unmeangiful raw data into meaningful information.

This raw data is called, ***Input*** and the generated information is called ***output*** in computer terminology.

Advantages of Computers

1. ***Fast speed*** Computers work at a fast speed, such that the calculations are complete in milliseconds or microseconds.
2. ***Storage capacity*** Computers have memory to store large data which can be retrieved at any desired time.
3. ***Accuracy*** Computers produce errors when the instructions given to then are wrong. Otherwise they produce results with amazing accuracy.
4. ***Versatility*** Truly, computers are versatile in their working as a variety of jobs can be done efficiently. Multiple tasks on computers from searching to mailing to listening to music can be achieved.
5. ***Reduced paperwork*** Computers store all data on hard disks. This data can be retrieved at any time. It has thus done away with reams of paper which were earlier used to keep records.
6. ***Reduction in manpower*** As computers are very fast in processing data, banks, industries and other offices have been able to reduce their manpower costs.

2. Analog vs Digital An analog device deals with the continuous measurement, recording or processing of information.

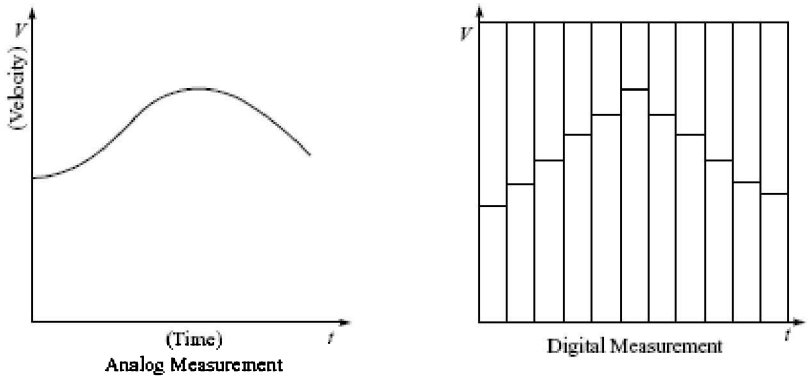


Fig. 2.12 *Analog and digital measurement*

A speedometer is an analog device which measures the speed of a vehicle continuously. Similarly, a slide-rule is an analog computing device.

A ***digital*** device deals with discrete samples of information. Both types of information can be converted to another with sufficient accuracy using either ADC (Analog to Digital Converter) or DAC (Digital to Analog Converter).

All modern computers are digital in nature. They require digital input and can only generate digital output. Any interfacing with an analog input device requires use of ADC circuits. Similarly, to produce an analog output, DAC circuits are required.

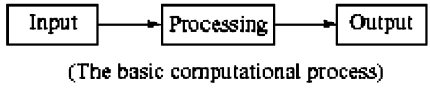


Fig. 2.13 *The basic computational process*

2.15 COMPONENTS OF A COMPUTER

A computer system is made up of three basic components:

1. Input devices
2. Output devices
3. Central Processing Unit (CPU)

2.15.1 Input Devices

It provides data for the computer to operate upon. Some commonly used input devices are

1. Keyboard (to enter data manually)
2. Mouse (to re-position the cursor on the screen)

The ***keyboard*** allows the entry of textual information. It has keys for characters (letters, numbers, and punctuation marks) and special commands. Pressing the keys tells the computer what to do or what to write. The ***mouse*** has a special ball that allows selection of a point on the screen by moving a screen cursor to the point and pressing the mouse button. Alternatively, devices to the mouse are tracker balls, light pens and touch-sensitive screens. Other types of input devices allow you to put images into the computer like ***scanner*** and ***digital camera.***

Besides these, there could be other specialised input devices, providing information about industrial automation system, control system to the computer, etc.



Fig. 2.14 *Input devices*

2.15.2 Output Devices

These are used to view or store the generated information. Some commonly used output devices are

1. Monitor (a TV screen to view results)
2. Printer (to print the results)
3. Speakers (outputs the sound)

The ***monitor*** is a cathode ray tube device like a TV which displays text and graphics. It allows you to 'see' what you and the computer are doing together. A ***printer*** is another common part of computer system. It takes computer data and generates a hard copy of that data. The most commonly used printers are the inkjet printer and laser printer. ***Speakers*** are output devices that allow you to hear sound from your computer. They are just like stereo speakers.



Monitor



Printer

Fig. 2.15 *Output devices*

2.15.3 Central Processing Unit (CPU)

The CPU is the brain of a computer. It is responsible for converting the raw data into meaningful information based on certain instructions. These instructions are called programs. All processing and calculations take place here. This is further divided into three parts.

1. Arithmetic and Logical unit (ALU) It performs all the mathematical functions of addition, subtraction, division and multiplication. Besides this, it performs logical operations like *greater than, less than* and *equal to.* A combination of these basic functions makes it possible for the A.L.U. to solve any kind of computer numerical problems.

2. Memory The computer requires a set of instructions and input data to produce results. In this computational process, it may also generate temporary data. A memory unit is required to store this data as well as the generated result until it can be passed on to the output device.

The memory is further classified into two types.

(a) Primary Memory The memory which resides inside the computer system (CPU) is known as primary memory It is further classified into two types.

(i) RAM (Random Access Memory) It is a dynamic memory, which can store temporary data created during the processing of a computer program. The data can be erased and re-written any number of times. RAM is volatile in nature. As soon as the power supply of the computer is turned off, the content stored in this type of memory will be erased. Essentially, more RAM in a computer system means faster processing.

(ii) ROM (Read Only Memory) This type of memory is used to store data, which is permanent in nature. This includes configuration data used to start a computer (BIOS—Basic Input Output System). Such information is related to hardware present in the system and does not change. Data stored in ROM cannot be erased or re-written.

(b) Secondary Memory Secondary memory residues outside the computer system (CPU). It is used to permanently store large amounts of data. Large amount of input data and the programs/instruction required to process this data into information, both reside on the secondary memory and can be accessed any time later. Data on the secondary memory has to be transferred to the primary memory (RAM), for the computer to utilise it.

The various types of secondary memory are floppy disk, hard disk and computer disk (CD). Some devices which were earlier in use were punched cards, magnetic tapes and magnetic

drums.

(c) Memory Sticks (Pen Drives) These are the latest memory devices. They are sleek, reliable and portable and have become a common medium to save and share data between laptops, personal computers, LCD projections and digital cameras. These memory sticks are available in storage capacity of 4 GB, 8 GB, etc

3. Control Unit It controls the functioning of the CPU. The flow of data between the ALU and memory is controlled by the control unit.



Fig. 2.16 *Memorystick*

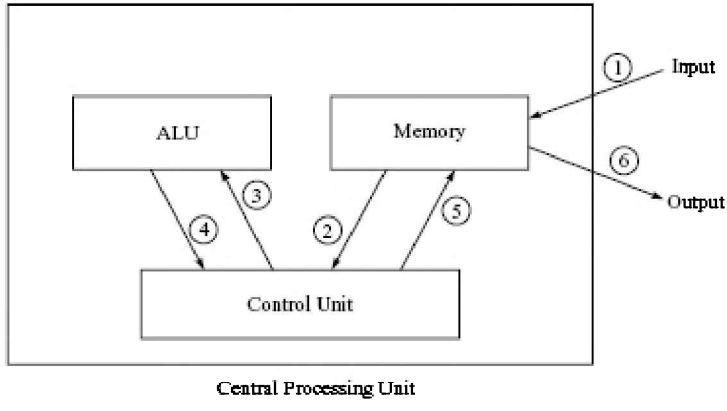


Fig. 2.17 *Central Processing Unit (CPU)*

It passes the input data present in the memory to the ALU for processing. Once the data is processed, it sends the generated information to the memory so that it can be passed on to the output devices.

2.16 HARDWARE AND SOFTWARE

Hardware is a collective term used for all the physical parts of a computer which we can see and touch. Hardware consists of the monitor, keyboard, mouse, internal parts of the computer like processor chips, Memory chips and other Integrated Circuits (I.Cs).

Software is set of programs/instructions required by the hardware of a computer to perform the desired data-processing functions. Software can be classified further into

1. System software
2. Application software
3. Utility programs

1. System Software Consists of programs that are required for the functioning of the computer system. The following can be the examples of system software.

(a) Operating System This software controls the loading of instructions stored in the disk (secondary memory) into the primary memory. The other components of OS help in controlling the overall flow of data to various parts of a computer. If also helps in proper functioning of various peripheral devices like printers, modems, etc. The most popular operating systems are Windows, Unix, Linux and MS-DOS.

(b) Instruction Interpreters (Languages) These sets of programs understand instructions written in English-like language and convert them into machine language (binary language) which the computer understands. If they convert programs written in English-like languages (called high-level languages) into machine language, line by line, they are called ***interpreters.*** If they convert the whole program together and then execute it, they are called ***compilers.*** Some of the interpreted languages are Basic, Java, some of the complied languages are C^{+}, C^{++}, Pascal.

Internally, all the programs are converted to an intermediate language called *assembly language* before getting converted to machine language. The program that converts assembly-language programs to machine language is called an ***assembler.***

2. Application Software These are sets of programs written to solve specific problems. These programs are specially written for applications like railway reservation, library management, weather forecasting, etc.

3. Utility Programs These are general-purpose programs written to store commonly faced problems/functions. These could be word-processing software (for creating a combination of text and graphics), photo-editing software, software for playing music on a computer, anti-virus software, etc.

2.17 BINARY SYSTEM

All information inside the computer and on external storage devices is represented in a form related to the binary number system. ***Binary is a number system which uses the base 2 instead of the base 10*** in the decimal system that is used in normal working. In the decimal system, a position number system is used which allows all numbers to be expressed using only the digits 0 → 9. Successive digits from the digit represent the number of the corresponding power of 10. Thus, 123 in decimal is

$$1 \times 10^2 + 2 \times 10^1 + 3 \times 10^\circ$$

that is, one hundred, plus two tens plus three units. But the binary number system builds all numbers from the bits 0 and 1, and power of 2.

101 in the binary number system represents the number $1 \times 2^2 + 0 \times 2^1 + 1 \times 2^\circ$ having value equal to 5 in the decimal system. The binary system allows all computation inside the computer to take place using cheap two-state electronic devices.

Modern computers organise information into small units called ***bytes*** which hold eight ***bits,*** each bit representing 0 or 1. Each byte may hold a single character of text or a small integer. Large numbers, computer instructions and character strings occupy several bytes.

Binary Arithmetic All digital computers represent data as a collection of bits. A bit is the smallest possible unit of information It can be in one two states—off or on, 0 or 1.

1 Bit ☐

can be 0 or 1

If one bit has two different states, how many states do two hits have? The answer is four. Likewise, three bits have eight states as represented bellow:

2 Bits = 4 States

0	0	0	1	1	0	1	1

3 Bits = 8 states

0	0	0	0	0	1	0	1	0	0	1	1
1	0	0	1	0	1	1	1	0	1	1	1

A common and convenient grouping of bits is the ***byte*** or ***octet,*** composed of eight bits. If two bits have four combinations, and three bits have eight combinations, how many combinations do eight bits have?

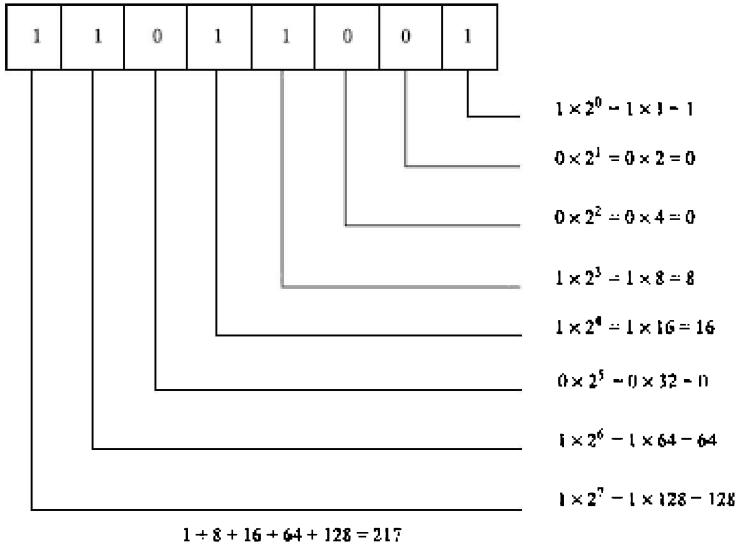
If you don't want to write out all possible byte patterns, just multiply eight twos together—one two for each bit, i.e.

$$2^8 = 256$$

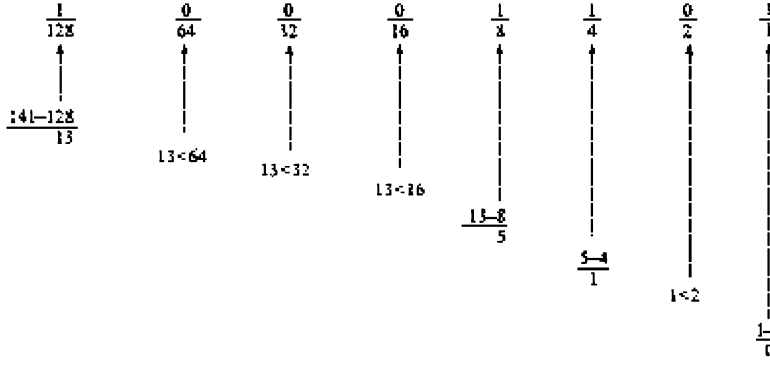
So, a byte has 256 possible states.

1 Byte = 8 Bits ☐☐☐☐☐☐☐☐

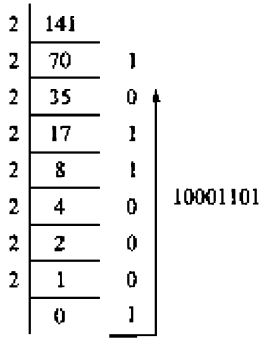
If a byte has 256 possible states, its exact state can be represented by a number from 1 to 256. However, since zero is a very important number, a byte is more typically represented by a number from 0 to 255. This is very common with bit pattern, 00000000 representing zero, and bit pattern 11111111 representing, 255. The numbers matching these two patterns, and everything in between, can be computed by assigning a weight to each bit, multiplying each bit's value (0 or 1) by its weight, and then adding the totals. For example, here's how 217 is represented as 11011001 in binary.



To convert a number from decimal to binary, begin at the leftmost bit position (128). If the number is larger than or equal to the bit's weight, write a 1 larger in the bit position, subtract the bit's weight from the number, and continue with the difference. If the number is less than the bit's weight, write a 0 in the position and continue without any subtraction. Here's an illustration of converting 141 to binary.



Another way of doing conversion from decimal to binary is to repeatedly divide the decimal number by 2, keeping only the whole part and noting down the reminder at each step, unit we reach zero. At the end of this, we have binary representation of the integer by reading the remainders in reverse order.



2.18 BINARY ARITHMETIC

1. Binary Addition we perform binary addition in the same way as we perform addition with decimal numbers. The following examples will illustrate.

Example 31 *Compute* $(1010)_2 + (1111)_2$

Solution: $(1010)_2 + (1111)_2 = (?)_2$

	1	1	1	⟶	carry
Augend		1	0	1	0
Addend		1	1	1	1
+					
	1	1	0	0	1

We start the addition from the RHS as we do in the decimal system. As soon as the sum becomes two or more, we carry 1 to the next position on the left and continue addition.

2. Binary Subtraction This is also performed in the same way as we do in the decimal System. While subtracting, a borrow is required when subtracting 1 from 0. In such a case, when 1 is borrowed from higher column on the LHS, the difference is also 1. The following example will illustrate.

Example 32 *Compute* $(1100)_2 - (11)_2$

Solution: $(1100)_2 - (11)_2 = (?)_2$

	1	1	0	0
−	0	0	1	1
	1	0	0	1

As in the decimal system, we start subtraction from the RHS. We need to borrow from the second column from the RHS. But the upper number in the second column is already 0. Thus, it needs to borrow from the third column from the RHS. It may be assumed that the second column borrows from the third column. The number in the third column becomes 0. In the second

column, it becomes 2, out of which 1 is borrowed by the number in the first column. The difference in the first column will be (2 – 1), i.e. 1. Now, 1 is left in the second column. The difference in the second column will be (1 – 1), i.e. 0. The upper number in the third column is now 0. Therefore, the difference in the third column will be (0 – 0), i.e. 0.

3. Binary Multiplication Binary multiplication is also similar to multiplication in the decimal system. The following example will illustrate.

Example 33 *Compute* $(1101)_2 \times (101)_2$

Solution:

$$\begin{array}{rrrrrrr} & & & 1 & 1 & 1 & 1 \\ \times & & & & 1 & 0 & 1 \\ \hline & & & 1 & 1 & 0 & 1 \\ & & 0 & 0 & 0 & 0 & \times \\ & 1 & 1 & 0 & 1 & \times & \times \\ \hline 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ \hline \end{array}$$

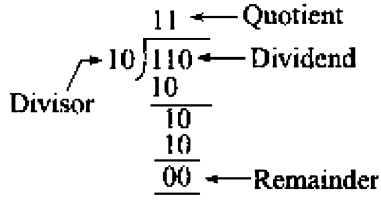
4. Binary Division Binary division is performed by successive subtraction of the division from the dividend. The quotient bits are thus framed. The following rules are obeyed:

$$0 \div 1 = 0$$
$$1 \div 1 = 1$$

Division by 0 has no meaning.
The following example will illustrate.

Example 34 *Compute* $(110)_2 \div (10)_2$

Solution:



Thus

$$(110)_2 \div (10)_2 = (11)_2$$

2.19 OPERATING SYSTEM

An operating system is a layer of software which takes care of technical aspects of a computer's operation. It shields the user of the machine from the low-level details of the machine's operation and provides frequently needed facilities. There is no universal definition of what an operating system is. You can think of it as being the software which is already installed on a machine, before you add anything on your own. Normally, the operating system has a number of

key elements:

1. A technical layer of software for driving the hardware of the computer, like disk drives, the keyboard and the screen.
2. A file system which provides a way of organising files logically.
3. A simple command language which enables users to run their own programs and to manipulate their files in the same way.
4. Some operating systems also provide text editors, compilers, debuggers and a variety of other tools. Since the operating system *(OS)* is in charge of a computer, all requests to use its resources and devices need to go through the OS. An *OS* therefore, provides legal entry points into its code for performing basic operations like writing to devices.

An operating system may be classified by how many tasks it can perform 'simultaneously'. and by how many users can be using the system 'simultaneously'. That is, single-user or multi-user and single tasking or multi-tasking.

1. Single-user Operating System We are all familiar with the concept of sitting down at a computer system and writing documents or performing some dask. Operating systems such as Windows 95, Windows NT, Workstation and Windows 2000 Professional are essentially single-user operating systems. They provide you the capability to perform tasks on the computer system such as writing programs and documents, printing and accessing files. In essence, a single-user operating system provides accesses to the computer system by a single user at a time. If another user needs access to the computer system, he must wait till the current user finishes what he is doing and leaves.

Students in computer labs at colleges and universities often experience this. You might also have experienced this at home, where you want to use the computer but someone else is currently using it. You have to wait for them to finish before you can use the computer system.

2. Multi-user Operating System A multi-user operating system lets more than one user access the computer system at one time. Access to the computer system is normally provided via a network, so that users access the computer remotely using a terminal or other computer.

In the early days of large multi-user computers, multiple terminals (keyboards and associated monitors) were provided. These terminals sent their command to the main multi-user computer for processing and the results were then displayed on the associated terminal monitor screen. Terminals were hard-wired directly to multi-user computer system.

Today these terminals are generally personal computers and use a network to send and receive information to the multi-user computer system. Examples of multi-user operating systems are Unix, Linux (a Unix clone) and mainframes such as the IBM A5400.

The operating system for a large multi-user computer system with many terminals is much more complex than a single-user operating system. It must manage and run all user requests, ensuring they do not interfere with each other.

Advantages and Disadvantages of Multi-user Operating Systems The advantages of having a multi-user operating system is that it lets a number of users share the very expensive hardware resources. Since the resources are shared, they are more likely to be in use than sitting idle and being unproductive.

One problem with a multi-user computer system is that as more people access it, the performance becomes slower and slower. Another disadvantage is the increased cost of memory devices, as the multi-user operating system requires a lot of a risk space and memory. In addition, the actual software for multi-user operating systems tend to cost more than single-user operating systems.

3. Multi-tasking Operating Systems A multi-tasking operating system provides the

ability to run more than one program at a time. For example, a user could be running a word-processing package, printing a document, copying files to the floppy disk and backing up selected files to a tape unit. Each of these tasks the user is doing appears to be running at the same time.

A multi-tasking operating system has the advantage of letting the user do more than one task at a time, so this leads to increased productivity. The disadvantage is that more the programs run by the user, more the memory required.

2.20 COMPUTER PROGRAMMING

Writing software or computer programs is a lot like writing down the steps it takes to do something. But, if what you need to do is not obvious, programming will challenge you like when you are solving puzzles.

A computer is very dumb. It does exactly what you tell it to do, which is necessarily what you wanted. Programming will help you learn the importance of clarity of expression.

These days, most people don't need to know how a computer works. Most people can simply turn on a computer and point the mouse at some little graphical image on the display, double-click the left mouse button, and a computer program starts up (like a Web browser); and, this is all they need to know about their computer.

To learn how to write computer programs, you need to know a little bit about how a computer works. Your job will be to instruct the computer to do things. These lists of instructions that you will write are computer programs, and the stuff that these instructions manipulate are different types of objects.

Basically, a computer perform operations on objects. A microprocessor, which is the heart of a computer, is really primitive but very fast. It takes a group of binary numbers representing parts of objects and moves them around, adds pairs together, subtracts one from another, compares a pair, etc.

Computers manipulate numbers, symbolic information (think characters), visual things (images), sound (MP3) and set of instructions (the computer's native language). As an example, computer displays consists of a bunch of coloured points called ***pixels.*** A pixel is an object. It has a position which consists of the row and column it is in. Its colour is specified as three numbers called RGB (Red, Green, Blue) values. So, like pixels are used to compose graphics and images, there are also standard representations for the other things: numbers, characters, sound and the computer's instructions. At the lowest level, everything is a bunch of ones and zeros (binary number).

4. Programming Languages (The Microprocessor's Language) Just like we have many different languages in use throughout the world for us humans to communicate with, there are different languages that we use to communicate with a computer. Computer languages are used to tell the computer what to do, you instruct it.

If you instructed a computer in its native language (machine language), you would have to write instructions in the form of binary numbers. This is very, very hard to do. Although, the pioneers of computers did this, no one does this these days.

One step above machine language is assembler language. In an assembler, the operations that the microprocessor knows how to do are given names. Addresses in memory can also be given meaningful names. This is a big step over binary, but still too tedious to do any large software program with. If still has its place for little pieces of software that need to interact directly with the microprocessor and/ or those that are executed many times. Here is an example of DEC system-10 assembler language that

1. Adds two numbers together,
2. Adds in a third number if it is greater than zero, and

3. Stores the result in a third position.

Table 2.3 *Assembly-language code*

Op. code	Accumulator	Operand
Move	T_1	Number 1
Add	T_1	Number 2
Skiple		Number 3
Add	T_1	Number 3
Move	T_1	Result

2. Programming Languages (High-Level Languages) Most software written today is in high-level languages. There are many and some are quite old. COBOL, FORTRAN, and Lisp were written in the 1950s. Higher-level languages make it easier to describe the pieces of a program you are creating. They abstract away the specifics of the microprocessor in your computer. Most come with large sets of common stuff you need to do.

High-level language programming does not require an initimate knowledge of the internal structure of the computer and can be ported over different computer architectures. High-level language programs are processed by a program known as compiler, which translates the high-level language program into an equivalent machine-language program. Thus, if a compiler was available for each machine architecture then a program could be run on any computer without change.



Fig. 2.18 *Computer programmers at work*

At the moment, there are several internationally standardised languages as given in the table below which are popular.

Table 2.4 *High-level languages*

Language	Application Area

COBOL	Business application
FORTRAN	Engineering and scientific calculations
C	General-purpose language
Prolog	Artificial intelligence
Lisp	Artificial intelligence
C++	Object-oriented version of C
Java	Object-oriented language widely used on the Web

Most popular high-level languages have been standardised by one or the other international body. Thus, if programs are written to conform strictly to the standard then they should execute correctly on any architecture for which there is a standard conforming compiler.

SUMMARY

1. The logarithm of a number with respect to a given base is the power to which the base must be raised to represent the number.
2. In Neparian logarithm, the base is *e* while in common logarithm, the base is 10.
3. The logarithm of a number consists of two parts. The integral part is called *characteristic* and the decimal part is called *mantissa.*
4. The curve of a function is sketched by plotting the value of *y* corresponding to different values of *x* and joining these points.
5. A *linear equation* is of the form $ax + by + c = 0$. In order to find the slope of the curve, we convert it into the form $y = mx + c$ where *m* is the slope of the line.
6. The *derivative* or differential coefficient of *y* w.r.t. *x* is denoted by
$$\frac{d(y)}{dx} = \underset{\delta x \to 0}{\text{Lt}} \frac{\delta y}{\delta x}$$
7. In a right-angled triangle, with the hypotenuse inclined at an angle of θ to the base,
$$\sin\theta = \frac{\text{Perpendicular}}{\text{Hypotenuse}} \text{ and } \cos\theta = \frac{\text{Base}}{\text{Hypotenuse}}$$
8. To determine the *maxima* and *minima* of a function $y = f(x)$, determine dy/dx and d^2y/dx^2. Determine the possible values of *x* by putting $dy/dx = 0$. Substitute these values one by one in the result of d^2y/dx^2. If the result is negative, the function has a maximum value at that value of x. If the result is positive, the function has a minimum value at that value of *x*.
9. *Integration* is just the reverse process of differentiation. A *definite integral* is one whose lower and upper limits are given.
10. The continued product of the first *n* natural numbers, i.e. product of all natural numbers beginning with 1 and ending with *n* is written as $\lfloor n$ or *n*! and read as *factorial n.*
11. The different arrangements that can be made with a given number of things taking some or all of them at a time are called *permutations.*

12. The different selections or groups that can be made out of a given number of things taking some or all of them at a time are called *combinations*.
13. The chance or possibility of occurrence of an event is called *probability*.
14. The *computer* is an electronic device which is able to process unmeaningful raw data into meaningful information.
15. Fast speed, storage capacity, accuracy, versatility, reduced paperwork and reduction in manpower are some of the *advantages* of computers.
16. A *computer system* is made up of three basic components, viz. input devices, output devices and central processing unit.
17. *Memory* of a computer consists of primary memory (RAM and ROM) and secondary memory.
18. *Software* can be clarified as system software, application software and utility software.
19. The information inside the computer and external storage devices is represented in a form related to the *binary number* system. Binary is a number system which uses the base 2 instead of the base 10.

EXERCISES

Based on Different University Papers
Objective Questions
(A) Fill in the Blanks

1. If $N = a^x$; then $\log_a N$ is equal to_____
2. The decimal part of logarithm of a given number is called_____
3. Derivative of e^x w.r.t. x is_____
4. $\cos (180 + \theta)° =$_____
5. $\int_1^2 x^2 dx$ is equal to _____
6. How many different words can be formed with the letters of the word 'LUCKNOW'?
7. A device which deals with the continuous measurement, recording or processing of information is called _____ device.
8. The CPU in a computer is responsible for converting raw data into_____based on certain instructions
9. _____number system uses the base 2 instead of 10 in decimal system that is used in normal working.
10. High-level language programs are processed by a program known as_____which translates the highlevel language program into machine-language program.

(B) Multiple-Choice Questions

1. $\log_a 1$ is equal to

   (a) 0

   (b) 1

(c) ∞

(d) 10

2. $\log_a m$ is equal to

(a) $\log_a m \times \log_b^a$

(b) $\log_b^m \times \log_a^b$

(c) $\log_m^b \times \log_a^b$

(d) $\log_m^b \times \log_a^b$

3. Characteristic of log 0.5828 is

(a) –2

(b) 1

(c) $\overline{2}$

(d) $\overline{1}$

4. For the curve $y = x^3 + 1$, the values of y corresponding to values of x as –2 and 2 are

(a) 7, –9

(b) –3, 6

(c) –7, 9

(d) 6, –3

5. Slope of the line $2x - y = 3$ is

(a) –2

(b) –1/2

(c) 1/2

(d) 2

6. Derivative of $x + \frac{1}{x}$ w.r.t. x is

(a) $1 - \frac{1}{x^2}$

(b) $1 + \frac{1}{x^2}$

(c) $-1 + \frac{1}{x^2}$

(d) $-1 - \frac{1}{x^2}$

7. Expression for $\sin C - \sin D$ is

(a) $2\cos\frac{C-D}{2}\sin\frac{C+D}{2}$

(b) $2\cos\frac{C+D}{2}\sin\frac{C-D}{2}$

(c) $2\sin\frac{C+D}{2}\sin\frac{C-D}{2}$

(d) $2\cos\frac{C+D}{2}\cos\frac{C-D}{2}$

8. Integration of x w.r.t. x within the limits $x = 2$ to $x = 4$ has the value

   (a) 60

   (b) 40

   (c) 20

   (d) 10

9. The value of $\frac{8!}{6!}$ is

   (a) 224

   (b) 28

   (c) 112

   (d) 56

10. The number of ways 5 English books and 4 Hindi books can be placed on a shelf so that the books on the same language always remain together is

    (a) 5! 4! 3!

    (b) 5! 4! 2!

    (c) 4! 3! 2!

    (d) 5! 3! 2!

11. The decimal equivalent of $(11001)_2$ is

    (a) 25

    (b) 50

    (c) 35

    (d) 15

12. A general-purpose computer language is

    (a) Prolog

    (b) COBOL

    (c) *C*

    (d) FORTRAN

13. Binary presentation of the decimal number 141 is

    (a) 10110001

    (b) 11110001

    (c) 10001111

    (d) 10001101

14. General-purpose programs written to solve commonly faced problems are called

    (a) system software

(b) application software
(c) utility programs
(d) none

15. The unit that performs the mathematical functions is
    (a) ALU
    (b) CPU
    (c) RAM
    (d) ROM

Answers

(A) Fill in the Blanks

1. x
2. mantissa
3. e^x
4. $-\cos \theta$
5. 7/3
6. 5040
7. analog
8. meaningful information
9. binary
10. compiler

(B) Multiple-Choice Questions

1. (a)
2. (b)
3. (d)
4. (c)
5. (d)
6. (a)
7. (b)
8. (a)
9. (d)
10. (b)
11. (a)
12. (c)
13. (d)
14. (c)

15. (a)

GENERAL QUESTIONS

Mathematical Concepts

1. If $x = 2^{\frac{-1}{3}\log_2 64}$, find the value of x $\left(\text{Ans}\ \frac{1}{4}\right)$

2. Integrate the following functions w.r.t x.

   (a) $e^{nx}dx$

   (b) a^{7x+8}

   Ans (c) $\dfrac{e^{-nx}}{-n}$

   (d) $\dfrac{a^{7x+8}}{7\log a}$

3. Evaluate the following integrals:

(a) $\int\left[\dfrac{2\cos x}{3\sin^2 x} + 5x^2 - 6\right]dx$ (b) $\int\dfrac{\sin^2 x}{1+\cos x}\,dx$

$$\left[\begin{array}{l}\text{Ans. (a)}\ \dfrac{-2}{3}\operatorname{cosec} x + \dfrac{5}{3}x^3 - 6x + C \\ \text{(b)}\ x - \sin x + C\end{array}\right]$$

4. Show that the total number of ways in which six '+' and four '–' signs can be arranged in a line such that no two '–' signs occur together is 35.

5. In a single throw of two dice, what is the probability of obtaining a total greater than 10? $\left(\text{Ans}\ \dfrac{1}{12}\right)$

6. Find the maximum and minimum values of

(a) $x^3 + 2x^2 - 4x + 8$

(b) $x^4 - 14x^2 + 21x + 9$

$$\left[\begin{array}{l}\text{Ans. (a) Maximum value} = 0 \text{ at } x = -2 \\ \qquad \text{Minimum value} = \dfrac{-256}{27} \text{ at } x = \dfrac{2}{3} \\ \text{(b) Maximum value} = 20 \text{ at } x = 1 \\ \qquad \text{Minimum value} = 17 \text{ at } x = 2\end{array}\right]$$

7. Find the inclination of a line whose gradient is

   (a) $\dfrac{1}{\sqrt{3}}$

   (b) $\sqrt{3}$

(c) 1

[**Ans.** (a) = 30° (b) 60° (c) 45°]

8. Evaluate (a) $\log_{43} 57$ (b) $\log_2 3$

[**Ans.** (a) 1.07 approx (b) 1.59 approx]

9. Solve graphically the equations

$$x + y = 3,\ 2x + 5y = 12$$

[**Ans.** $x = 1, y = 2$]

10. How many different words containing all the letters of the word 'TRIANGLE' can be formed?

[Ans. 40320]

11. Integrate the following functions w.r.t x.

(a) a^{5x+7}

(b) $x^a + a^x + e^x a^x + \sin a$

(c) $\sin x \sec^2 x$

[**Ans.** (a) $\frac{a^{5x+7}}{5 \log a}$ (b) $\frac{x^{11}}{11}$ (c) sec x]

12. Show that the equation $y - y_1 = m\,(x - x_1)$ for different values of m and (x_1, y_1) fixed represents a family of concurrent lines.

13. Prove that $\sin (x + y)$ is equal to $\sin x \cos y + \cos x \sin y$.

14. If $x = a\cos^3 t$ and $y = a \sin^3 t$ evaluate $\frac{dy}{dx}$

[**Ans.** $-\tan t$]

15. Evaluate $\int (\tan x + \cot x)\, dx$

[**Ans.** $\log(C \tan x)$]

Computers

1. Define *computer*. Give the terms used for raw data and the information generated by a computer.
2. Differentiate clearly between analog and digital devices. Give one example of each.
3. What are the components of a computer? Classify the following into input device and output device.
   (a) Keyboard
   (b) Printer
   (c) mouse
   (d) monitor
4. (a) What do you mean by 'program'?
   (b) Explain the function of *arithmetical and logical unit.*
5. Give the classification and subclassification of *memory.*
6. Give a schematic diagram for the flow of data between the ALU and Memory.

7. Explain the following terms:
   (a) Hardware
   (b) Software
8. What are utility programs? Explain giving examples.
9. What is binary system used in computers? Differentiate between byte and bit.
10. What are the advantages and disadvantages of a multi-user operating system?
11. Give the application areas of the following programing languages:
   (a) COBOL
   (b)LISP
   (c) C^{++}
   (d) FORTRAN
12. Find the binary equivalent of $(72)_{10}$

[**Ans.** $(1001000)_2$]

13. Find the decimal equivalent of $(11001)_2$

[**Ans.** 25]

14. Compute $(1010)_2 + (1101)_2$

[**Ans.** $(10111)_2$]

15. Compute $(1111)_2 - (1010)_2$

[**Ans.** $(0101)_2$]

16. Compute $(1111)_2 \times (101)_2$

[**Ans.** $(1001011)_2$]

17. Compute $(10000111)_2 \div (1001)_2$

[**Ans.** $(01111)_2$]



Gaseous State

3

LEARNING OBJECTIVES

- Understand kinetic theory of gases and derive the kinetic gas equation
- Derive the gas laws from the kinetic gas equation
- Follow Maxwell distribution of velocities
- Differentiate between most probable, average and RMS velocities
- Understand degree of freedom and principle of equipartition of energy
- Understand collision diameter, collision frequency and mean free path
- Derive barometric formula
- Understand the cause of deviation of real gases from ideal behaviours
- Derive the van der Waals equation for real gases
- Study the critical phenomenon and understand critical volume, critical temperature and critical pressure
- Follow the isotherms of carbon dioxide and appreciate continuity of state
- Learn about liquefaction of gases by Linde's process and Claude's process

3.1 INTRODUCTION

The well-known laws of gaseous behaviours, viz. Boyle's law, Charles' law, Graham's law, Dalton's law of partial pressure and Avogadro's law were enunciated as empirical generalisation based on experimental observations. There was no theoretical background to justify them. The first reliable measurements on properties of gases were made by the Anglo-Irish scientist Robert Boyle in 1662. Jaccques Charles and Joseph Lewis Gay Lussac were motivated to discover additional laws by the attempts of people to fly in air with the help of air balloons. A significant contribution to formulate gas laws was made by Avogadro and others. However, we had to wait for more time till clausius, Maxwell, Boltzmann and others developed the kinetic theory of gases. This theory provided a strong theoretical background to the gas laws which had been enunciated till that time.

There are three states of matter, namely gas, liquid and solid. A gas consists of molecules separated by wide distances. The molecules are free to move about in the space in which they are contained. Intermolecular space in liquids is much less. However, the molecules are free to move throughout the liquid. Molecules in a solid occupy fixed positions. They cannot move about; however, they can vibrate slightly from the fixed positions. Some important characteristics of gases are listed below:

1. They fill up the whole vessel in which they are placed.
2. They exert pressure on the walls of the vessel in which they are taken.
3. They can be compressed by applying pressure.
4. Cooling and compression of the gas brings about its liquefaction.
5. They exhibit the property of intermixing with one another, a property known as ***diffusion.***

6. At ordinary conditions of temperature and pressure, their densities are low.

3.2 KINETIC THEORY OF GASES_

Maxwell and Boltzmann developed a mathematical theory to explain the behaviour of gases. The main points of the theory are the following:

1. Every gas is made up of a large number of small particles called molecules. All the molecules of a particular gas are identical in mass and size and differ from gas to gas.
2. The molecules of a gas are separated from each other by a large distance so that the actual volume of the molecules is negligible as compared to the total volume of the gas.
3. The distances of separation between the molecules are so large that the forces of attraction or repulsion between them are negligible.
4. The molecules are supposed to be moving continuously in different directions with different velocities. Hence, they keep on colliding with one another (called molecular collisions) as well as on the walls of the containing vessel.
5. Since the molecules are moving with different velocities, they possess different kinetic energies. However, the average kinetic energy of the molecules of a gas is directly proportional to the absolute temperature of the gas.
6. The pressure exerted on the walls of the containing vessel is due to the bombardment of the molecules on the walls of the containing vessel.
7. The force of gravitation on the molecules is also supposed to be negligible.
8. Molecules are supposed to be perfectly elastic hard spheres so that no energy is lost when the molecules collide with one another or with the walls of the vessel.

3.2.1 Derivation of Kinetic Gas Equation, $PV = \frac{1}{3} mnu^2$

Kinetic gas equation is derived as under: Consider a cubical vessel containing the gas (Fig. 3.3). Suppose,

Total number of molecules present in the gas = n,

Mass of each molecules of the gas = m,

Length of each side of the cube = l cm

According to the kinetic theory of gases, the molecules of the gas are moving in different directions with different velocities. Consider any one molecule moving with a velocity v_1 cm/s in any direction. The velocity can be resolved into three mutually perpendicular components v_x, v_y and v_z parallel to x-axis, y-axis and z-axis respectively as shown in Fig. 3.3. Then mathematically,

$$v_1^2 = v_x^2 + v_y^2 + v_z^2 \qquad \ldots(3.1)$$

Consider the motion of the molecule due to component v_x only. Due to this component, the molecule will strike the opposite faces A and B which are at right angles to the x-axis.

Momentum of molecule due to component v_x just before it strikes the face A

$$= mv_x$$



Fig. 3.1 *Ludwig Edward Boltzmann (1844–906) was an Austrian physicist. Boltzmann was one of the greatest theoretical physicists, but his work was not recognised by other scientists in his lifetime. He suffered severe depression and committed suicide in 1906.*

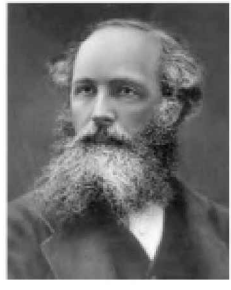


Fig. 3.2 *James Clerk Maxwell (1831–1879) was a Scottish physicist. He received recognition as one of the greatest theoretical physicists. His work covered kinetic theory of gases, thermodynamics, and electricity and magnetism.*

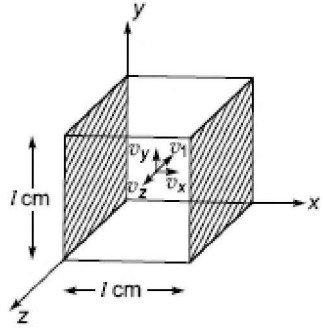


Fig. 3.3 *A cubical vessel containing n molecules of a gas*

As the molecules are supposed to be perfectly elastic, after colliding with the face A, the molecule will return with the same velocity. As the direction has changed, the velocity will now be taken as $-u_x$. Hence,

Momentum of the molecule due to component u_x just after it strikes the face $A = m \times (-u_x) = -mu_x$

$\therefore$ change of the momentum of the molecule in one collision on the face A due to component u_x

$$= mv_x - (-mv_x) = 2mv_x$$

Let us calculate the number of collisions which take place on the face *A* in one second due to the component v_x.

For the next collision on the face A, the molecule has to travel from face *A* to *B* and then back from *B* to *A*, i.e. a total distance of

$$l + l = 2\,l \text{ cm}$$

As the component being considered is v_x cm/s, this means that the distance travelled by the molecule in one second is v_x cm.

∴ number of collisions which take place on the face *A* in one second due to the component v_x

$$= \frac{v_x}{2l}$$

The change of momentum in one collision is $2mv_x$.

∴ change of momentum of the molecule in one second is due to the component v_x for collisions on face

$$A = 2mv_x \times \frac{v_x}{2l} = \frac{mv_x^2}{l}$$

Similarly, change of momentum of the molecule in one second due to component v_x for collisions on the face *B*

$$= \frac{mv_x^2}{l}$$

∴ change of momentum of the molecule in one second due to component v_x for collisions on the opposite faces perpendicular to *x*-axis

$$= \frac{mv_x^2}{l} + \frac{mv_x^2}{l} = \frac{2mv_x^2}{l}$$

Similarly, change of momentum of the molecule in one second is due to the component v_y, for collisions on the opposite faces perpendicular to the *y*-axis and due to the component v_z for collisions on the opposite faces perpendicular to the *z*-axis will be respectively.

$$\frac{2mv_y^2}{l} \text{ and } \frac{2mv_z^2}{l}$$

Thus, change of momentum of the molecule in one second due to all the components for collisions on all the six faces. 2

$$= \frac{2m}{l}\left(v_x^2 + v_y^2 + v_z^2\right) = \frac{2mv_1^2}{l} \text{ from Eq. (3.1)}$$

Similarly, the change of momentum in one second for molecules having velocities v_2, v_3, v_4... v_n will be respectively

$$\frac{2mv_2^2}{l}, \frac{2mv_3^2}{l}, \frac{2mv_4^2}{l} \cdots \frac{2mv_n^2}{l}$$

∴ total change of momentum in one second for all *n* molecules for collisions on all the six faces will be

$$= \frac{2mv_1^2}{l} + \frac{2mv_2^2}{l} + \frac{2mv_3^2}{l} + \ldots \frac{2mv_n^2}{l}$$

$$= \frac{2m}{l}\left(v_1^2 + v_2^2 + v_3^2 + \ldots + v_n^2\right)$$

$$= \frac{2m}{l} \times n \times \frac{v_1^2 + v_2^2 + v_3^2 + \ldots + v_n^2}{n}$$

$$= \frac{2mn}{l} \times u^2$$

where $u = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \ldots + v_n^2}{n}}$ is called root mean square velocity.

But the change of momentum in one second according to Newton's second law is equal to the force. Hence, the force (F) exerted by all the 'n' molecules on all the six faces is

$$F = \frac{2\,mnu^2}{l}$$

As pressure

$$= \frac{\text{Force}}{\text{Area}}$$

and area of all the faces = $6\,l^2$

Pressure (P) exerted on the walls of the cubical vessel will be

$$P = \frac{2\,mnu^2}{l} \times \frac{l}{6l^2} \cdot \frac{1}{3}\frac{mnu^2}{l^3}$$

But l^3 is the volume of the cubical vessel and hence is equal to the volume (V) of the gas

$\therefore$

$$P = \frac{1}{3}\frac{mnu^2}{V}$$

or

$$PV = \frac{1}{3}mnu^2$$

This is called ***kinetic gas equation.***

Bringing Chemistry to Life

You must have learnt about air bags in luxury cars as safety devices in case of accidents. These bags are filled with NaN_3. In case of a collision, the following reaction takes place:

$$2\,NaN_3\,(s) \rightarrow 2\,Na\,(s) + 3\,N_2\,(g)$$

An approximate 50 g of NaN_3 that is filled in each bag produces around 40 L N_2 at 85°C and 1 atm pressure. The bag is suddenly filled up with this volume of N_2 and protects the driver from collision with the steering wheel. This is how the properties of gases come to the rescue of humans.



Fig. 3.4 *Air bags are useful in car crashes*

3.2.2 Derivation of Boyle's Law, Charles' Law and Avogadro's Law from Kinetic Gas Equation

1. Boyle's Law According to the kinetic gas equation,

$$PV = \frac{1}{3} mnu^2 = \frac{2}{3} \cdot \frac{1}{2} mnu^2 = \frac{2}{3} \cdot \frac{1}{2} Mu^2$$

(where $m \times n = M$ is the total mass of the gas)

But $\frac{1}{2} Mu^2$ = Kinetic energy of the gas

$$\therefore \quad PV = \frac{2}{3} \text{KE} \tag{3.2}$$

Further, according to one of the postulates of the kinetic theory of gases

KE $\propto$ Absolute temperature *(T)*

or KE = $k'T$

where k' is a constant of proportionality. Putting this value in Eq. (3.2), we get

$$PV = \frac{2}{3} k' T$$

As $\frac{2}{3}$ is a constant quantity, k is also a constant. Therefore, if T is kept constant, $\frac{2}{3} k' T$ will be constant. Hence,

PV = constant, if T is kept constant

Boyle's law is thus deduced.



Fig. 3.5 *Robert Boyle (16271691) was a British chemist and natural philosopher. He made significant contribution to the fields of chemistry and physics, Boyle's law being one of them.*



Fig. 3.6 *Jacques Alexander Cesar Charles (1746-1823) was a French physicist. He was the first person to use hydrogen to inflate balloons. He was a pioneer in designing scientific apparatus and was a talented lecturer. He was a balloon enthusiast. In fact, it was Charles and Gay-Lussac both who first gave a temperature-volume relationship for gases.*



Fig. 3.7 *Joseph Louis Gay-Lussac (1778-1850) was a French chemist and physicist. As a balloon enthusiast, he once ascended to an altitude of 20,000ft. to collect air samples for analysis.*

2. Charles' Law Consider Eq. (3.2) deduced under Boyle's law

$$PV = \frac{2}{3} kT$$

This may be rewritten as

$$\frac{V}{T} = \frac{2}{3}\frac{k}{P}$$

Now $\frac{2}{3}$ is a constant quantity and k is also constant; therefore, if P is kept constant, the whole quantity on the right-hand side becomes constant.

Charles's law is thus deduced.

3. Avogadro's Law Consider any two gases. According to the the kinetic gas equation,

For Gas 1 $$P_1 V_1 = \frac{1}{3} m_1 n_1 u_1^2 \qquad \ldots(3.3a)$$

For Gas 2 $$P_2 V_2 = \frac{1}{3} m_2 n_2 u_2^2 \qquad \ldots(3.3b)$$

where P_1 = Pressure of Gas 1
V_1 = Volume of Gas 1
m_1 = Mass of each molecule of Gas 1
n_1 = Total number of molecules of Gas 1
u_1 = Root mean square velocity of the molecules of Gas 1

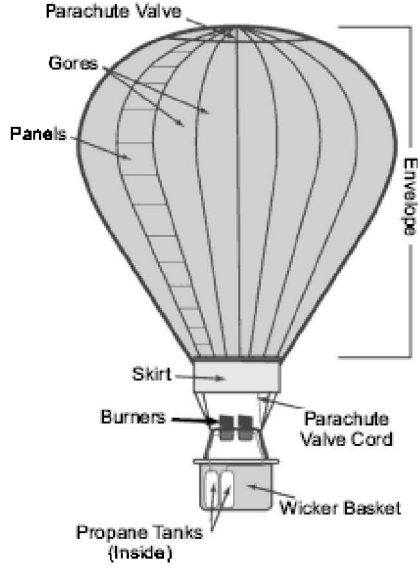


Fig. 3.8 *Airballoons provide popularsports and recreation these days*

P_2, V_2, m_2 and u_2 are the corresponding values for Gas 2.

If conditions of pressure are similar for both the gases then

$$P_1 = P_2 \qquad \ldots (3.4a)$$

If equal volumes of both the gases are taken then

$$V_1 = V_2 \qquad \ldots (3.4b)$$

Combining equations (3.4a) and (3.4b), we get

$$P_1V_1 = P_2V_2 \qquad \ldots (3.5)$$

Thus, left-hand sides of equations (3.3a) and (3.3b) are equal. Hence, right-hand sides must also be equal, i.e.

$$\frac{1}{3} m_1 n_1 u_1^2 = \frac{1}{3} m_2 n_2 u_2^2$$

or $$m_1 n_1 u_1^2 = m_2 n_2 u_2^2 \qquad \ldots (3.6)$$

Further, according to one of the postulates of the kinetic theory of gases,

Average KE of a gas $\propto$ Absolute temperature

Since conditions of temperature are similar in both the cases,

$\therefore$ Average KE of first gas = Average KE of second gas

i.e. $$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2$$

or $$m_1 u_1^2 = m_2 u_2^2 \qquad \ldots (3.7)$$

Dividing Eq. (3.6) by Eq. (3.7), we get

$$n_1 = n_2$$

Thus, equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

Thus, Avogadro's law is proved.

3.2.3 Derivation of Ideal Gas Equation, Graham's Law of Diffusion and Dalton's Law of Partial Pressure from Kinetic Gas Equation

1. Ideal Gas Equation According to kinetic gas equation,

$$PV = \frac{1}{3} mnu^2 = \frac{2}{3} \cdot \frac{1}{2} mnu^2$$

$$= \frac{2}{3} \text{KE}$$

$$\left(\because \frac{1}{2} mnu^2 = \text{KE of the gas}\right)$$

But $\text{KE} \propto T$ (one of the postulates of kinetic theory)

or $$\text{KE} = k'T$$

where k' is the constant of proportionality.

$\therefore$ $$PV = \frac{2}{3} k'T$$

$\frac{2}{3}$ is a constant quantity and k' is also constant.

$\therefore \frac{2}{3}k' = R$, another constant, called gas constant.

Hence,

$$PV = RT$$

which is the equation of state for 1 mol of the ideal gas.

Combining Boyle's law, Charles' law and Avogadro's law, we find that volume of a gas depends upon pressure, temperature and number of moles.

or $$V \propto \frac{1}{P}, \quad V \propto T \text{ and } \quad V \propto n$$

Combining the three relations, we have

$$V \propto \frac{nT}{P} \quad \text{or } V = R\frac{nT}{P} \quad \text{or } PV = nRT$$

where R, the proportionality constant is the gas constant.

Gas Constant One mole of an ideal gas occupies a volume of 22.414 dm^3 at NTP. From the equation $PV = nRT$,

$$R = \frac{PV}{nT} = \frac{(1 \text{ atm})(22.414 \text{ dm}^3)}{(1 \text{ mol})(273.15 \text{ K})} = 0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

In SI units,

$$R = \frac{PV}{nT} = \frac{(1.03125 \times 10^5 \text{ Nm}^{-2})(22.414 \times 10^{-3} \text{ m}^3)}{(1 \text{ mol})(273.15 \text{ K})}$$

$$= 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \qquad (\text{J} = \text{N} \times \text{m})$$

Note: *Although IUPAC recommends the use of SI units, the scientific community in general has been rather slow in adopting the same. Hence, we have retained the C.G.S. units also along with the SI units in the calculations and numerical problems. However, at any time, conversion from one set of units to the other may be done wherever felt necessary.*

2. Graham's Law of Diffusion According to the kinetic gas equation

$$PV = \frac{1}{3}mnu^2 = \frac{1}{3}Mu^2 \qquad (\because mn = M \text{ total mass of the gas})$$

or $$u^2 = \frac{3PV}{M} = \frac{3P}{MV} = \frac{3P}{d} \qquad (\because \frac{M}{V} = d \text{ is the density of the gas})$$

or $$u = \sqrt{\frac{3p}{d}} \qquad \ldots(3.8)$$

Greater the velocity (u) of the molecules, greater is the rate of diffusion (r) of the gas,

i.e $$r \propto u \qquad \ldots(3.9)$$

Combining equations (3.8) and (3.9), we get

$$r \propto \sqrt{\frac{3p}{d}}$$

Hence, if pressure *(P)* is kept constant then

$$r \propto \sqrt{\frac{1}{d}}$$

Thus, Graham's law follows from the kinetic gas equation.

3. Dalton's Law of Partial Pressure Let us consider two gases. According to the kinetic gas equation

$$PV = \frac{1}{3} mnu^2$$

or

$$P = \frac{1}{3} \frac{mnu^2}{V}$$

Now, if only the first gas is enclosed in the vessel of volume V, the pressure exerted would be

$$P_1 = \frac{1}{3} \frac{m_1 n_1 u_1^2}{V}$$

Again, if only the second gas is enclosed in the same vessel (so that V is constant) then the pressure exerted would be $_2$

$$P_2 = \frac{1}{3} \frac{m_2 n_2 u_2^2}{V}$$

Lastly, both the gases are enclosed together in the same vessel. Since the gases do not react with each other, their molecules behave independent of each other. Hence, the total pressure exerted would be

$$P = \frac{1}{3} \frac{m_1 n_1 u_1^2}{V} + \frac{1}{3} \frac{m_2 n_2 u_2^2}{V}$$
$$= P_1 + P_2$$

Similarly, if more than two gases are present, it follows that

$$P = P_1 + P_2 + P_3 + \ldots$$

Scuba divers and mountain climbers suffer the effects of sudden changes in pressure. At higher altitudes on the mountains, the pressure is significantly lower than at sea level. The pressure deep under water is, however, higher than at sea level. In both the activities of diving and climbing, the players suffer problems. A lower total pressure means lower partial pressure of oxygen, and insufficient oxygen (or ***hypoxia)*** can cause altitude sickness leading to headache, dizziness and nausea. Under severe conditions, death can occur. To prevent this, mountaineers wear oxygen gas masks.



Fig. 3.9 *Scuba divers*



Fig. 3.10 *Mountaineering*

In the case of scuba diving, the divers should never hold their breath during ascent to the surface. During underwater ascent, the air in the diver's lungs expands because of lower pressure outside. If the air is not expelled, it causes overexpansion. This leads to a condition called burst lung, causing air to escape into chest cavity. Such a condition can cause a heart attack or stroke.

3.2.4 Derivation of Relations between Molecular Velocity, Pressure, Temperature, Volume and Density of the Gas

According to the kinetic gas equation,

$$PV = \frac{1}{3}mnu^2$$

or $$u^2 = \frac{3PV}{mn} = \frac{3PV}{M} \qquad (\because mn = M \text{ is the mass of the gas})$$

If 1 mole of the gas is taken, M will be equal to the molecular weight of the gas,

$$u = \sqrt{\frac{3PV}{M}} \qquad \ldots(3.10)$$

Further, for 1 mole of the gas,

$$PV = RT$$

$$\therefore \quad u = \sqrt{\frac{3PV}{M}} \qquad \ldots(3.11)$$

Equation (3.10) can be written as

$$u = \sqrt{\frac{3P}{M/V}} \qquad \ldots(3.12)$$

But $\frac{m}{V} = d$ (where d is the density of the gas)

Equation (3.12) takes the form

$$u = \sqrt{\frac{3P}{d}}$$

3.2.5 Derivation of Relation between Kinetic Energy and Temperature

For 1 mol of the gas containing n molecules, each of mass m, the kinetic energy will be

$$\text{KE} = \frac{1}{2} mnu^2$$

According to the kinetic gas equation

$$PV = \frac{1}{3} mnu^2$$

or $$mnu^2 = 3\,PV$$

$$\therefore \quad \frac{1}{2} mnu^2 = \frac{3}{2} PV$$

$$\text{K.E.} = \frac{3}{2} PV$$

Further, for 1 mol of the ideal gas,

$$PV = RT$$

$$\text{KE} = \frac{3}{2} RT$$

The average translational kinetic energy of ***one molecule*** of an ideal gas is given by

$$\varepsilon = \frac{K.E}{N_A} = \frac{3}{2}\frac{RT}{N_A} = \frac{3}{2} kT$$

where N_A is Avogadro's constant and k is the Boltzmann constant. The value of k is 1.38×10^{35} J K^{-1}

The value of R depends upon the units in which P, V and T are measured. Volume of one mole of an ideal gas under STP conditions, i.e. 273.15 K and 1 bar pressure is 22.710981 L mol^{-1}. The value of R for one mole of an ideal gas can be calculated under these conditions as

$$PV = RT$$

or
$$R = \frac{PV}{T} = \frac{(10^5 \text{ Pa} \times 22.71 \times 10^{-3} \text{ m}^3)}{273.15 \text{ K}}$$

$$= 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \text{ (SI units)}$$
$$= 8.314 \text{ ¥ } 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1}$$
$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

At STP conditions used earlier (0°C and 1 atm pressure), the value of R is 8.20578×10^{-2} L atm $K^{-1}mol^{-1}$

PROBLEMS FOR PRACTICE

1. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27°C?

[**Ans.** 8.314×10^4 *Pa*]

2. The drain cleanser Drainex contains small bits of aluminum which reacts with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and one bar will be released when 0.15 g of Al reacts?

[**Ans.** 202.5 mL]

3. 2.9 g of a gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C at the same pressure. What is the molar mass of the gas?

[**Ans.** 40 g mol^{-1}]

4. A 10.0 dm^3 cylinder of O_2 gas at 4.00 atm pressure and 17°C developed a leak. When the leak was repaired, the gas which remained in the cylinder was found to register a pressure of 2.5 atm at 17°C. How many moles of the gas escaped?

[**Ans.** 0.63 mole]

5. Calculate the density of CO_2 gas at 0°C and 1 atm pressure.

[**Ans.** 1.96 kg m^{-3}]

3.3 MAXWELL DISTRIBUTION OF VELOCITIES

Molecules of a gas are in a state of continuous motion in different directions with different velocities. Hence, they keep on colliding with one another. However, the collisions are supposed to be perfectly elastic and there is no net loss of kinetic energy. In other words, whereas some molecules are speeded up, the others are slowed down after collision. Maxwell suggested that at a particular temperature, the fractions of molecules possessing particular velocities remain almost constant. Such a state is called a ***steady state.*** On the basis of the laws of probability, he calculated that the fraction of the molecules having velocities between C and $C + dc$ is given by

$$\frac{dn_c}{n} = 4\pi \left[\frac{M}{2\pi RT}\right]^{3/2} e^{-Mc^2/2RT} c^2 dc \qquad \ldots(3.13)$$

where ***dn*** represents the number of molecules having velocities between C and C + dc. Out of a total of n molecules of the gas, and M and T are the molecular weight and absolute temperature of the

gas respectively. The above equation may be rewritten as

$$\frac{1}{n}\cdot\frac{dn_c}{dc}=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}e^{-Mc^2/2RT}\,c^2 \qquad \ldots(3.14)$$

The quantity $\frac{1}{n}\cdot\frac{dn_c}{dc}$, is called the probability (p) of finding molecules with velocity C.

The significance of the above equation may be seen by plotting the probability $\left(p=\frac{1}{n}\cdot\frac{d_{nc}}{d_c}\right)$ versus the velocity c at a particular temperature T. Such a plot is known as Maxwell's distribution of velocities and is shown in (Fig. 3.11) and represents the most probable velocity.

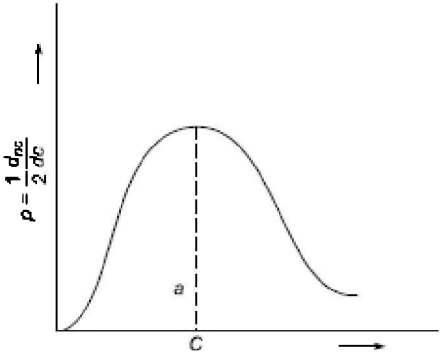


Fig. 3.11 *Maxwell distribution of velocities*

Example 1 *Calculate the average transitional kinetic energy of an ideal gas per molecule* ***(ε)*** *and per mole (E) at 35°C.*

Solution:

$$\varepsilon=\frac{3}{2}kT=\frac{3}{2}(1.38\times10^{-23}\text{ J K}^{-1})(308\text{ K})$$
$$=6.38\times10^{-21}\text{ J per mole}$$
$$E=\frac{3}{2}RT=\frac{3}{2}(8.314\text{ J K}^{-1}\text{ mol}^{-1})(308\text{ K})$$
$$=3.84\times10^{3}\text{ J mol}^{-1}$$

The area between two ordinates separated by ***dc*** represents ***dn/n,*** i.e. the fraction of the total number of molecules possessing velocities between c and $c + dc$ (Fig. 3.12). Hence, the area under the whole curve is equal to the total number of molecules and the height of the ordinate corresponding to any velocity is a measure of the fraction of the molecules which have that velocity. From the Maxwell's distribution of velocities as given in Fig. 3.11 it may be observed that the fraction of molecules having zero velocity, i.e. of molecules which are motionless is zero and the fractions of molecules having velocities greater than zero increase with increase of velocities, reach a maximum value corresponding to a particular velocity and then begin to decrease. Thus, it may be concluded that

1. The fractions of molecules having very low velocities or very high velocities are very small, and
2. There is a velocity (α) corresponding to which the fraction of molecules is maximum.

In other words, α is the velocity possessed by the maximum fraction of the molecules. ***This***

velocity is called the most probable velocity. This most probable velocity may be defined as the velocity possessed by the maximum fraction of the molecules of the gas at a particular temperature.

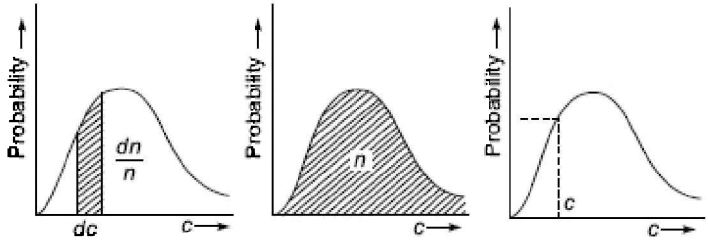


Fig. 3.12 *Interpretation of Maxwell's distribution of velocities*

3.3.1 Effect of Temperature on Maxwell's Distribution of Velocities

With increase of temperature, the curve makes a shift as shown in Fig. 3.13. Two important changes may be noticed:

1. The peak of the curve shifts forward.
2. The peak of the curve shifts downward and is flattened.

The following two important conclusions may be drawn g from the above observations.

1. With increase of temperature, the value of the most probable velocity increases.
2. The fraction of molecules possessing the most probable velocity decreases with increase of temperature ($f_2 < f_1$).

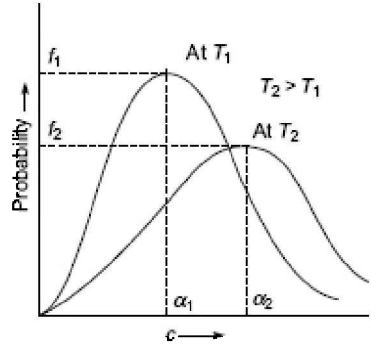


Fig 3.13 *Distribution of velocities at two different temperatures.*

3.3.2 Mathematical Representation of Maxwell's Distribution of Energies

Eqnation (3.13) and (3.14) in section 3.3 representing the distribution of velocities can be converted so as to represent the distribution of energies as follows:

$\frac{1}{2} Mc^2$ can be replaced by E, the kinetic energy of the gas per mole.

$$\frac{1}{2} Mc^2 = E \qquad \ldots(3.15)$$

To change c^2 dc into the energy terms Eq. (3.15) can be rewritten as

$$Mc^2 = 2E \qquad \ldots(3.16)$$

Differentiating both sides, we get

$$2\,Mc\,dc = 2dE$$

or
$$Mc\,dc = dE \qquad \ldots(3.17)$$

Taping square roots of *both* sides of Eq. (3.16), we get

$$M^{1/2}\,c = (2E)^{1/2} \qquad \ldots(3.18)$$

$$c^2\,dc = \frac{(2E)^{1/2}\,dE}{M^{3/2}} \qquad \ldots(3.19)$$

Substituting the value of $\frac{1}{2}Mc^2$ from Eq. (3.15) and that of $c^2\,dc$ from Eq. (3.19) in Eq. (3.13), we get

$$\frac{dn_c}{n} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-E/RT}\,\frac{(2E)^{1/2}\,dE}{M^{3/2}}$$

or
$$\frac{dn_c}{n} = \frac{2\pi}{(\pi RT)^{3/2}}\,e^{-E/RT}\,E^{1/2}\,dE \qquad \ldots(3.20)$$

where dn/n now represents the fraction of the total number of molecules having kinetic energies between E and dE.

Equation (3.20) can be rewritten as

$$P' = \frac{1}{n}\frac{dn_c}{dE} = \frac{2\pi}{(\pi RT)^{3/2}}\,e^{-E/RT}\,E^{1/2} \qquad \ldots(3.21)$$

where p' represents the probability of molecules having energy E.

The plots of p' (probability) vs E obtained are similar to those for the distribution of velocities.

3.4 MOST PROBABLE VELOCITY (α), AVERAGE VELOCITY (υ) AND ROOT MEAN SQUARE (RMS) VELOCITY (u)

1. Most Probable Velocity (α) The most probable velocity of a gas at a particular temperature represents the velocity possessed by the maximum fraction of the total number of molecules at that temperature. It is usually represented by 'α'.

2. Average Velocity (υ) It is defined as the arithmetic mean of the velocities possessed by the different molecules of a gas at a particular temperature. It is usually represented by υ. It is expressed in two different ways.

(a) If all the n molecules of the gas are supposed to have different velocities, say υ_1, υ_2, υ_3, ... υ_n

$$\upsilon = \frac{\upsilon_1 + \upsilon_2 + \upsilon_3 + \cdots + \upsilon_n}{n}$$

(b) If n_1 molecules of the gas have velocity υ_1 cm/s, n_2 have velocity υ_2 cm/s, n_3 have velocity υ_3 cm/s, and so on then

$$\upsilon = \frac{n_1\upsilon_1 + n_2\upsilon_2 + n_3\upsilon_3 + \ldots}{n_1 + n_2 + n_3 + \ldots (= n)}$$

3. Root Mean Square Velocity (u) It is defined as the square root of the mean of the squares of the different velocities. It is usually represented by '*u*'. Like the average velocity, it can be expressed in two different ways.

(a) Assuming all the *n* molecules to have different velocities viz, v_1, v_2 ... v_n cm/s, we have

$$u = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \ldots + v_n^2}{n}}$$

(b) Assuming n_1 molecules have velocity v_1, n_2 molecules have velocity v_2, n_3, have v_3, and so on, we have

$$u = \sqrt{\frac{n_1 v_1^2 + n_2 v_2^2 + m v_3^2 + \ldots}{n_1 + n_2 + n_3 + \ldots (= n)}}$$

3.4.1 Derivation of Expression for Most Probable Velocity (α). Average Velocity (v), Root Mean Square Velocity (u) from Maxwell Distribution of Velocities

1. Most Probable Velocity (α) Maxwell's distribution law equation can be used mathematically to get the condition for the maximum in the probability distribution curve. The condition obtained is

$$c = \sqrt{\frac{2RT}{M}}$$

Representing the most probable velocity by *a* in place of c, we have

$$\alpha = \sqrt{\frac{2RT}{M}} \qquad \ldots(3.22)$$

This result is obtained by differentiating right-hane side of Eq. (3.14) in Section 3.3 w.r.t. *c* and equation the result to zero, we get

$$\left(1 - \frac{Mc^2}{2RT}\right) c e^{-Mc^2/2RT} = 0$$

Taking $1 - \frac{Mc^2}{2RT} = 0$, we get $\frac{Mc^2}{2RT} = 1$

or $c = \sqrt{\frac{2RT}{M}}$

2. Average Velocity (υ) By using Maxwell's distribution law equation, we can derive mathematically that

$$v = \sqrt{\frac{8RT}{\pi . M}} \qquad \ldots(3.23)$$

[This result is obtained by making use of the fact that

$$v = \frac{\int_0^\infty c dn_c}{n}$$

and then substituting the value of dn_c from Eq. (3.13) in Section 3.3 and solving it.]

3. Root Mean Square Velocity (u) From the kinetic gas equation,

$$PV = \frac{1}{3} m N u^2 = \frac{1}{3} M u^2 \qquad (mN = M \text{ gram molecular mass})$$

or $$u^2 = \frac{3PV}{M} = \frac{3RT}{M} \qquad (\because PV = RT \text{ for 1 mol of an ideal gas})$$

or $$u = \sqrt{\frac{3RT}{M}} \qquad \ldots(3.24)$$

3.4.2 Relationships Between Most Probable Velocity, Average Velocity and Root Mean Square Velocity

Expressions for α, v and u are respectively given as under:

(i) $\alpha = \sqrt{\frac{2RT}{M}}$,

(ii) $v = \sqrt{\frac{8RT}{\pi M}}$

(iii) $u = \sqrt{\frac{3RT}{M}}$

Combining (i) with (iii), we get

$$\alpha = \sqrt{\frac{2}{3}} u$$

i.e. $$\alpha = 0.816\, u \qquad \ldots(3.25)$$

Combining (ii) with (iii), we get

$$v = \sqrt{\frac{8}{3\pi}} u$$

i.e. $$v = 0.921\, u \qquad \ldots(3.26)$$

Alternatively, the relationship between α, v and u are

$$\alpha : v : u = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= 1.414 : 1.595 : 1.732$$

$$\alpha : v : u = 1 : 1.128 : 1.224 \qquad \ldots(3.27)$$

Example 2 *Calculate the root mean square velocity, average velocity and most probable velocity of sulphur dioxide molecules at 427°C.*

Solution:

(a) *Calculation of root mean square velocity*

$$u = \sqrt{\frac{3RT}{M}}$$

Here, $T = 427°C, 427 + 273 = 700$ K

M = mol. wt. of $SO_2 = 32 + 32 = 64$

$R = 8.314 \times 10^7$ ergs/degree/mol (CGS units)

Putting the values in the above equation, we get

$$u = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 700}{64}}$$

$$= \sqrt{\frac{3 \times 8.314 \times 10^8 \times 70}{64}}$$

$$= \sqrt{\frac{3 \times 8.314 \times 70}{64}} \times 10^4 = 5.224 \times 10^4 \text{ cm s}^{-1}$$

$$= \mathbf{52240 \text{ cm s}^{-1}}$$

(b) *Calculation of average velocity (υ)*

$$v = 0.9213 \times u = 0.9213 \times 52240 \text{ cm s}^{-1}$$

$$= \mathbf{48128 \text{ cm s}^{-1}}$$

(c) *Calculation of most probable velocity (α)*

$$\alpha = 0.816 \times u = 0.816 \times 52240 \text{ cm s}^{-1}$$

$$= \mathbf{42628 \text{ cm s}^{-1}}$$

Example 3 *Oxygen has a density of 1.429 g/l at NTP Calculate the RMS and average velocity of oxygen molecules.*

Solution:

(a) The RMS velocity (u) is given by the formula

$$u = \sqrt{\frac{3P}{d}}$$

Here, $P = 1$ atm $= 76 \times 13.6 \times 981$ dynes/sq cm

$$d = 1.429 \text{ gL}^{-1} = \frac{1.429}{1000} \text{ g cm}^{-3} \text{ (CGS units)}$$

$$= 0.001429 \text{ g cm}^{-3}$$

Putting these values in the above formula, we get

$$u = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001429}}$$

$$= \sqrt{\frac{30.42}{1429} \times 10^8}$$

$$= 4.61 \times 10^4 = \mathbf{46100 \text{ cm s}^{-1}}$$

(b) Calculation of average velocity ($υ$)

$$v = 0.9213 \times u = 0.9213 \times 46100$$
$$= \mathbf{42461\ cm\ s^{-1}}$$

Example 4 *Calculate the temperature at which the hydrogen molecules will have an average speed of 176400 cm s^{-1}.*

Solution: We are given that

$$v = 176400 \text{ cm } s^{-1}$$

Applying the formula

$$v = \sqrt{\frac{8RT}{\pi M}}$$

Putting $R = 8.314 \times 10^7$ ergs/degree/mol

$$M = 2 \text{ (for } H_2\text{)}$$

$$176400 = \sqrt{\frac{8 \times 8.314 \times 10^7 \times 7}{22/7 \times 2}}$$

or

$$T = \frac{176400^2 \times 22 \times 2}{7 \times 8 \times 8.314 \times 10^7} = 300\ K \text{ or } 27°C$$

Example 5 *At what temperature will the root mean square velocity of chlorine gas be equal to that of SO_2 at NTP?*

Solution: The root mean square velocity is given by the equation

$$u = \sqrt{\frac{3RT}{M}}$$

For SO_2, $T = 273$ K

$M = 64$

$$\therefore \quad u_{SO_2} = \sqrt{\frac{3R \times 273}{64}}$$

For Cl_2 $T = ?$

$M = 71$

$$u_{Cl_2} = \sqrt{\frac{3R \times T}{71}}$$

But $u_{SO_2} = u_{Cl_2}$

$$\therefore \quad \sqrt{\frac{3R \times 273}{64}} = \sqrt{\frac{3R \times T}{71}}$$

$$\frac{3R \times 273}{64} = \frac{3R \times T}{71}$$

$$T = \frac{273 \times 71}{64} = 302.9\ K$$

$$= 302.9 - 273 = \mathbf{29.0°C}$$

Example 6 *Calculate the root mean square velocity of nitrogen at NTP ($R = 8.314 \times 10^7$ ergs/degree/mol).*

Solution : For N_2 at NTP,

$P = 760$ mm $= 76$ cm $= 76 \times 13.6 \times 981$ dynes cm^{-2} (CGS units)

$V = 22400$ cm^3

$M = 28$

Putting these values in the equation

$$u = \sqrt{\frac{3PV}{M}}$$

$$u = \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{28}}$$

$$= 4.92 \times 10^4 \text{ cm s}^{-1}$$

Example 7 *Calculate the root mean square velocity of chlorine molecules at 17°C and 800 mm pressure.*

Solution: This numerical problem involves two steps as follows:

Step 1 To calculate the volume under given conditions (for one mole of gas). One mole of a gas

at NTP occupies 22400 cm^3.

Applying the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{760 \times 22400}{273} = \frac{800 \times V_2}{290}$$

$$\therefore \quad V_2 = \frac{760 \times 22400 \times 290}{273 \times 800} = 22600 \text{ cm}^3$$

Step 2 To calculate the rms velocity using the equation

$$u = \sqrt{\frac{3PV}{M}}$$

Here, $P = 800 \text{ mm} = 80 \text{ cm} = 80 \times 13.6 \times 981$ dynes/sq. cm (CGS units)

$V = 22600 \text{ cm}^3$

$M = 71$ (for Cl_2)

$$u = \sqrt{\frac{3 \times 80 \times 13.6 \times 981 \times 22600}{71}}$$

$$= \sqrt{10.18 \times 10^8} = \mathbf{3.19 \times 10^4 \text{ cm s}^{-1}}$$

Example 8 *Calculate translational KE of 2 moles of a gas at 27°C.*

Solution: For 1 mol of a gas, $\text{KE} = \frac{3}{2}RT$

∴ for 2 moles of the gas,

$$\text{KE} = \left(\frac{3}{2}RT\right) \times 2$$

Putting $R = 8.314 \times 10^7$ ergs/degree/mol

$T = 27°\text{C} = (27 + 273)\text{ K} = 300\text{ K}$

We get $\text{KE} = 3 \times 8.314 \times 10^7 \times 300$ ergs (CGS units)

$= 7482.5 \times 10^7$ ergs

$= \mathbf{7482.6 \text{ joules}}$

Example 9 *For hydrogen gas, calculate (a) the average velocity, and (b) most probable velocity at 0°C in SI units.*

Solution: The molar mass M of $H_2 = 2.016 \text{ g mol}^{-1} = 2.016 \times 10^{-3} \text{ kg mol}^{-1}$

$$\text{Average velocity} = \left[\frac{8\,RT}{\pi\,M}\right]^{\frac{1}{2}} = \left[\frac{(8)\,(8.314\ \text{J K}^{-1}\text{mol}^{-1})\,(273.15\ \text{K})}{(3.1416)\,(2.016\times10^{-3}\ \text{kg mol}^{-1})}\right]^{\frac{1}{2}}$$

$$= 1.69\times10^{3}\ \text{m s}^{-1}$$

$$\text{Most probable velocity} = \left[\frac{2RT}{M}\right]^{\frac{1}{2}} = \left[\frac{(2)\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\,(273.15\ \text{K})}{2.016\times10^{-3}\ \text{kg mol}^{-1}}\right]^{\frac{1}{2}}$$

$$= 1.50\times10^{3}\ \text{m s}^{-1}$$

Example 10 *Calculate the root mean square velocity of nitrogen at 27°C and 70 cm pressure. Density of Hg = 13.6 g cm^{-3}.*

Solution: Volume of nitrogen at 27°C and 70 cm pressure can be obtained using the general gas equation $P_2\,V_2/T_2 = P_1\,V_1/T_1$. Substituting the values, we have

$$\frac{70\ \text{cm}\times V_2}{300\ \text{K}} = \frac{76\ \text{cm}\times0.0224\ \text{m}^3}{273\ \text{K}}$$

or $$V_2 = 0.026725\ \text{m}^3$$

$$P_2 = \left(\frac{70}{76}\right)\times(101325\ N\,\text{m}^{-2}) \qquad (\because 1\ \text{atm} = 101325\ N\,\text{m}^{-2})$$

$$\text{RMS velocity} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3PV}{M}\right)^{\frac{1}{2}}.$$

Substituting the values, we have

$$\text{RMS velocity} = \left[\frac{(3)(70/76)\times101325\ \text{Nm}^{-2})\,(0.026725\ \text{m}^3\text{mol}^{-1})}{28\times10^{-3}\ \text{kg mol}^{-1}}\right]^{2}$$

$$= 517\ \text{m s}^{-1} \qquad (1\ \text{N} = 1\ \text{kg m s}^{-2})$$

PROBLEM FOR PRACTICE

1. At what temperature will the root mean square velocity of SO_2 be the same as that of O_2 at 27°C?

[Ans. 327°C]

3.5 DEGREE OF FREEDOM

The number of coordinates required to specify the position of all the mass points, i.e. atoms in a molecule is called the *degree of freedom*. To represent one atom, we need three conditions.

Therefore, a molecule made up of N atoms has $3N$ degree of freedom.

According to kinetic theory of matter, when thermal energy is absorbed by a molecule, it is stored within the molecule in the form of

1. translational motion of the molecule
2. internal movement of the atoms within the molecule, i.e. rotational motion and vibrational motion

The transitional motion of the molecule represents the motion of the centre of mass of the molecule as a whole. The centre of mass of the molecule can be represented by three coordinates.

Hence, there are ***three translational degrees of freedom.*** The remaining ($3N$ – 3) coordinates represent the ***internal degrees of freedom.***

However, as already mentioned, the internal degrees of freedom may be subdivided into

1. rotational degrees of freedom, and

2. vibration degrees of freedom.

For a rotational motion, there are two degrees of freedom for a linear molecule and three for a nonlinear molecule as shown in Fig. 3.14.

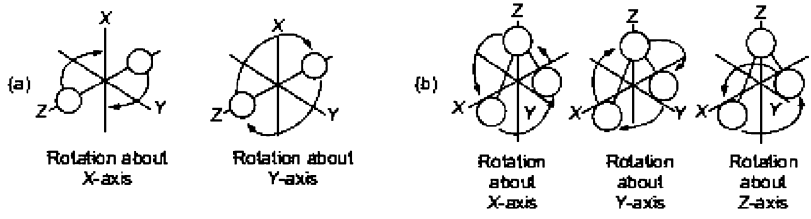


Fig. 3.14 *(a) Rotations of a linear molecule about two mutually perpendicular axes (b) Rotations of a non-linear molecule about three mutually perpendicular axes*

Remaining degrees of freedom for the linear molecules are equal to ($3N$ – 5) and for the non-linear molecules they are equal to ($3N$ – 6). These describe the motion of the nuclei with respect to one another and thus represent the number of ***vibrational degrees of freedom.***

Hence,

Vibrational degrees of freedom of a linear molecule containing N atoms = $3N - 5$

Vibrational degrees of freedom of a non-linear molecule containing N atoms = $3N - 6$

The following examples illustrate calculation of vibrational degree of freedom of molecules.

1. As a diatomic molecule is always linear, its vibrational degrees of freedom = $3N - 5$

$$= 3 \times 2 - 5 = 1$$

2. For the linear polyatomic molecule, HC ≡ CH, (N = 4), the vibrational degrees of freedom = $3N - 5 = 3 \times 4 - 5 = 7$

3. For the non-linear polyatomic molecule, HCHO, (N = 4) the vibrational degrees of freedom = $3N - 6 = 3 \times 4 - 6 = 6$

It may be summarised that a molecule consisting of N atoms has the following degrees of freedom:

	Translational	Rotational	Vibrational
For linear molecule	3	2	3N – 5
For non-linear molecule	3	3	3N – 6

Thus, the total degrees of freedom in each case = $3N$

3.6 PRINCIPLE OF EQUIPARTITION OF ENERGY

According to kinetic theory of gases, the molecules of a gas are moving in different directions with different velocities. Consider any one gas molecule moving in any direction with velocity υ. The velocity υ can be resolved into three components υ_x, υ_y and υ_z along the three mutually perpendicular axes (Fig. 3.15) such that

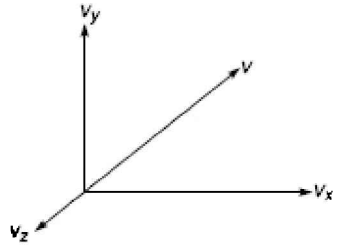


Fig. 3.15 *Resolution of a velocity into three mutually perpendicular components*

$$v^2 = v_x^2 + v_y^2 + v_z^2 \qquad \ldots(3.28)$$

Multiplying both sides of the equation by ½ *m*, we get

$$\frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \qquad \ldots(3.29)$$

i.e. KE of the gas molecule = $(KE)_x + (KE)_y + (KE)_z$ ….(3.30)

Considering all the molecules of the gas and taping their average value, we can say,

$$\overline{K.E} = (\overline{K.E})_x + (\overline{K.E})_y + (\overline{K.E})_z \qquad \ldots(3.31)$$

Since the molecules of the gas move in a random manner and do not have any preference for a particular direction, therefore, it follows that

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \qquad \ldots(3.32)$$

The mean value of any velocity component such as $\overline{v_x}$ is zero because all directions are equally possible so that there are equal possibilities for components in opposite direction,

i.e., v_x and $-v_x$ are equally probable. But $\overline{v_x^2}$ is not zero because the squares are always positive.

Multiplying throughout by $\frac{1}{2}m$, we get

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}m\overline{v_x^2} \qquad \ldots(3.33)$$

or $$(KE)_x = (KE)_y = (KE)_z \qquad \ldots(3.34)$$

Combining equations (3.32) and (3.34), it becomes clear that the average translational kinetic energy of a molecule is the sum of their components along the three mutually perpendicular axes and these three components are equal to one another. From kinetic theory of gases, as the total translational kinetic energy of a molecule is $\frac{3}{2}kT$, therefore, each component will be $\frac{1}{2}kT$ where *k* is Boltzmann constant and *T* is the absolute temperature.

Now consider the rotational and vibrational energies associated with the gas molecules. Just as translational kinetic energy of a molecule is the sum of the three squared terms, each squared term contributes $\frac{1}{2}kT$ to the total energy of the molecules, the rotational energy is kinetic in nature and is represented by one squared term ($\frac{1}{2}I\omega^2$ where, *I* is the moment of interia and ω is the angular velocity of rotation). Each type of rotation (i.e. each squared term) contributes $\frac{1}{2}kT$ to the energy of the molecule. However, vibrational energy is partly kinetic and partialy potential and is represented by

the sum of two squared terms. Each squared terms contributes $\frac{1}{2}kT$ to the energy of the molecule so that each mode of vibration contributes kT to the enery of the molecule.

The above discussion leads to following generalisation known as the ***"principle of equipartition of energy!"***

The total energy of a molecule is divided equally among the different degrees of freedom, the amount of energy associated with each degree of freedom being equal to $\frac{1}{2}kT$ where the term 'degree of freedom' refers to the number of independent square terms (i.e. terms involving the square of a co-ordinate or momentum/velocity) required to express the total energy of the molecule.

It may be summarised that

Energy contributed by each translational degree of freedom = $\frac{1}{2}kT$

Energy contributed by each rotational degree of freedom = $\frac{1}{2}kT$

Energy contributed by each vibrational degree of freedom (or vibrational mode) = kT

Example 11 *Calculate the average energy of the molecule of C_2H_6 as well as the molar energy at 300K as predicted by the law of equipartition of energy.*

Solution: As C_2H_6 is a non-linear molecule, and $N = 8$.

$\therefore$ Translational degrees of freedom = 3

Rotational degrees of freedom = 3

Vibrational degrees of freedom = $(3N - 6) = 18$

$\therefore$
$$\begin{aligned}\overline{\varepsilon} &= \overline{\varepsilon_t} + \overline{\varepsilon_r} + \overline{\varepsilon_v} \\ &= \left(3 \times \frac{1}{2}kT\right) + \left(3 \times \frac{1}{2}kT\right) + (18 \times kT) \\ &= \frac{3}{2}kT + \frac{3}{2}kT + 18\,kT = 21\,kT \\ &= 21 \times \frac{8.314}{6.022 \times 10^{23}} \times 300 \\ &= 8.70 \times 10^{-20} \text{ joules}\end{aligned}$$

Average energy per mol will be given by

$$\begin{aligned}\overline{E} &= \overline{\varepsilon} \times N \\ &= 8.70 \times 10^{-20} \times 6.022 \times 10^{23} \text{ joules} \\ &= 52.39 \text{ kJ}\end{aligned}$$

Example 12 *At what temperature would ethane molecules have the same RMS velocity as methane molecules at 27°C?*

Solution: RMS velocity = $\sqrt{\frac{3RT}{M}}$

For methane, RMS velocity at 27°C (300 K),

$$= \sqrt{\frac{3R \times 300}{16}}$$

Let ethane possess the same velocity at T K. Then

$$\sqrt{\frac{3RT}{30}} = \sqrt{\frac{3 \times R \times 300}{16}} \quad \text{or} \quad \frac{T}{30} = \frac{300}{16} \quad \text{or} \quad T = \frac{30 \times 300}{16}$$

$$T = 562.5 \text{ K} \quad \text{or} \quad 289.5^{\circ}\text{C}$$

Example 13 *Calculate the average internal energy of a diatomic molecule at 300 K using the law of equipartition of energy.*

Solution: For a diatomic molecule, as it is linear, and $N = 2$

Average translation energy

$$(\overline{\varepsilon_t}) = 3 \times \frac{1}{2} kT = \frac{3}{2} kT$$

Average rotational energy

$$(\overline{\varepsilon_r}) = 2 \times \frac{1}{2} kT = kT$$

Average vibrational energy

$$(\overline{\varepsilon_v}) = (3N - 5)_x \, kT = (3 \times 2 - 5)\, kT = kT$$

Hence, the average internal energy of the molecule is

$$\begin{aligned} \bar{\varepsilon} &= \overline{\varepsilon_t} + \overline{\varepsilon_r} + \overline{\varepsilon_v} \\ &= \frac{3}{2} kT + kT + kT = \frac{7}{2} RT \\ &= \frac{7}{2} \times \frac{8.314}{6.022 \times 10^{23}} \times 300 \text{ joules} \\ &= \mathbf{1.45 \times 10^{-20} \text{ joules}} \end{aligned}$$

3.7 COLLISION DIAMETER, COLLISION NUMBER, COLLISION FREQUENCYAND MEAN FREE PATH

1. Collision Diameter Collision is an event in which the centers of two identical molecules come within a distance σ from one another as shown in Fig. 3.16.

Sigma (σ) which is the distance between centres of the molecules at the point of closest approach is called the ***collision diameter.***

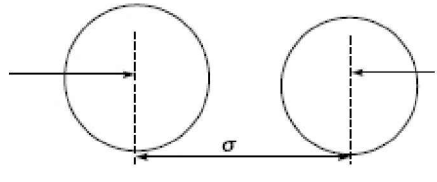


Fig. 3.16 *Collision diameter*

2. Collision Number The number of molecules with which a single molecule will collide per unit time per unit volume of the gas is called collision number. It is given by

$$Z_1 = \sqrt{2}\,\pi\,\sigma^2\,\bar{c}\,\rho \qquad \ldots(3.35)$$

where Z_1 = Collision number

σ = Diameter of molecule

$\bar{c}$ = Average velocity

ρ = No. of molecules per unit volume of the gas

3. Collision Frequency It represents the number of molecule collisions occurring per unit time per unit volume of the gas. Total number of molecules colliding per unit volume per unit time is obtained by multiplying collision number density ρ. Thus total number of collisions molecule = $= \sqrt{2}\,\pi\,\sigma^2\,\bar{c}\,\rho^2$

Since each collision involves two molecules of the same type, number of collisions is given by one half of this

$$Z_{11} = \frac{1}{2}\cdot\sqrt{2}\,\pi\sigma^2\bar{c}\,\rho^2 \qquad \ldots(3.36)$$

$$= \frac{1}{\sqrt{2}}\pi\sigma^2\bar{c}\,\rho^2 \qquad \ldots(3.37)$$

It readily follows that number of collisions of molecules of Type 1 with those of Type 2 would be given by

$$Z_{12} = \frac{1}{\sqrt{2}}\pi\sigma^2\,\bar{c}\,\rho_1\,\rho_2 \qquad \ldots(3.38)$$

where ρ_1 and ρ_2 are densities of molecules of type 1 and 2 respectively.

4. Mean Free Path Mean free path (λ) represents the mean distance travelled by a gas molecule between two successive collision. Thus,

$$\lambda = \frac{\bar{c}}{Z_1} = \frac{\bar{c}}{\sqrt{2}\,\pi\,\sigma^2\bar{c}\,\rho^2} \quad \text{[Substituting from (3.35)]} \qquad \ldots(3.39)$$

Also $PV = nRT = nN_A\,kT$

where N_A = Avogadro's number

and k = Boltzmann constant

[Gas constant (R) = Avogadro's no. (N_A) × Boltzmann constant]

or $$P = \frac{nN_A kT}{V} = \frac{NkT}{V}$$

where N (= $n\,N_A$) is total noumber of molecules in n moles of the gas

Since ρ is the number of molecules per unit volume, $\rho = \frac{N}{V}$

Thus $$P = \rho RT \quad \text{or} \quad \rho = \frac{P}{RT} \qquad \ldots(3.40)$$

Substituting the value of ρ of in (3.39),

$$\lambda = \frac{\bar{c}}{\sqrt{2}\,\pi\sigma^2\,\bar{c}\,P/kt} = \frac{kT}{\sqrt{2}\,\pi\,\sigma^2 P}$$

Mean free path is also related to the velocity of the gas. It is given by the equation

$$\lambda = \eta \sqrt{\frac{3}{Pd}}$$

where P = Pressure of the gas
d = Density of the gas
η = Coefficient of viscosity of the gas

3.7.1 Effect of Temperature and Pressure on Mean Free Path and Collision Frequency

Let us first take ***mean free path.*** It is given by the equation

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$ [Refer to previous section.]

Clearly, the variables on the RHS of the equation are P and T. Other quantities are constants, T appears in the numerator and P in the denominator. We can say that

$$\lambda \propto \frac{T}{P}$$

or λ varies directly as the temperature and varies inversely as the pressure.

Taking the case of ***collision frequency,***

Collision frequency $$Z_{11} = \frac{1}{\sqrt{2}} \pi\sigma^2 \bar{c}\, \rho^2$$ ...(3.41)

1. Effect of Temperature From the above equation, $Z_{11} \propto \bar{c}$

Also $$\bar{c} \propto \sqrt{T}$$

(RMS velocity and average velocity vary directly as the square root of absolute temperature)

$\therefore$ $$Z_{11} \propto \sqrt{T}$$

Thus, collision frequency varies directly as the square root of absolute temperature.

2. Effect of Pressure From Eq. (3.41) above,

$$Z_{11} \propto \rho^2$$

But $P \propto \rho$ (Pressure of a gas is directly proportional to ρ, i.e. number of molecules present in per unit volume of the gas)

$\therefore$ $$Z_{11} \propto P^2$$

or collision frequency varies directly as the pressure of the gas.

Example 14 *At 0°C and 1 atmosphere pressure, molecular diameter of a gas is 4×10^{-8} cm. Calculate the mean free path of its molecules.*

Solution: Mean free path is given by the equation

$$\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2\rho}$$

where σ is molecular diameter.

22400 ml of a gas at 0°C and 1 atm pressure contains 6.02×10^{23} molecules.

Hence, number of molecules per cc

$$\rho = \frac{6.02 \times 10^{23}}{22400} = 2.689 \times 10^{19}$$

Substituting the values in the above equation,

$$\lambda = \frac{1}{1.414 \times 3.14(4 \times 10^{-8})^2 \times 2.689 \times 10^{19}}$$

$$= 0.524 \times 10^{-5}\,\text{cm}$$

Example 15 *The RMS velocity of hydrogen at STP is 1.85 × 10^5 cm s^{-1} and its mean free path is 1.75 × 10^{-5} cm. Calculate the collision number.*

Solution:

RMS velocity, $u = 1.85 \times 10^5\ \text{cm s}^{-1}$

Average velocity $\bar{c} = 0.9213 \times \text{RMS velocity}$

$= 0.9213 \times 1.85 \times 10^5\ \text{cm s}^{-1}$

$$\text{Mean free path} = \frac{\text{Average velocity}}{\text{Collision number}}$$

$$1.75 \times 10^{-5} = \frac{0.9213 \times 1.85 \times 10^5}{\text{Collision number}}$$

or

$$\text{Collision number} = \frac{0.9213 \times 1.85 \times 10^5}{1.75 \times 10^{-5}}$$

$$= 9.734 \times 10^9\ \text{sec}^{-1}$$

Example 16 *Calculate for oxygen gas at 25°C and 1 atm pressure (a) the mean free path, and (b) number of collisions per second per molecule. The collision diameter of the oxygen molecule is 361 picometres. SI units may be used for calculation.*

Solution:

(a) $1\ \text{atm} = 1.01325 \times 10^5\ \text{Nm}^{-2}$

$T = 25°\text{C} = 298\ \text{K}$

$\sigma = 361\ \text{pm} = 361 \times 10^{-12}\ \text{m} = 3.61 \times 10^{-10}\ \text{m}$

$$\lambda = \frac{kT}{\sqrt{2}\,\pi\,\sigma^2 P} = \frac{(1.38 \times 10^{-23}\ \text{JK}^{-1})(298\ \text{K})}{1.4142 \times 3.1416 \times (3.61 \times 10^{-10}\ \text{m})^2 (1.01325 \times 10^5\ \text{Nm}^{-2})}$$

$= 7.02 \times 10^{-8}\ \text{m} = 70.2\ \text{nm}$ $\quad [1\,\text{J} = 1\ \text{kgm}^2\text{s}^{-2} = 1\,\text{Nm}]$

(b)

Average velocity $\bar{c} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left[\frac{8(8.314\ \text{J K}^{-1}\text{mol}^{-1})(298\ \text{K})}{3.1416 \times 32 \times 10^{-3}\ \text{kg mol}^{-1}}\right]^{\frac{1}{2}}$

$= 444.0\ \text{ms}^{-1}$

Collision number Z_1 is given by

$$Z_1 = \sqrt{2}\,\pi\sigma^2\,\bar{c}\,\rho$$

As $\rho = \frac{P}{kT}$, the value of Z_1 can be writhen as

$$Z_1 = \frac{\sqrt{2}\,\pi\,\sigma^2\,\bar{c}\,P}{kT} \qquad (k \text{ is the Boltzmann constant})$$

Substituting the values of σ, $\bar{c}$, P, k and T, we have

$$Z_1 = \frac{(1.4142)(3.1416)(3.61 \times 10^{-10}\ \text{m})^2(444.0\ \text{m s}^{-1})(1.01325 \times 10^5\ \text{Nm}^{-2})}{(1.38 \times 10^{-23}\ \text{J K}^{-1})(298\ \text{K})}$$

$$= 6.32 \times 10^9\ \text{s}^{-1}$$

3.8 VISCOSITY OF GASES

Like liquids, gases also exhibit the property of viscosity. It is a property by virtue of which it tends to oppose the relative motion between two adjacent layers. In gases, the viscosity arises from the transfer of momentum between two adjacent layers of the gas. The coefficient of viscosity η is given by the equation

$$F = -\eta\left(\frac{dv_y}{dz}\right) \quad \text{If } \frac{dv_y}{dz} = 1, \quad \text{then } F = -\eta \quad \text{or } \eta = -F$$

Coefficient of viscosity is defined as the force per unit area required to establish a unit velocity gradient between two adjacent layers of the gas (or fluid), a unit distance apart. The negative sign comes from the fact that if F is in the positive 7-direction, the velocity v_y decreases in successive layers and $\frac{dv_y}{dz}$ is negative.

In SI units, F has the units of kg m s^{-2}/m^2 (it is the force per unit area) and $\frac{dv_y}{dz}$ has the units of ms^{-1}/m. Therefore, units of η are kg m^{-1} s^{-1}. CGS unit of η is called poise (P). A poise is one tenth of the SI unit

or $$1\text{P} = 0.1\ \text{kg m}^{-1}\ \text{s}^{-1}$$

Viscosity in Terns of Momentum Transfer

As a result of collision between the molecules of a gas, the momentum of the faster layer is deceased by the entry of molecules from the slower layer. The collision between the molecules is responsible for the transfer of momentum. These factors that control the rate of momentum transfer are average molecular speed, the mean free path and the concentration of molecules.

Maxwell, using the kinetic theory of gases, showed that η is given by

$$\eta = \frac{1}{3}\lambda \bar{c}\, m\rho \qquad \ldots(3.42)$$

where m is the mass of the molecule and ρ is density defined by $\rho = N/V$, i.e. number of molecules per unit volume. It has been evaluated in previous sections that $\rho = P/kT$ where P is the pressure and k is Boltzmann constant. It has been derived under the section on collision frequency and collision diameter that

$$\lambda = \frac{kT}{\sqrt{2}(\pi\sigma^2)P} \qquad \ldots(3.43)$$

Substituting the values in Eq. (3.42), we have

$$\eta = \frac{1}{3}\left(\frac{kT}{\sqrt{2}(\pi\sigma^2)P}\right)\left(\frac{\delta kT}{\pi m}\right)^{\frac{1}{2}} m\left(\frac{P}{kT}\right) \qquad \ldots(3.44)$$

Multiplying numerator and denominator on RHS by N_A, Avogadro's number and simplifying, we get

$$\eta = \frac{2(MRT)^{\frac{1}{2}}}{3\pi^{1/2}N_A(\pi\sigma^2)} = \frac{2(MRT)^{\frac{1}{2}}}{3\pi^{3/2}N_A\sigma^2} \qquad \ldots(3.45)$$

Here, $\pi\sigma^2$ represents the collision cross section of the gas.

However, a more rigorous treatment by Chapman places the numerical coefficient in Eq. (3.42) as $\frac{1}{2}$ in place of $\frac{1}{3}$

$$\therefore \qquad \eta = \frac{1}{2}\lambda \bar{c}\, m\rho \qquad \ldots(3.46)$$

1. Calculation of Mean Free Path λ from Viscosity Measurement According to this equation,

$$\lambda = \frac{2\eta}{\bar{c}\rho'} \qquad \ldots(3.47)$$

where $\bar{c}$ is the average velocity and ρ' is the density of the gas

As $$V = \frac{RT}{p}, \text{ hence } \rho' = \frac{M}{V} = \frac{PM}{RT} \qquad \ldots(3.48)$$

Also, we know average velocity $\bar{c} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$

Substituting the value of $\bar{c}$ from Eq. (3.49) in Eq. (3.47), we get

$$\lambda = \frac{1}{\sqrt{2}\rho'}\left[\frac{\pi RT}{M}\right]^{\frac{1}{2}}\eta \qquad \ldots(3.50)$$

Thus from the value of η, we can calculate λ.

2. Calculation of Collision Diameter σ from Viscosity Measurement We have the relation (Eq. (3.41) Art. 3.7)

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2}$$

Comparing this equation with Eq. (3.50), above,

$$\frac{1}{\sqrt{2}\rho}\left(\frac{\pi RT}{M}\right)^{\frac{1}{2}}\eta = \frac{kT}{\sqrt{2}\rho\pi\sigma^2} \qquad \ldots(3.51)$$

Boltzmann constant

$$k = \frac{R}{N_A}$$

$$\therefore \quad \sigma^2 = \frac{(MRT)^{\frac{1}{2}}}{\pi^{3/2}N_A\eta} \qquad \ldots(3.52)$$

Thus, from viscosity measurement, we can obtain the collision diameter, σ.

Example 17 *At 20°C, coefficient of viscosity of CO_2 gas is 1.48 × 10^{-5} kg m^{-1} s^{-1}. Calculate the collision diameter of CO_2*

Solution: Moles mass M of CO_2 = 44.01 g mol^{-1} = 44.01 × 10^{-3} kg mol^{-1}

From Eq. (3.52) given above,

$$\sigma^2 = \frac{(MRT)^{\frac{1}{2}}}{\pi^{3/2}N_A\eta} = \frac{[(44.01\times10^{-3}\text{kg mol}^{-1})(8.314\text{ JK}^{-1}\text{ mol}^{-1})(293.15\text{ K})]^{\frac{1}{2}}}{(3.416)^{3/2}(6.022\times10^{23}\text{ mol}^{-1})(1.48\times10^{-5}\text{ kg m}^{-1}\text{s}^{-1})}$$

$$= 20.865\times10^{-20}\text{ m}^2$$

or $$\sigma = 4.568\times10^{10}\text{ m}$$

3. Thermal Conductivity of Gases Consider a gas in a container with two parallel walls at two different temperatures. We find from the experiments that the rate at which heat is transferred from the hotter wall to the colder wall is proportional to the area of the walls and the temperature gradient *(dT/dz)* between the walls. After the steady state has been achieved, the temperature gradient becomes constant. Mathematically, this can be put as

$$\frac{dq}{dt} = -\kappa_T A\left(\frac{dT}{dz}\right) \qquad \ldots(3.53)$$

where κ_T is thermal conductivity of the gas and *dq/dt* is the rate of heat transfer We see from the kinetic-theory treatment that

$$\kappa_T = \frac{1}{3}\lambda\bar{c}\,C_v\rho = \frac{\bar{c}\,C_v}{3\sqrt{2}\pi\sigma^2} \qquad \ldots(3.54)$$

C_v = Molar heat capacity
σ = Collision diameter
ρ = Density of the gas
λ = Collision frequency

We have used the fact that $\lambda = kT/(\sqrt{2}\pi\sigma^2 P)$ and $\rho = P/kT$

We find from Eq. (3.54) that κ_T is independent of pressure.

Although a greater number of molecules are available to bring about transmission of energy at higher pressure, presence of more molecules limits the value of mean free path λ. The two effects balance each other and, therefore, K_T is independent of pressure.

4. Diffusion in Gases Transport of mass across a concentration gradient causes diffusion in gases. If *dn/dt* is the number of gas molecules transferred per second across a vertical plane of cross-sectional area *A* and the concentration gradient is *dc/dz* then according to *Fick's first law of diffusion,*

$$\frac{dn}{dt} = -DA\left(\frac{dc}{dt}\right) \qquad \ldots(3.55)$$

Equation (3.55) can be written as

$$J_z = \frac{1}{A}\frac{dn}{dt} = -D\left(\frac{dc}{dz}\right) \qquad \ldots(3.56)$$

where

j_z = Flux along *Z*-direction due to diffusion

D = Diffusion coefficient

D has the SI units of $m^2\ s^{-1}$. The negative sign in Eq. (3.56) arises from the fact that if the concentration *c* increases in the positive *Z*-direction, *dc/dz* is positive but the flux is in the negative *Z*-direction because the flow is in the direction of lower concentration.

We come to know from a simple kinetic theory treatment that

$$D = \frac{1}{3}\bar{c}\,\lambda = \frac{kT\bar{c}}{3\sqrt{2}\pi\sigma^2 P} = \frac{(4k^3T^3/9\pi m)^{\frac{1}{2}}}{(\pi\sigma^2)P} \qquad \ldots(3.57)$$

The refined theory of diffusion in gases gives

$$D = \frac{3}{16}\bar{c}\,\lambda \qquad \ldots(3.58)$$

As $\bar{c}$ (average velocity), is inversely proportional to $M^{1/2}$ (refer to the equation of average velocity), we can understand Graham's law of diffusion of gases which states: Rate of diffusion of a gas is inversely proportional to the square root of the molar mass. From Eq. (3.57), we observe that *D* deceases with increase of pressure (*P*). This is because λ is inversely proportional to *P*. Hence, *D* the diffusion coefficient decreases with increase of pressure. At high pressure, the number of collisions increases and, therefore, the progress of movement of molecules along any given direction slows down.

3.9 THE BAROMETRIC FORMULA

As we move higher, the pressure of the atmosphere decreases. Barometric formula gives us the variation of atmospheric pressure with altitude.

Let us suppose the pressure at the altitude *x* is *P* and that at altitude $x + dx$ is $P + dP$. The pressure difference $-dP$ is equal to the weight (not mass) per unit area of a layer of gas of thickness *dx* and is given by

$$-dP = \rho g\, dx$$

(minus sign indicates that the pressure decreases as altitude increases)

Here, ρ is the density of the gas, and *g* is the acceleration due to gravity. Density of an ideal gas is given by $\rho = PM/RT$ where *M* is the molar mass.

$$-dP = \frac{P M g dx}{RT}$$

or $$\frac{dP}{P} = -\frac{Mg}{RT}dx, \text{ Integrating}$$

$$\ln P = -\frac{Mgx}{RT} + I \qquad \ldots(3.59)$$

where I is the constant of integration when Thus,

when $x = 0, P = P_o$

Thus, $$\ln P = -\frac{Mgx}{RT} + \ln P_o$$

or $$\ln \frac{P}{P_o} = -\frac{Mgx}{RT}$$

Taking antilog, $$P = P_o e^{\frac{-Mgx}{RT}} \qquad \ldots(3.60)$$

This is called barometric formula. P_o is the atmospheric pressure at sea level.

Example 18 *Calculate the atmospheric pressure at a hill station situated at a height of 2000 m above sea level, if the pressure at sea level is 1 atm and the temperature is 25°C (M = 29 g mol^{-1}).*

Solution: Equation (3.60) above after taking logarithm of both sides can be writhen as

$$\ln \frac{P_o}{P} = \frac{Mgx}{RT}$$

Substituting the data in this equation,

$$\log\left(\frac{1}{P}\right) = \frac{(29 \times 10^{-3}\ \text{kg mol}^{-1})(9.81\ \text{m s}^{-2})(2000\ \text{m})}{2.303 \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})} (1\ \text{J} = 1\ \text{kg m}^2\text{s}^{-2})$$

$$= 0.0996$$

$$\log P = -0.0996 = \bar{1}.9004$$

Taking antilog $$P = 0.795\ \text{atm}$$

3.10 IDEAL GAS AND REAL GAS

1. Ideal Gas A Gas Which Obeys Boyle's law, Charles law, etc. **under all conditions of temperature and pressure is known as an ideal gas or a perfect gas.** An ideal gas may also be defined as

A gas which obeys the gas equation (PV = nRT) under all conditions of temperature and pressure is called an ideal gas.

We find that there is no gas which obeys the gas laws or the gas equation under all conditions of temperature and pressure. The gases are found to obey the gas laws fairly well if the pressure is low or the temperature is high.

2. Real Gas A real gas is one which obeys the gas laws fairly well under low pressure or high temperature.

All gases are real gases. They show more and more deviations from the gas laws as the pressure is increased or the temperature is decreased.

Deviation of Real Gases from Ideal Behaviour

According to Boyle's law, PV = constant at constant temperature. This means that the product PV should remain constant at all pressure provided temperature is kept constant. Thus, a plot of PV vs P should be a horizontal straight line parallel to the X-axis. However, in actual practice, it is found that no gas gives a straight-line plot. Two types of curves are generally obtained.

(a) For gases like CO and CH_4, the product PV first decreases with increase of pressure, reaches a minimum value and then begins to increase (see Fig. 3.17.)

(b) For gases like hydrogen and helium, the product PV continuously increases with increases of pressure (see Fig. 3.17.)

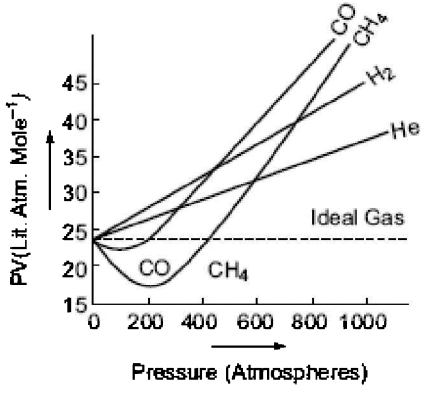


Fig. 3.17 *Plots of PV vs P for different gases at* 0°C (273 K)

3.10.1 Deviation of Real Gases from Boyle's and Charles' Law in Terms of Compressibility Factor, z

The effect of temperature and pressure on the behaviour of a gas may be studied in terms of quantity '*z*' called *compressibility factor*, which is defined as

For an ideal gas, $z = 1$ at all temperature and pressures. ***In case of real gases, the factor*** z varies from values less than 1 to values greater than 1, with changes of temperature and pressure. For example, the plots of compressibility factor z vs. pressure P at different constant temperatures for nitrogen gas are shown in (Fig 3.18). From these plots, it is observed that as the temperature increases, the minimum in the curves shift upwards. Ultimately, a temperature is reached at which the value of z remains close to 1 over an appreciable range of pressure. For example, in case of nitrogen gas, at 50°C, the value of z remains close to 1 up to nearly 100 atmospheres. ***This temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point because at this temperature Boyle's law is obeyed over a range of pressures.*** Obviously, above the Boyle temperature, a gas shows positive deviations only.

$$z = \frac{PV}{nRT}$$

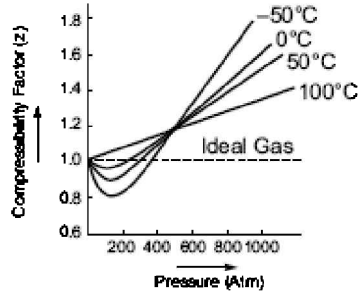


Fig. 3.18 *Plot of Z vs P for N_2 different temperatures*

Deviations from Charles Gay-Lussac's Law According to Charles Gay-Lussac's law, the coefficient of volume expansion of every gas should be same [i.e. 1/273 of its volume at 0°C] independent of pressure. However, experiments have shown that this is true only at low pressures. Appreciable deviations are observed at high pressure.

Example 19 *Calculate the volume of 10 moles of methane at 100 atm pressure and 0°C. At this temperature and pressure, Z = 0.75.*

Solution:

$$Z = \frac{PV}{nRT}$$

$\therefore$

$$V = \frac{ZnRT}{P}$$

$$= \frac{0.75 \times 10 \times 0.0821 \times 273}{100}$$

$$= 1.68 \text{ litres}$$

3.10.2 Causes of Deviation of Real Gas from Ideal Behaviour

The gas laws are derived from kinetic theory of gases which is based upon certain assumptions. Thus there must be something wrong with certain assumptions. A careful study shows that at high pressure or low temperature, the following two assumptions of kinetic theory of gases become invalid.

1. **The volume occupied by the gas molecules is negligible as compared to the total volume of the gas.**
2. **The forces of attraction or repulsion between the gas molecules are negligible.**

The above two assumptions are valid only if the pressure is low or the temperature is high so that the distance between the molecules is large. However, if the pressure is high or the temperature is low, the gas molecules come close together.

Under these conditions:

1. The forces of attraction or repulsion between the molecules are not negligible.
2. The volume of the gas is so small that the volume occupied by the gas molecules cannot be neglected.

3.10.3 Derivation of van der Waals Equation for Real Gases

van der Waals obtained the equation for real gases by applying the corrections for volume and pressure as explained below:

1. Correction for the Volume Suppose u is the actual volume occupied by one mole of the gas molecules. Then since the gas molecules are in motion, it has been found that the effective volume occupied by the gas molecules is four times the actual volume i.e., equal to 4 u. Let it be represented by b. The volume b is also called co-volume or excluded volume. Thus, the free space available for the movement of the gas molecules is $(V - b)$. Hence, in the real gas equation, V should be replaced by $(V - b)$ [see Fig. 3.19].

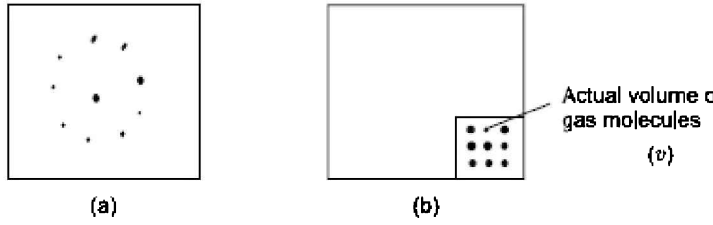


Fig. 3.19 *(a) Gas molecules are dispersed in the whole space of the container (b) Actual volume of the gas molecules*

2. Correction for the Forces of Attraction, i.e. Pressure Correction A gas molecule lying in the interior of the gas such as molecule A in Fig. 3.20 is attracted by all other gas molecules surrounding it. Hence, the net force of attraction exerted on such a molecule by the other molecules is zero. However, for a molecule lying near the wall of the container, such as molecule B in Fig. 3.20, the molecules lying inside the bulk of the gas exert some net inward pull. Thus, the effect of such an inward pull is "dragging back" of the molecule. Consequently, the pressure with which the gas molecule strikes the wall of the vessel is less than the pressure that would have been exerted if there were no such inward pull.

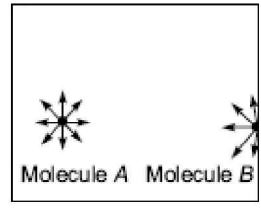


Fig. 3.20 *intermolecular forces of attraction*

Thus, the ideal pressure would be greater than the observed pressure by a factor p where p is the "correction factor due to the inward pull. This inward pull on the gas molecules lying near the wall depends upon

(a) Number of molecules surrounding a molecule.

(b) Total number of molecules

Each of these factors in turn depends upon the density (ρ) of the gas. Hence, correction factor, $p \propto \rho^2$

But for a given mass of the gas,

$$\rho \propto \frac{1}{V}$$

where V is the volume of the gas.

$$\therefore \quad p \propto \frac{1}{V^2}$$

or
$$p = \frac{a}{V^2}$$

where a is a constant, depending upon the nature of the gas. Thus,

$$\text{corrected pressure} = P + \frac{a}{V^2}$$

Putting the corrected values of volume and pressure in the ideal gas equation, $PV = RT$, for 1 mole of the gas, the equation is modified to

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This equation is known as van der Waals equation. The constants a and b are called van der Waals constant whose values depend upon the nature of the gas and are independent of the temperature and pressure.

For* n *moles of the gas, $\rho \propto \frac{n}{V}$ and effective volume = nb. Hence, the van der Waals equation takes the form

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = n\,RT$$



Fig. 3.21 *Johannes Diderick van der waals (1837-1923) was a Dutch physicist. He received the Nobel prize in 1910 for his work on the properties of gases and liquids.*

3.10.4 Significance of van Der Waals Constants a and b

It is found that the values of a for the easily liquefiable gases are greater than those for the so-called permanent gases like H_2 and He. Moreover, the value of a increases with the ease of liquefaction of the gas. We know that a gas which is more easily liquefiable has greater intermolecular forces of attraction. Hence, 'a', is ***a measure of the intermolecular forces of attraction in a gas.***

'b' is the 'effective volume' of the gas molecules. The constancy in the value of b for any gas over a wide range of temperature and pressure confirms that ***the gas molecules are incompressible.***

3.10.5 Behaviour of Real Gases Using van Der Waals Equation

1. A Low Pressure At extremely low pressure, V is very large. Hence, the correction term $\frac{a}{V^2}$ is very small. Similarly, the correction term b is also very small as compared to V. Thus, both the correction terms can be neglected so that the van der Waals equation reduces to $PV = RT$. This is why at extremely low pressure, the gases obey the ideal gas equation.

2. At Moderate Pressure As the pressure is increased, the volume decreases and hence the factor a/V^2 increases. Thus, the factor a/V^2 can no longer be neglected. However, if the pressure is not too high, the volume V is still sufficiently large so that b can be neglected in comparison with V. Thus, the van der Waals equation reduces to

$$\left(P + \frac{a}{V^2}\right) V = RT$$

or
$$PV + \frac{a}{V} = RT$$

or
$$PV = RT - \frac{a}{V}$$

Thus, PV is less than RT by a factor $\frac{a}{V}$. As the pressure increases, V decreases, so that the factor $\frac{a}{V}$ increases. Thus, PV decreases as the pressure is increased. This explains why a dip in the plots of PV vs P of real gases is obtained (see Fig. 3.17).

3. At High Pressure As the pressure is increased further so that it is fairly high, $V$is so small that b can no longer be neglected in comparison with V. Although under these conditions, the factor a/V^2 is quite large but since P is very high so a/V^2 can be neglected in comparison with P. Thus, the van der Waals equation reduces to

$$P(V - b) = RT$$

or
$$PV - Pb = RT$$

or
$$PV = RT + Pb$$

Thus, PV is greater than RT by a factor Pb. Now as the pressure is increased, the factor Pb increases more and more. This explains why after the minima in the curves, the product PV increases continuously as the pressure is increased more and more (Fig. 3.17).

4. At High Temperature At any given pressure, if the temperature is sufficiently high, V is very large so that as in case 1, the van der Waals equation reduces to $PV = RT$. Hence, at high temperature, real gas behaves like an ideal gas.

3.10.6 Exceptional Behaviour of Hydrogen and Helium

In case of hydrogen and helium, their molecules have very small masses. Hence, in the case of these gases, intermolecular forces of attraction are extremely small even at high pressures. In other words, the factor a/V^2 is negligible at all pressures. Hence, the van der Waals equation is applicable in the following form at all ***pressures and ordinary temperatures.***

$$P(V - b) = RT \text{ or } PV = RT + Pb$$

This explains why hydrogen and helium show positive deviation only which increases with increase in the value of P.

Example 20 *Two moles of ammonia gas are enclosed in a vessel of 5-litre capacity at 27°C.*

Calculate the pressure exerted by the gas. assuming that

(a) The gas behaves like an ideal gas (using ideal gas equation)

(b) The gas behaves like a real gas (using van der Waals' equation)

Given that for ammonia, a = 4.17 atm litre^2 mol^{-2} (or 4.17 atm dm^6 mol^{-2}) and b = 0.037 litre mol^{-1} (or 0.037 dm^3 mol^{-1})

Solution: We are given that

n = 2 moles

V = 5 litres or dm^3

T = 27°C = (27 + 273) K = 300 K

a = 4.17 atm litre^2 mol^{-2} or atm dm^6 mole^2

b = 0.037 litre mol^{-1} or dm^3 mol^{-1}

We know that

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1} \text{ atm or dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

(a) If the gas behaves like an ideal gas, we have,

$$PV = nRT$$

$$\therefore \quad P = \frac{nRT}{V}$$

$$= \frac{2 \times 0.0821 \times 300}{5} = 9.85 \text{ atm}$$

(b) If the gas behaves like a real gas, we apply. van der Waals equation, i.e.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$= \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.031} = \frac{4.17 \times (2)^2}{(5)^2}$$

$$= 9.33 \text{ atm}$$

Example 21 *Calculate the pressure exerted by one mole of carbon dioxide gas in a 1.32 dm^3 vessel at 48°C using the van der Waals equation. The van der Waals'constants are a = 3.59 dm^6 atm mot^{-2} and b = 0.0427 dm^3 mol^{-1}*

Solution: The van der Waals equation can be written as

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Substituting the values for different quantities, we have

$$P = \frac{(1 \text{ mol})(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(321 \text{ K})}{(1.32 \text{ dm}^3) - (1 \text{ mol})(0.0427 \text{ dm}^3 \text{ mol}^{-1})} - \frac{(1 \text{ mol})^2 (3.59 \text{ dm}^6 \text{ atm mol}^{-2})}{(1.32 \text{ dm}^3)^2}$$

$$= 20.62 \text{ atm} - 2.06 \text{ atm} = 18.56 \text{ atm}$$

Example 22 *Calculate from the van der Waals equation the temperature at which 3 moles of SO_2*

would occupy a volume of 0.01 m^3 at 1519875 Nm^{-2} pressure (a = 0.679 $Nm^4\ mot^{-2}$, $b = 5.64 \times 10^{-5}$ $m^3\ mol^{-1}$, R = 8.314 $J\ K^{-1}\ mol^{-1}$).

Solution: The van der Waals equation may be written as

$$T = \frac{1}{nR}\left(P + \frac{an^2}{V^2}\right)(V - nb)$$

Substituting the values which are in SI units,

$$T = \frac{1}{3 \times 8.314}\left(1519875 + \frac{0.679 \times 3^2}{(0.01)^2}\right)(0.01 - 3 \times 5.64 \times 10^{-5})$$

$$= \frac{1}{24.942} \times 1580985 \times 0.0098308$$

$$= 623.1\ \text{K}$$

3.10.7 Kammerlingh-Onnes (Virial) Equation of State for Real Gases

It is an empirical equation which expresses PV as a power series of pressure P at any given temperature. It is written as

$$PV = A + BP + CP^2 + DP^3 + \ldots$$

where P is the pressure in atmospheres and V is the molar volume in litres. The coefficients A, B, C etc., are known respectively as the first, second, third, etc., **virial coefficients.** The following points may be noted about the above equation:

1. The virial coefficients are different for different gases.
2. At very low pressure, only the first virial coefficient is significant and it is equal to RT, i.e.
$$A = RT$$
3. At higher pressures, the other virial coefficients also become important and must also be considered.
4. For any particular gas, the values of A, B, C, etc., are constant at constant temperature. Their values change with change of temperature. The first virial coefficient A is always positive and increases with temperature. On the other hand, the second virial coefficient B is negative at low temperatures. With increase of temperature, it increases to zero and then becomes more and more positive. The temperature at which $B = 0$ is called ***Boyle temperature.*** At this temperature, Boyle's law is valid over a fairly wide pressure range.

The other form in which the Onnes equation is often written is by expressing the compressibility factor (Z) as a power series in $1/V$, i.e.

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots$$

or

$$PV = RT\left[1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\right]$$

Where the coefficients B, C, etc. (called second, third virial coefficient, etc.) for a particular gas depend only on the temperature and not on the pressure.

Example 23 *What is the molar volume of N_2 (g) at 500 K and 600 atm according to (a) the perfect gas law, and (b) the virial equation? The virial coefficient B of N_2 (g) at 500 K is 0.0169 litre mot^{-1}.*

Solution:

(a) According to the perfect gas law,

$$V = \frac{RT}{P} = \frac{0.0821 \times 500}{600} = 0.0684 \text{ litre}$$

(b) $$PV = RT\left(1 + \frac{B}{V}\right) = RT + \frac{RT}{V}B$$

or $$PV = RT + PB$$

or $$V = \frac{RT + PB}{P}$$

or $$V = \frac{RT}{P} + B = \left(\frac{0.0821 \times 500}{600}\right) + 0.0169$$

$$= 0.0684 + 0.0169 = 0.0853 \text{ litre mol}^{-1}$$

3.10.8 Boyle's Temperature

It is the temperature at which a gas behaves like an ideal gas. This temperature is given by

$$T_B = \frac{a}{Rb}$$

Boyle's temperature may be derived from the van der Waal's equation as follows:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

It may be written in the form

$$PV = RT - \frac{a}{V} + bp + \frac{ab}{V^2} \qquad \ldots(3.61)$$

As both a and b are small, and if the pressure is not too high so that V is not so small, $\frac{ab}{V^2}$ can be neglected.

Further, V in the correction term a/V may be replaced by RT/P.

Then Eq. (3.61) reduces to

$$PV = RT - \frac{aP}{RT} + bP$$

$$= RT + P\left(b - \frac{a}{RT}\right)$$

Since the gas behaves ideally at Boyle's temperature, $PV = RT$

Hence the second term on RHS should be zero.

Since P has a finite value,

$$b - \frac{a}{RT} = 0 \quad \text{or} \quad T = \frac{a}{Rb}$$

or Boyle's temperature

$$T_b = \frac{a}{Rb} \qquad \ldots(3.62)$$

3.10.9 Second Virial Coefficient using van der Waals Equation

The general equation of state as given by Onnes is

$$PV = RT\left[1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\right] \qquad \ldots(3.63)$$

The second virial coefficient B of this equation can be obtained by comparing it with van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

which may be rewritten in the form

$$PV = RT + bp + \frac{ab}{V^2} - \frac{a}{V}$$

or

$$PV = RT + bp - \frac{a}{V} + \frac{ab}{V^2}$$

As a and b are very small and if the pressure is not too high, $\frac{ab}{V^2}$ can be neglected. Further, P may be replaced by $\frac{RT}{V}$.

Hence, we get

$$PV = RT + b\frac{RT}{V} - \frac{a}{V}$$

or

$$PV = RT\left[1 + \frac{1}{V}\left(b - \frac{a}{RT}\right)\right] \qquad \ldots(3.64)$$

Comparing Equation (3.63) and (3.64), we get

$$\boxed{B = b - \frac{a}{RT}}$$

Thus, the second virial coefficient can be calculated from a knowledge of the van der Waals constant a and b of the gas at temperature T.

Example 24 *The van der Waals constant b for CO_2 is 4.28×10^{-2} dm^3 mol^{-1}. Assuming the CO_2 molecule to be spherical, calculate its molecular diameter.*

Solution: For 1 mole of the gas,

$$b = 4\,N\upsilon_m$$

where N is Avogadro's number and υ_m is the actual volume of the gas molecule.

$$v_m = \frac{n}{4V} = \frac{0.0428}{4 \times 6.022 \times 10^{23}} \text{ litres}$$

$$= 1.777 \times 10^{-26} \text{ litres}$$

$$= 1.777 \times 10^{-23} \text{ cm}^3$$

But $$v_m = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3$$

$\therefore$ $$\sigma^3 = \frac{6v_m}{\pi} = \frac{6 \times 1.777 \times 10^{-23}}{3.143}$$

$$= 33.92 \times 10^{-24}$$

which gives $$\sigma = 3.24 \times 10^{-8} \text{ cm or } 3.24 \text{ A}^\circ$$

3.10.10 Other Equations of State

Besides van der Waals equations and virial equation, a number of other equations have been worked out to give P–V–T relation in case of real gases. Some of these are described as under. In all these gases, the quantity of gas considered is one mole.

1. Berthelot Equation Berthelot proposed the following equation to explain the behaviour of real gases:

$$\left(P + \frac{a}{TV^2}\right)(V - b) = RT$$

Here, the correction term for pressure is a/TV^2 in place of a/V^2.

2. Dieterici Equation Dieterici proposed the following equation for the P–V–T behaviour of real gases:

$$Pe^{a/RTV}(V - b) = RT$$

or $$P(V - b) = RT\, e^{-a/RTV}$$

This equation gives satisfactory results at moderate pressure in line with the van der Waals equation. However, at higher pressures, it gives results in greater agreement with experimented data.

3. Radlich-Kwong Equation This equation may be written as

$$\left[P + \frac{a}{V(V + b)T^{\frac{1}{2}}}\right](V - b) = RT$$

This equation has been found to be the best two-parameter equation of state for real gases. The constant a is temperature dependent. It is being frequently used because of its simplicity.

4. Clausius Equation To account for the variation of a with temperature, Clausius used the following equation:

$$\left[P + \frac{a}{T(V + c)^2}\right](V - b) = RT$$

c is an additional constant. The Clausius equation explains fairly well the behaviour of real gases.

3.11 CRITICAL PHENOMENON_

Andrews studied the pressure-temperature conditions for liquefaction of several gases. He observed that for each gas, there is a temperature above which the gas cannot be liquefied, however high pressure we may apply. This temperature is called ***critical temperature*** which is different for different gases.

At critical temperature and pressure, the gas becomes identical with its liquid and is said to be in ***critical state.*** The smooth merging of the gas with its liquid state is referred to as the ***critical phenomenon.***

3.11.1 Critical Temperature, Critical Pressure and Critical Volume

Critical temperature (T_c) of a gas may be defined as that temperature above which the gas cannot be liquefied, howsover high pressure we may apply on the gas. The minimum pressure required to liquefy the gas at the critical temperature is called the ***critical pressure (P_c).*** The volume occupied by one mol of the gas at the critical temperature and pressure is called is called the ***critical volume (V_c).***

The critical temperature, critical pressure and critical volume of a gas are collectively called the ***critical constants*** of the gas. For example, the critical constants of carbon dioxide (CO_2) are

$$T_c = 31.1°C \text{ or } 304.2 \text{ K}$$

$$P_c = 72.9 \text{ atmospheres}$$

$$V_c = 95.65 \text{ cm}^3 \text{ mol}^{-1}$$

3.11.2 Measurement of Critical Constants (T_c, P_c and V_c)

1. Measurement of T_c and P_c The measurement of critical temperature (T_c) is based upon the observation that when a liquid, e.g. ether or carbon disulphide, is heated in a closed space, the surface of separation between the liquid and the vapour disappears at a definite temperature and on cooling, the surface of separation reappears at the same temperature. The temperature at which this occurs is the critical temperature.

The apparatus used for the measurement of the critical temperature is shown in Fig. 3.22. It helps to measure critical pressure simultaneously. It consists of a glass bulb B containing only the liquid and its vapour sealed over mercury. The bulb is connected to a manometer M containing air above the mercury.

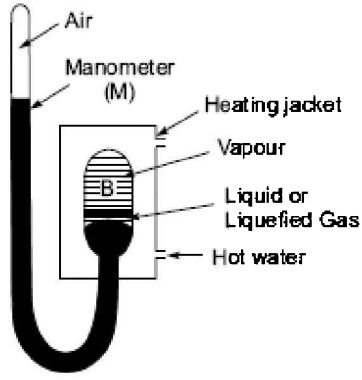


Fig. 3.22 *Measurement of critical temperature and pressure*

The bulb *B* is surrounded by a heating jacket as shown in the Fig. 3.22. The bulb *B* is heated gently by circulating hot water in the heating jacket and the temperature is noted at which the meniscus disappears. The bulb is then allowed to cool till the meniscus reappears or the cloudiness appears on the surface of the bulb due to condensation of vapour. The mean of the two temperatures gives the critical temperature of the liquid/gas enclosed in the bulb *B*.

Corresponding pressure from the manometer at the two stages is noted and taking their mean, gives the critical pressure *(P_C)*.

2. Measurement of V_C The measurement of critical volume (V_C) is based upon a rule which states that the mean of the densities of any substance in the state of liquid and saturated vapour at the same temperature is a linear function of the temperature.

Thus, to determine the critical volume of any substance, the densities of the substance in the liquid state and those of the vapour in equilibrium with it are determined at a number of temperatures. If these densities are plotted against temperature, the curve obtained is as shown in Fig. 3.23. The densities of the vapour lie along the curve *AC* while those of the liquid lie along the curve *BC*. The two curves meet at the point *C* which corresponds to the critical temperature. If the mean values of densities $\left(\frac{d_l + d_v}{2}\right)$ are plotted against temperature, a straight line *CD* is obtained. The line on extrapolation meets the density axis at *D* which corresponds to the critical density. Dividing the molecular weight of the substance by the critical density, ***critical volume*** is obtained.

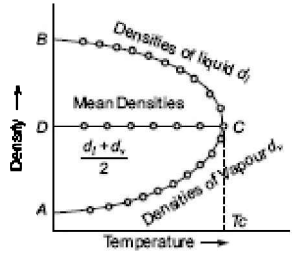


Fig. 3.23 *Determination of critical density*

3.11.3 Andrews' Experiments on Critical Phenomenon (Isotherms of Carbon Dioxide)

Andrews, in 1861, studied the effect of temperature and pressure on the volume of carbon dioxide. Each time, keeping the temperature constant at a particular value, he measured the volume of carbon dioxide at different pressures. He then plotted the volumes against pressures, at the constant temperature. Such a plot of *P* vs *V* at constant *T* is called an ***isotherm.*** A number of such isotherms were obtained at different temperatures as shown in Fig. 3.24.

At the lowest temperature, i.e. 13.1°C (286.2 K), at low pressure, carbon dioxide exists as a gas, as shown at the point *A*. As the pressure is increased, the volume of the gas decreases along the curve *AB*. At the point *B*, the liquefaction of the gas starts. Hence, the volume decreases rapidly along *BC* because the liquid has much less volume than the gas. At the point *C*, the liquefaction is complete. Now the increase of pressure has very little effect upon the volume because liquids are hardly compressible. Hence, a steep curve *CD* is obtained as shown in Fig. 3.24. Thus, along the portion *AB*, carbon dioxide exists only as gas, along the portion *BC*, the liquid and the vapour are in equilibrium with each other and along *CD*, carbon dioxide exists only as liquid.

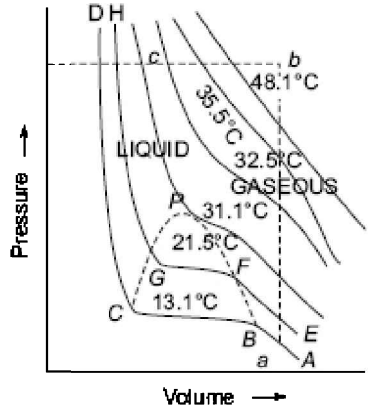


Fig. 3.24 *Isotherms of carbon dioxide*

The isotherm *EFGH* at 21.5°C is similar to that at 13.1°C except that the horizontal portion over which the liquefaction occurs is shorter. In fact, as the temperature is raised, this portion becomes smaller and smaller and finally at 31.1°C, it is reduced only to a point. In the isotherms above 31.1°C, the horizontal position completely disappears. This shows that above 31.1°C, the liquefaction of the gas does not take place at all howsoever high pressure may be applied. Thus, 31.1°C is the critical temperature of carbon dioxide. The pressure required to liquefy the CO_2 gas at 31.1°C (304.2 K) is found to be 72.9 atmospheres, which is, therefore, the critical pressure for CO_2.

It has been observed that in case of all other gases, similar isotherms are obtained. However, lengths of the horizontal portions and the peak of the dotted parabola are different, depending upon the nature of the gas.

3.11.4 Continuity of State

If the ends of the horizontal portions of the different isotherms are joined together, a parabolic curve (shown by dotted lines in Fig. 3.24) is obtained. The peak of this parabola represents the critical point. Within the parabola, the liquid and the vapour exist together in equilibrium. Outside the parabola, the substance exists only as a gas under the conditions represented on the right side and only as liquid under the conditions represented on the left side. A close examination reveals that below the critical temperature, it is possible to change a substance from gaseous state to liquid state without having both the phases present together at any stage. This is explained as under:

Suppose the substance under consideration is CO_2 so that Fig. 3.24 may be referred again. At 13.1°C, if pressure and volume correspond to the point *a*, the substance is gaseous. Keeping the volume constant, if the gaseous CO_2 is heated till it has pressure corresponding to the point *b*, the path *ab* is followed. Now keeping the pressure constant, suppose the gaseous CO_2 is cooled and the volume decreases along the path *bc*. At *c*, CO_2 will exist as liquid. Thus, nowhere along the path *abc*, there has been more than one phase present. This is expressed by saying that the change of state from gaseous to liquid is ***continuous*** or it is referred to as the ***continuity of state***.

3.11.5 Expression for Critical Constants in Terms of van der Waals Constants a and b

For 1 mol of a gas, the van der Waals equation is written as

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

On simplification, it gives

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

Multiplying throughout by V^2, we get

$$PV^3 + aV - PbV^2 - ab = RTV^2$$

Dividing throughout by P, we get

$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} = \frac{RT}{P}V^2$$

Rearranging in the descending powers of V, we get

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 - \frac{a}{P}V - \frac{ab}{P} = 0 \quad \ldots (3.65)$$

Using the appropriate values of the van der Waals constants a and b and the gas constant R for any constant value of T (used by Andrews in his experiments), the values of V can be obtained for different values of P. The ***theoretical isotherms*** thus obtained are shown in Fig 3.25. These curves are similar to those obtained experimentally (Fig. 3.25), except that in the curves below the critical temperature, the horizontal portions are replaced by curved portions. For example, in the isotherms at 13.1°C, the horizontal portion BC has been replaced by the curved portion $BXYZC$. This is expected because the van der Waals equation is cubic in V, as written above. Hence, for every value of pressure P, it has three roots (i.e. three values of V), all of which may be real or one may be real and the other two may be imaginary. Below the ***critical temperature,*** all the three roots are real in a certain pressure range, and these values come closer as the isotherm moves upwards. At the ***critical temperature,*** all the roots become equal for a particular pressure. ***Above the critical temperature,*** for any value of P, there is only one real root, i.e. only one value of V.

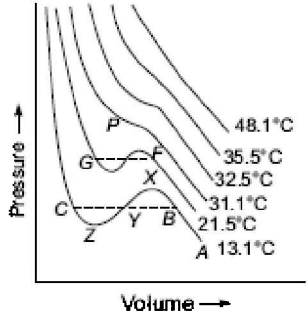


Fig. 3.25 *Theoretical isotherms of CO_2*

It has been found that the portions BX, XYZ and ZC represent metastable conditions and can be actually obtained in practice by careful experimentation.

As stated above, at the critical temperature, the three values of V become identical for a particular value of pressure P. If we represent critical volume by V_c,

$$V = V_c \text{ or } (V - V_c)^3 = 0$$

Expanding this, we get

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad \ldots (3.66)$$

Further, as already explained, the van der Waals equation may be written in the form

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

At the critical point, the terms P and T may be replaced by the critical values P_c and T_c. Hence, the above equation may be written as

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 \quad \ldots (3.67)$$

At the critical point, equations (3.66) and (3.67) must be identical. Hence, the coefficients of similar powers of V must be equal in both the equations. Equating the coefficients of terms of similar power of V, we obtain the following relations:

$$3V_c = b + \frac{RT_c}{P_c} \quad \ldots (3.68)$$

$$3V_c = \frac{a}{P_c} \quad \ldots (3.69)$$

and

$$V_c^3 = \frac{ab}{P_c} \quad \ldots (3.70)$$

These equations can be solved to calculate the critical constants V_c, P_c and T_c in terms of van der Waals constant a and b. Dividing Eq. (3.70) by (3.69), we get

... (3.71)

Substituting this value in Eq. (3.69), we get

... (3.72)

Substituting the values of V_c and P_c in Eq. (3.68), we get

... (3.73)

3.11.6 Derivation of Relation between the Critical Constant P_c, V_c and T_c

Writing again the equations between critical constants and van der Waals constants,

... (3.74a)

... (3.74b)

... (3.74c)

To obtain a relationship between P_c, V_c and T_c, we need to eliminate a and b from equations. From Eq. (3.74a),

... (3.75a)

Substituting this value of b in Eq. (3.74b), we get

... (3.75b)

Substituting the value of a and b from equations (3.75a) and (3.75b) in Eq. (3.74c), we get

... (3.76)

3.11.7 van der Waals Constants a and b in Terms of Critical Constants

Expressions for a and b in terms of P_c and V_c are

Expressions in terms of P_c and T_c are

These equations can be obtained by eliminating a and b separately using the equations.

... (3.77)

Example 25 *The critical temperature and critical pressure of chlorine are 146°C and 93.5 atmosphere respectively. Calculate the values of the van der Waals constants a and b.*

Solution: Here, we are given that

The relations between critical constants are

Dividing Eq. (ii) by Eq. (i), we get

Taking R = 0.0831 litre atm degree^{-1} and mol^{-1} and putting the given values of T_c and P_c in equations (iii) and (iv), we get

Solution in terms of SI units

Example 26 *The critical temperature of carbon dioxide gas is 31.1°C and its critical density is 0.455 g/cm^3. Find out the values of a, b and P_c for the gas (R = 0.082 litre/atm/degree/mol).*

Solution:

Dividing (ii) by (iii), we get

Substitute the value of b from (i) in the above equation,

3.11.8 Reduced Equation of State and the Law of Corresponding States

The pressure, volume and temperature of a gas can be expressed in terms of the critical pressure, volume and temperature respectively as under:

... (3.78)

Thus, the quantities π, ϕ and θ may be defined as

The quantities π, ϕ and θ are called reduced pressure, reduced volume and reduced temperature respectively.

Substituting the values of P, V and T given by Eq. (3.78), in van der Waals equation

we get

Substituting the values of P_c, T_c and V_c in terms of van der walls constants, viz.

This equation which relates the reduced pressure, volume, temperature (i.e. π, ϕ and θ) is called the ***reduced equation of state.*** A significant point about this equation is that this does not involve the constant a, b and R and hence is applicable to all substances in the liquid and the gaseous state.

Another important conclusion drawn from the above equation is as follows: ***If two substances have the same reduced pressure and the same reduced temperature, they must have the same reduced volume.*** The above statement is called the ***law of corresponding states*** and the substances having the same reduced pressure and same reduced temperature and, hence, the same reduced volume are said to be in the corresponding states.

Example 27 *The reduced volume and temperature of a gas are 10.2 and 0.7. What will be its pressure if its critical pressure is 42 atm?*

Solution: It is given that

Reduced volume $\phi = 10.2$, reduced temperature, $\theta = 0.7$, critical pressure $P_c = 42$ atm

According to the reduced equation of state,

Substituting the value of ϕ and θ, we get

Example 28 *Calculate the pressure exerted by one mole of CO_2 at 40°C when confined to a volume of 0.17dm^3 by making use of the law of corresponding states. The values of the critical pressure (P_c), critical volume (V_c) and critical temperature (T_c) are 73 atmosphere 0.0957 dm^3 and 30.42°C respectively.*

Solution :

Substitute in the reduced equation of state and calculate π.

PROBLEMS FOR PRACTICE

1. Calculate the critical temperature of a real gas for which P_c is 100 atm and b is 50 cm^3 mol^{-1}

[Ans. 487.2 K]

2. A certain gas has the following values of critical constants:

$P_c = 45.6$ atm, $V_c = 0.0987$ dm^3 mol^{-1} and $T_c = 190.6$ K.

Calculate the van der Waals constants of this gas.

[Ans. $a = 1.333$ dm^6 atm mol^{-2}, $b = 0.0329$ dm^3 mol^{-1}]

3. The van der Waals constants of a gas are $a = 0.751$ dm^6 atm mol^{-2} and $b = 0.0226$ dm^3 mol^{-1}. Calculate its critical constants.

[Ans. $V_c = 0.0678$ dm^3 mol^{-1}, $P_c = 54.5$ atm, $T_c = 120$ K]

3.12 LIQUEFACTION OF GASES

On lowering the temperature and increasing the pressure, the molecules of a gas come close to one another. A stage reaches when the gas liquefies and appears as a liquid. Certain gases like carbon dioxide can be liquefied by applying pressure even at room temperature. There are others which require slightly higher pressure than the atmospheric pressure and the temperature of freezing mixtures like sodium cholide and ice is enough to achieve liquefaction. Faraday liquefied a number of gases by a technique as shown in Fig. 3.26 below.

Fig. 3.26 *liquefaction by Faraday's method*

3.12.1 Liquefaction of Gas by the Adiabatic Expansion of Compressed Gas—Linde's Process

This process is based upon Joule-Thomson effect which is stated as follows:

When a gas under high pressure is allowed to expand adiabatically through a fine orifice (hole) into a region of low pressure, it is accompanied by cooling.

The reason for the cooling is that when the gas expands from a region of high pressure to the region of low pressure, the intermolecular distances increase. Some work is done in separating the molecules apart. This is done at the cost of kinetic energy of the gas. Thus, the kinetic energy of the gas decreases and therefore, the temperature falls.

It may be mentioned here that in case of hydrogen and helium, heating takes place instead of cooling. These gases are warmed up if allowed to expand as above, under ordinary temperature. However, if these gases are first cooled to some particular temperature and then allowed to expand, they behave like other gases. The temperature to which a gas should thus be cooled to given normal Joule-Thomson effect is called the ***inversion temperature.*** The inversion temperatures for hydrogen and helium are –80°C and –240°C respectively. The process based upon the above principle is known as ***Linde's process.*** The apparatus used is shown in Fig. 3.27.

Fig. 3.27 *Linde's process for liquefaction of air*

This apparatus was used by Linde for the liquefaction of air. The procedure adopted is as follows:

The air is first compressed to about 200 atmospheres in the compressor and then passed through the condensing coils. As a result, the air is cooled and the water vapours present condense to form the liquid which is removed. The dry air is than passed through the copper spiral which terminates into a jet. The air expands through the jet into the chamber where the pressure of the air falls down to about 50 atmospheres. Thus, as a result of Joule-Thomson effect, the air is cooled.

As this cooled air moves up, it further cools the incoming air. The cooled air is sent to the compressor again and the process is repeated a number of times till ultimately the air is cooled to such an extent that it liquefies. The liquefied air collects at the bottom of the chamber and can be drawn off. Any uncondensed air is recirculated.

3.12.2 Liquefaction by the Adiabatic Expansion of Compressed Gas Involving Mechanical Work—Claude's Process

This process is based upon the principle that when a gas expands adiabatically against a piston in an engine, it does some external work. Hence, its internal energy falls and consequently the temperature of the gas falls. This principle combined with the Joule-Thomson effect, has been applied in Claude's process for the liquefaction of air. The apparatus used is shown in Fig. 3.28.

Fig. 3.28 *Claude's process*

The purified air, i.e. air freed from carbon dioxide and water vapour, is first compressed to about 200 atmospheres. The compressed air then passes through the tube T which bifurcates at the point X. A part of the air goes into the cylinder fitted with an airtight piston and the rest of the air passes through the coil C having a jet J at its end. The air that goes into the cylinder pushes the piston and thus does some external work. As a result, the internal energy of the air falls and hence the temperature falls. The cooled air then enters the chamber D at the point Y. The air then passes through the coil C, cooled by the Joule-Thomson effect as it comes out of the jet J into the chamber D. The cooled air going upwards in the chamber D further cools the incoming air in the coil C. The cooled air is led to the compressor and the process is repeated a number of times till the air is cooled to such an

extent that it liquefies. The liquefied air collects in the chamber and can be withdrawn.

3.12.3 Liquefaction by Adiabatic Demagnetisation

The process is based upon the principle that when a magnetised body is demagnetised adiabatically (i.e. in such a way that heat can neither enter nor leave the system), the temperature of the body must fall. When a suitable solid is magnetised, the order is increased, since various magnetic entities are aligned. When demagnetisation is allowed to occur, the disorder returns and, therefore, the entropy increases Thus, heat is absorbed and the cooling of the substance and its surroundings takes place. Nowadays, lower temperatures are commonly attained by this method.

PROBLEMS FOR PRACTICE

1. If van der Waals equation of a gas is given by $(V - 0.0024) = 0.0041\ (273 + t)$, calculate T_c and P_c, if $R = 0.082\ L\ \text{atm}\ K^{-1}\ \text{mol}^{-1}$

   [Ans. $P_c = 50.54$ atm, $T_c = 236.39$ K]

2. A certain gas has the following critical constants: $P_c = 45.6$ atm., $V_c = 0.0987\ l\ \text{mol}^{-1}$ and $T_c = 190.5$ K. Calculate van der Waals constants for the gas. Estimate the radius of the molecule, assuming it to be spherical.

   [Ans. $a = 1.333\ L^2\ \text{atm mol}^{-2}$ $b = 0.0329\ L\ \text{mol}^{-1}$ $r = 2.35$ Å]

3. What is the mean free path of argon at 2988 K and a pressure of 1 atm? Given $\sigma = 1.86$ Å

   [Ans. 1115 Å]

4. van der Waals constant for CO_2:

   Calculate the critical temperature and critical volume, $R = 0.0821$ L atm K^{-1} mol^{-1}

   [Ans. 3PC, 12.34×10^{-2} L mol^{-2}]

5. van der Waals constant '*b*' for O_2 gas is 0.0318 L mol^{-1}. Calculate the diameter of the O_2 molecule.

   [Ans. 2.934×10^8 cm]

6. Calculate the pressure exerted by 10 g of N_2 enclosed in a 1 L flask at 298 K, assuming ideal behaviour.

   [Ans. 8.73 atm]

7. 1 mole of CO_2 has a volume of 1.5 L at 300 K. If $R = 0.0821$ L atm K^{-1} mol^{-1} then the values of '*a*' and '*b*' are 1.04 and 0.04 respectively. Find the pressure of the gas using van der Waals equation.

   [Ans. 16.39 atm]

8. The critical temperature and pressure of chorine are 4.19 K and 9.474×10^6 Nm^{-2} respectively Calculate van der waals constants '*a*' and '*b*' Given = 8.314 JK^{-1}

   [Ans. $a = 0.54\ \text{Nm}^4\ \text{mol}^{-2}$, $b = 4.59 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$]

9. Calculate the compressibility factor of a van der Waals gas at the critical point [Hint: Compressibility factor Z of a gas is given by

   Substitute the value of critical constants

10. 1 mole of the gas occupies a volume of 10.7 litres at 313 K. Calculate the pressure using
    (a) ideal gas equation
    (b) van der Waals equation

[Ans. 2.40 atm. 2.891 atm].

11. Find the temperature at which the r.m.s. velocity of CO_2 gas is the same as that of Cl_2 at 293 K.

[Ans. 181.57 K]

12. Calculate the r.m.s. velocity of N_2 at 298 K. The molecular weight of N_2 is 28.02

[Ans. $u = 5.14 \times 10^4$ cm sec^{-1}]

13. Calculate the root mean square velocity and average velocity of CO_2 at 291 K and 400 mm pressure.

[Ans. $u = 48390$ cm sec^{-1}, $c = 40920$ cm sec^{-1}]

SOLVED PROBLEMS

Example 29 *An ideal gas can never be liquefied. Justify.*

Solution: According to kinetic theory of gases, which is applicable to ideal gases, there are no forces of attraction between the molecules of a gas. In the absence of forces of attraction, it is not possible to bring them together and obtain them in the liquefied state.

Example 30 *Prove that van der Waals equation reduces to ideal gas equation at Boyle 's temperature.*

Solution: At Boyle's temperature, the gas behaves in an ideal manner. Therefore, the van der Waals equation reduces to ideal gas equation.

Example 31 *The values of van der Waals constant 'a' for two gases are x and y respectively (x >> y). Which of these can be liquefied easily?*

Solution: Force of attraction between the molecules of a gas is a factor that governs the liquefaction process. The quantity '*a*' in van der Waals equation for real gases is related to force of attraction between the molecules. A greater value of '*a*' means greater force of attraction, which in then means greater chance of liquefaction. Thus, the gas having '*x*' as the value of '*a*' can be liquefied more easily.

Example 32 *Can a gas of the type P (V – b) = RT be liquefied? Explain.*

Solution: In the above equation, the quantity '*a*' which refers to the force of attraction between gaseous molecules, does not occur. In the absence of a force of attraction, it is not possible to liquefy the gas.

Example 33 *The compressibility factor for N_2 at 223 K at 800 atm. pressure is 1.95 and at 373 Kand 200 atm., it is 1.10. A certain mass of N_2 occupied a volume of 1 L at 223 K and 800 atm. Calculate the volume occupied by the quantity of N_2 at 373 Kand 800 diameters.*

Solution: at temperature T_1, volume V_1 and pressure P_1

Similarly,

SUMMARY

1. An ideal gas is one that has no intermolecular forces of attraction or repulsion. Kinetic gas equation is PV where u is root mean square velocity
2. Kinetic energy of an ideal gas is related to temperature.
3. Maxwell distribution of molecular velocities is given by the expression

4. *Collision diameter* σ is the distance between the centre of two molecules at the point of closest approach. Mean free path λ is defined as the distance travelled by a gas molecule between two collisions. Mathematically, for an ideal gas,
5. Number of coordinates required to specify the position of all the mass points, i.e. atoms in the molecule, is called the degrees of freedom
6. Total energy of a molecule is divided equally amongst the various degrees of freedom of the molecule. This is called the principle of *equipartition of energy*. According to this principle, C_v = 3*R*/2 for mono-atomic gases, = 2.7 *R* for diatomic gases and = 3.3 *R* for triatomic gases.
7. Viscosity of a gas is defined as the property by virtue of which it tends to oppose the motion between two adjacent layers of a gas. Coefficient of viscosity, η, is given by $F = -\eta (du_y/dz)$.
8. A *real* gas is one which obeys the gas laws fairly well under low pressure and high temperature.
9. The effect of temperature and pressure on the behaviour of a gas may be studied in terms of quantity z called *compressibility factor* given by the relation

10. The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called *Boyle 's temperature*.
11. Causes of deviation of real gases from ideal behaviour are (a) the force of attraction between the molecules are not negligible, and (b) the volume occupied by the gas molecules is not negligible compared to the volume of the gas.
12. For *n* moles of the gas, the van der Waals equation is given by

    where *a* and *b* are called van der Waals constants
13. For each gas, there is a temperature above which the gas cannot be liquefied, however high pressure we may apply. This temperature is called *critical volume* (T_c). The volume occupied by one mole of the gas and pressure exerted by the gas at critical temperature are called *critical volume* (V_c) and *critical pressure* (P_c) respectively.
14. The relation between critical constants and van der Waals constants are given by

15. When a gas under high pressure is allowed to expand adiabatically through a fine orifice (hole) into a region of low pressure, it is accompanied by cooling. This is called Joule-Thomson effect.
16. The temperature to which a gas must be cooled to give Joule-Thomson effect is called inversion temperature.
17. The liquefaction of a gas can be carried out by the following methods:
    (a) Linde's process
    (b) Claude's process
    (c) Adiabatic demagnetisation

EXERCISES

Based on Different University Papers

1. Objective Questions

(A) Fill in the Blanks

1. There is no effect of_____on the velocity of gas molecules.
2. For an ideal gas, $C_P - C_V$ is equal to_____
3. Average velocity =_____× RMS
4. The distance covered by an atom of a gas between the consecutive collisions is called_____
5. The value of R is 0.0821. The unit of this is_____
6. Moistured air diffuses_____through a small hole in comparison with dry air.
7. Pressure-volume curves drawn at constant temperature are called_____
8. The temperature at which real gases behave like ideal gases is called_____
9. Heat capacity of a diatomic gas is_____than that of monoatomic gas.
10. Deviation from ideal behaviour of a gas is more prominent at_____

(B) Multiple-Choice Questions

1. A real gas closely approaches the behaviour of an ideal gas at
   (a) 15 atmospheres and 220 K
   (b) 1 atm and 273 K
   (c) 0-5 atm and 500 K
   (d) 15 atm and 500 K
2. An ideal gas cannot be liquefied because
   (a) its critical temperature is always above 0°C
   (b) its molecules are relatively smaller or in size
   (c) it solidifies before becoming a liquid
   (d) forces operative between its molecules are negligible
3. A real gas will approach the behaviour of ideal gas at
   (a) low temperature and low pressure
   (b) low temperature and high pressure
   (c) high temperature and high pressure
   (d) high temperature and low temperature
4. The gas that is heated up during Joule-Thomson effect at ordinary temperature is:
   (a) O_2
   (b) CO_2
   (c) H_2
   (d) SO_2
5. The temperature at which the second virial coefficient of a real gas is zero is called:
   (a) critical temperature
   (b) eutactic point
   (c) boiling point
   (d) Boyle's temperature

6. The van der Waals equation explains the behaviour of
   (a) ideal gas
   (b) real gases
   (c) vapours
   (d) non-real gases
7. Which one of the following gases has the maximum value of root mean square velocity?
   (a) CH_4
   (b) CO_2
   (c) H_2
   (d) CO
8. Degrees of freedom in a water molecule are
   (a) 1
   (b) 2
   (c) 3
   (d) 4
9. Expansion of a gas above inversion temperature creates
   (a) cooling
   (b) heating
   (c) constant temperature
   (d) none
10. The value of C_p/C_v for inert gases is
    (a) 1.33
    (b) 1.66
    (c) 2.13
    (d) 1.99
11. Which is not true in case of an ideal gas?
    (a) It cannot be converted into a liquid.
    (b) There is no interaction between the molecules.
    (c) All molecules of the gas move with same speed.
    (d) At a given temperature, PV is proportional to the amount of the gas.
12. A gas is said to behave like an ideal gas when the relation PV/T = constant. When do you expect a real gas to behave like an ideal gas?
    (a) When the temperature is low
    (b) When both the temperature and pressure are low
    (c) When both the temperature and pressure are high
    (d) When the temperature is high and pressure is low
13. The gas which can be liquefied under high pressure and 40°C is
    (a) nitrogen
    (b) hydrogen
    (c) oxygen

(d) ammonia

14. Which set of conditions represent easiest way to liquefy a gas?
    (a) Low temperature and high pressure
    (b) High temperature and low pressure
    (c) Low temperature and low pressure
    (d) High temperature and high pressure
15. Gases deviate from the ideal gas behaviour because their molecules
    (a) possess negligible volume
    (b) have forces of attraction between them
    (c) are polyatomic
    (d) are not attracted to one another
16. An ideal gas, obeying kinetic theory of gases, can be liquefied:
    (a) It cannot be liquefied at any P and T
    (b) Its pressure is more than P at a temperature less than T
    (c) Its temperature is more than critical temperature T
    (d) Its pressure is more than critical pressure P
17. Formula for inversion temperature is
    (a)
    (b)
    (c)
    (d)
18. The correct representation of van der Waals equation is
    (a) $PV = RT$
    (b)
    (c)
    (d)
19. Critical temperature means above this temperature at any pressure, any gas can be
    (a) liquefied
    (b) not liquefied
    (c) both statements are correct
    (d) Solified
20. According to the van der Waals correction to get the pressure of ideal gas in observed pressure a definite fraction for correction is
    (a) subtracted
    (b) added
    (c) divided
    (d) unchanged

Answers

(A) Fill in the Blanks

1. Gravitational
2. R
3. 0.9213
4. Mean free path
5. Lit atm K^{-1} mol^{-1}
6. Faster
7. Isotherms
8. Boyle's temperature
9. Greater
10. High temperature and low pressure

(B) Multiple-Choice Questions

1. (c)
2. (d)
3. (d)
4. (c)
5. (d)
6. (b)
7. (c)
8. (c)
9. (b)
10. (b)
11. (c)
12. (d)
13. (d)
14. (a)
15. (b)
16. (b)
17. (c)
18. (b)
19. (b)
20. (b)

GENERAL QUESTIONS

1. (a) State the law of corresponding states.
   (b) Derive the equation

   (c) What are the units of van der Waals constants 'a' and 'b'?
2. (a) What do you understand by principle of corresponding states? Deduce the expression of

corresponding states from van der Waals equation.

(b) What do you understand by continuity of state? Explain with the help of isotherm of carbon dioxide.

3. (a) What is the physical meaning of the constant 'a' and 'b' in the van der Waals equation

Show by deriving a relationship between the parameters of this equation and the critical constant that

(b) The critical volume for methane (CH_4) is 99 ml mol^{-1}. Assuming the molecules to be spherical, estimate the diameter of methane molecule.

(c) Draw the isotherm of CO_2 below and above its critical temperature. Write briefly how these isotherms are used to understand the principle of liquefaction of gases.

4. (a) Using the principle of equipartition of energy and taking various degrees of freedom of motion into consideration, estimate the value of C_V for SO_2 (a bent molecule).

(b) What is the equation for the fraction of gas molecule with speed in a certain range according to Maxwell distribution law of speeds? Also illustrate the effect of temperature on

(i) the distribution, and

(ii) the most probable speed with the help of curves.

(c) Write the van der Waals equation for n moles of a real gas. Also calculate the van der Waals constants of CO_2 for which the critical constants are

(Ans. $b = 4.28 \times 10^{-2}$ L mol^{-1} $a = 3.612$ atm. mol^{-2})

5. Explain, what is meant by critical constants of a gas. Derive the relations you will use to calculate these from van der Waals constants.

6. (a) Derive the following:

where the symbols have their usual meanings.

(b) When temperature of a gas is increased, what happens with the following?

(a) Most probable velocity

(b) Number of molecules with higher velocity

(c) Distinguish between an ideal and a real gas.

(d) If van der Waals equation of a gas is given by

calculate T_c and P_c ($R = 0.082$ L atm K^{-1} mol^{-1})

7. (a) State Maxwell's law for distribution of velocities among the molecules of a gas. How does change in the temperature of a gas influence this distribution?

(b) Explain the following with reasons:

(i) The molar volumes of various liquids are studied at their boiling points.

(ii) An ideal gas cannot be liquefied.

(iii) Real gases show ideal behaviour at very low pressure

(c) The reduced volume and temperature of a gas are 10.2 and 0.7. What will be the pressure if its critical pressure is 40 atmospheres?

8. (a) Write van der Waals equation of state for n moles of a real gas and write the significance of van der Waals constant 'a' and 'b'.

   (b) A gas cannot be liquefied above 304 K but the same can be liquefied by applying a pressure of 7396725 Nm^2 at 304 K. Calculate van der Waals constant (R = 8.314 JK^{-1} mol^{-1}).

   (c) State the law of corresponding states and deduce the equation.

   What is the limit of its applicability?

9. (a) State and explain the principles used in the liquefaction of gases by

   (i) Claude's process

   (ii) Linde's process

   (b) What is the limitation of equipartition of energy?

   (c) A 10 dm^3 flask contains 64 g of oxygen at 300 K. Calculate the pressure of the gas in kPa:

   (i) If oxygen is an ideal gas

   (ii) If oxygen is a real gas

10. (a) Briefly describe Maxwell's distribution of velocities of gases.

    (b) Explain the following with reasons:

    (i) Why cannot H_2 gas be liquefied at room temperature?

    (ii) Gases cannot be liquefied merely by the application of pressure above their critical temperature.

    (iii) An ideal gas cannot be liquefied.

    (c) Derive the kinetic gas equation.

11. (a) Outline the basic assumptions of the kinetic theory of gases. Show that the total pressure (P) exerted by an ideal gas containing N molecules (each of mass m) and occupying volume V is given by

    where u^2 has the standard meaning of mean square velocity for molecules.

    (b) Draw the curve showing Maxwell distribution of molecular velocities at a definite temperature in a gas and indicate on the curve the positions of the average (υ), most probable (υ_{mp}) and the root mean square ($\upsilon_{r.m.s}$) velocities. Also describe/illustrate how this distribution changes with an increase in temperature.

    (c) How many vibrational degrees of freedom are there in the nonlinear O_3 molecule?

12. Write down the assumptions of the kinetic theory of gases and point out those assumptions which were later on found valid for real gases. Also derive the kinetic gas equation.

13. (a) Isotherms of CO_2 at different temperatures have helped in establishing a relationship between critical constants and van der Waals constants. Justify.

    (b) What is an ideal gas? What are the causes for deviation of real gases from ideal behaviour?

    (c) The reduce volume and temperature of the gas are 10.2 and 0.7. What will be its pressure if its critical pressure is 42 atmospheres?

    [Ans. 6.7 atm]

14. What are the limitations of the kinetic gas equation?

    (a) Give an account of the improvement suggested by van der Waals.

(b) Calculate the pressure exerted by one mole of CO_2 gas at 40°C confined to a volume of 0.107 dm^3 using the law of corresponding states. The critical constants of the gas are V_c = 0.0957 dm^3, T_c = 304 K, P_c = 72 atm

[Ans. 74.46 atm]

15. (a) What is the principle of equipartition of energy?

(b) What is Z called in the following equation?

Also write the value of Z for an ideal gas.

16. What is the virial equation of state?

(a) Express the van der Waals equation of state in the form of virial equation of state. Calculate Boyle's temperature.

(b) Calculate the volume occupied by 1 mole of a slightly imperfect gas at 4.75 atm and 17°C. The second virial coefficient is 0.028 L mol^{-1}.
[*Hint:* Due to slight imperfect nature of the gas,
the gas behaves more ideal. The pressure correction, i.e.

The equation of state of the gas becomes

Second virial coefficient

17. (a) What are the limitations of the equation $PV = RT$? What improvements have been suggested by van der Waals?

(b) Define compressibility factor and Boyle's point. What is the value of compressibility factor for an ideal gas? Under what conditions of temperature and pressure, does nitrogen gas behave almost as an ideal gas?

(c) Write the virial equation in terms of

(i) Pressure

(ii) Volume

(d) One mole of ammonia gas is enclosed in a vessel of 2.5 dm^3 at 300 K. What will be the pressure of a real gas when

18. (a) State the law of corresponding state and deduce the equation

Boiling points are approximately the corresponding temperature. Justify this statement.

(b) Calculate the root mean square velocity for the following set of molecules: 10 molecules moving at 5×10^2 ms^{-1}, 20 molecules moving at 10×10^2 ms^{-1} and 5 molecules moving at 15×10^2 ms^{-1}

[Ans. $u = 2.8 \times 10^2$ ms^{-1}]

19. (a) What is an ideal gas? What are the causes for deviation of real gases from ideal behaviour?

(b) Show that van der Waals equation for one mole of a gas can be written in the form

(c) Derive the kinetic gas equation.

(d) van der Waals constant '*b*' for NO gas is 0.0278 dm^3 mol^{-1}. Calculate the diameter of NO molecule.

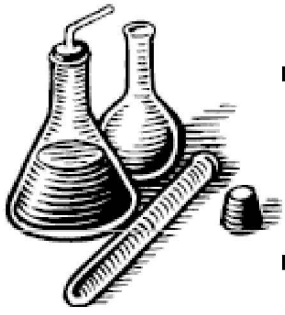
20. (a) Derive the equation of state for a gas in critical state.

(b) The critical temperature and critical pressure of Cl_2 gas are 146°C and 93.5 atm respectively. Calculate the value of van der Waals constants '*a*' and '*b*'.

[Ans. 1 atm, 101325 Nm^{-2}]

(c) Explain Linde's process for the liquefaction of gases.

(d) Define the principle of equipartition of energy.



The Liquid State

4

LEARNING OBJECTIVES

- Gain an insight into the molecular arrangement in liquids
- Study different intermolecular forces in liquids like dipole-dipole interactions, London forces and hydrogen bonding
- Understand the terms surface tension, and interfacial tension and study the methods of determination of surface tension
- Study methods for the determination of vapour pressure of a liquid
- Study the term parachor and its applications in the determination of structure of compounds
- Define the terms viscosity and fluidity and study the methods for determination of viscosity
- Study the relationship between viscosity and chemical constitution
- Understand the terms refractive index, specific refractivity and molar refractivity and the application of molar refractivity in the determination of structure of a compound.
- Study the liquid crystal state and different kinds of liquid crystals
- Learn the swarm theory of liquid crystals
- Learn the applications of liquid crystals

4.1 INTRODUCTION

A liquid may be regarded as a condensed gas or a molten solid. Molecules of a solid are rigidly fixed and, therefore, it has a definite shape and a definite volume. On the other hand, molecules of a gas show random movement and, therefore, it neither has a definite shape nor a definite volume. The situation in a liquid is intermediate between those of the solid and the gas. Molecules in a liquid are not as rigidly fixed as in solids but at the same time it is much more restricted than in gases. Therefore, liquids do not possess a definite shape although they possess a definite volume.

4.1.1 Differences Between Solids, Liquids and Gases in Terms of Structure

We may discuss the structures of solids, liquids and gases in terms of kinetic molecular theory. Molecules in a gas are in a state of constant random motion. The space between the molecules is large and, therefore, there is a negligible force of attraction between the molecules. In liquids, the force of attraction between the molecules are sufficiently strong to hold them in contact with one another. But, the molecules can move past one another through the vacant spaces or holes here and there. A liquid may be defined as *a collection of molecules held close to one another but showing random motion through the intervening empty spaces.* In solids, there are strong intermolecular forces, which fix the position of each molecule. The molecules in a solid are not able to leave their position, However, small oscillations around the mean position are possible. Structures of gases, liquids and solids may be represented with the help of Fig. 4.2.

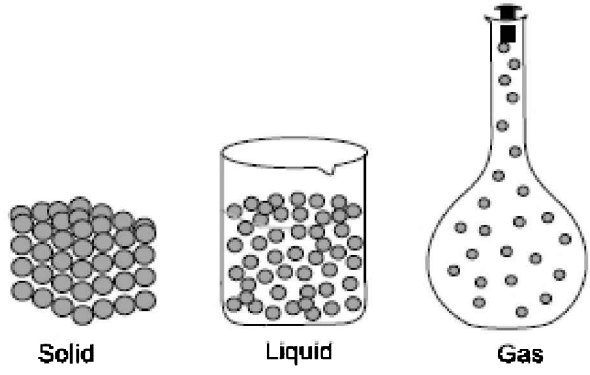


Fig. 4.1 *There is very little space between the molecules in a solid, greater space between those in a liquid and a large space between the molecules in a gas.*

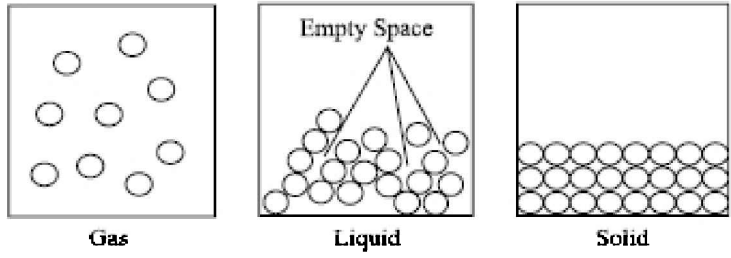


Fig. 4.2 *Molecular structures of gas, liquid and solid.*

Ering and Ree proposed in 1961 a theory that intermolecular space in a liquid is not randomly distributed but contains holes of molecular size. The liquid is thus considered a congregation of holes and molecules as shown in Fig 4.3. Based on these assumptions, Ering and Ree calculated the melting point, boiling point, critical constants, etc., of argon gas. There was a striking resemblance between the theoretical and experimental

values.

Free Volume in a Liquid We observe that molecules in a liquid move over an infinitesimally small distance before colliding with another molecule. This is in contrast to gases where the molecules move comparatively much larger distances before striking other molecules. This can be explained by saying that each molecule in a liquid is surrounded by almost 10 to 12 molecules forming a spherical cage as shown in Fig. 4.4 such that r_2 is only slightly bigger than r_1. The central molecule can move in a limited volume. This volume for one mole of the gas is called free volume.

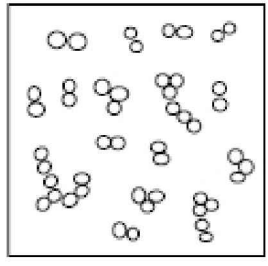


Fig. 4.3 *Holes and molecules in a liquid*

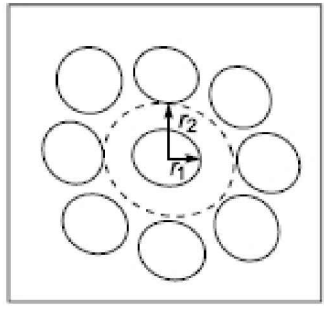


Fig. 4.4 *Free volume in a liquid*

A new algorithm could help understand the structure of liquids and how they flow through porous media. Theoretical physicist Moumita Maiti and colleagues at the Jawaharlal Nehru Centre for Advanced Scientific Research in Bangalore, India, have now implemented an algorithm for analysing void space in sphere packing, where the spheres need not all be the same size. This method could be applied to analyse the geometry of liquids present between multi-sized spheres that are akin to a model for porous materials. This provides a tool for studying the flow of such fluids through porous materials.

4.1.2 Intermolecular Forces in Liquids

The intermolecular forces in liquids can be discussed under three heads.

1. Dipole-dipole Interactions Such interactions occur in polar molecules. Take the

example of HCl. It is a polar molecule with one end having a partial positive charge and the other end having a partial negative charge. Such molecules are called dipoles. The positive end of one molecule attracts the negative end of another molecule. There is a net attractive force between the polar molecules; such attractive forces are called dipole-dipole attraction. The strength of such forces is generally 1% of that of a covalent bond. It is observed that attractive forces between the opposite poles are stronger than the repulsive forces between like poles. Thus, there is a net force of attraction. It is illustrated in Fig. 4.6.



Fig. 4.5 *Structure of liquids*

$$H^{\delta+} — Cl^{\delta-}$$

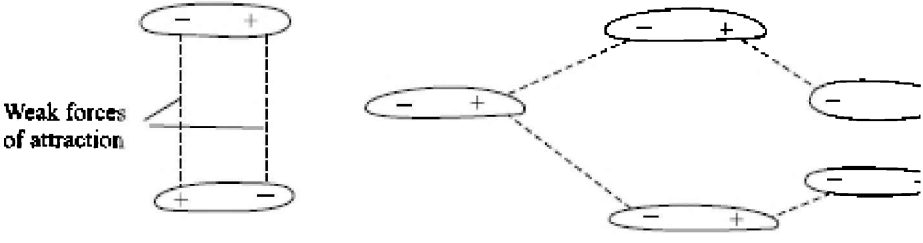


Fig. 4.6 *Weak forces of attraction between polar HCl molecules*

2. London Forces Fritz London in 1930 explained the force of attraction between non-polar molecules. A non-polar molecule is formed between the atoms of similar electronegativity by sharing of electrons. The shared electron pairs lie exactly in the middle.

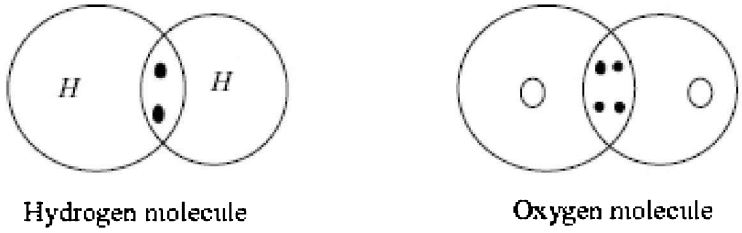


Fig. 4.7 *Hydrogen molecule and oxygen molecule*

Even these molecules exhibit weak attractive forces. London explained this by saying that according to the principle of probability, at a particular instant, the electrons may shift to one side of the molecule making that side negative and the other side positive. This creates a dipole.

Such a dipole is called ***instantaneous dipole.*** The negative pole of such a molecule repels the electrons of neighbouring nonpolar molecules making that end positive and the other end negative

Thus, an induced dipole is created. This instantaneous dipole and induced dipole will now attract each other. Because of the mobile nature of electrons, instantaneous dipole may disappear the next moment and another dipole is formed. Attraction between instantaneous and induced dipole is responsible for attractive forces between nonpolar molecules. This illustrated in Fig. 4.8. Momentary attractions between the instantaneous dipole and induced dipole in liquid molecules gives rise to ***London forces.*** The strength of London forces depends upon the number of electrons in the outer orbit and the size of the molecule. Thus, argon with a greater number of electrons and large molecular size has higher b.p. than helium.

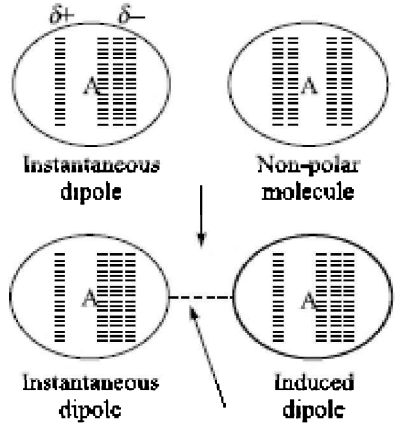
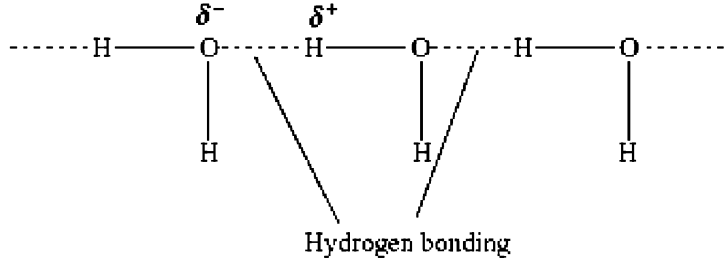


Fig. 4.8 *Representation of London forces*

3. Hydrogen Bonding Hydrogen bond occurs in molecules containing hydrogen and an electronegative atom like O, N and F, covalently bonded. Take the case of H_2O molecule. In this molecule, oxygen being electronegative attracts the shared pain of

electrons towards itself making H slightly positive and O slightly negative.

Now negative O is attracted by positive H of the second molecule and a weak bond is created between the two, which is called hydrogen bond. Hydrogen bonds between the molecules of water are shown below:

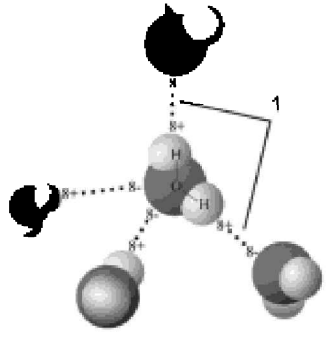


Hydrogen bond is the strongest of all intermolecular forces including the dipole-dipole interactions and London forces.

It may be noticed that all the three intermolecular forces mentioned above are collectively called van der Waals' forces.

4.1.3 Evaporation and Condensation

According to the postulates, kinetic theory of gases and liquids, the molecules are constantly moving in all possible directions and with all possible velocities. Some of the liquid molecules are moving with small velocities. They are associated with smaller kinetic energies. Such molecules continue moving in the liquid state. However, there are molecules moving faster. Such molecules possess higher kinetic energies and they have a tendency to leave the liquid phase and move into the space above the liquid. Such molecules constitute the vapour phase above the liquid phase. ***This phenomenon of high energy molecules leaving the liquid phase and moving into the vapour phase is called evaporation.***



We are able to use water for drinking, cooking, washing, and cleaning only because ofhydrogen bonding

The molecules in the vapour phase collide with one another and also with the walls

of the container. In this process, some of them lose a part of their energy and revert to the liquid state. ***Transference of molecules from the vapour phase to the liquid phase is called condensation.*** At equilibrium, as many molecules leave the liquid surface and move to the vapour phase as the molecules that move from vapour phase to liquid phase. This keeps the concentration of the substance in the two phase constant.

4.2 VAPOUR PRESSURE OF A LIQUID

Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour present above the liquid in equilibrium with the liquid at that temperature. Vapour pressure exerted by the vapours obtained from the liquid may be illustrated as shown in Fig. 4.9.

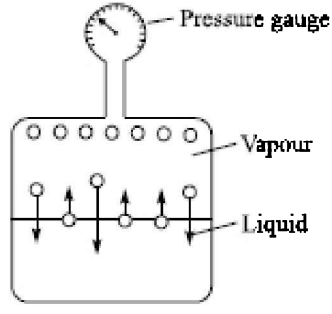


Fig. 4.9 *Illustration of Vapour pressure.*

Cooling Caused by Evaporation

When a liquid evaporates, the more energetic molecules leave the liquid. As a result, the average kinetic energy of remaining liquid decreases and hence the temperature falls.

4.2.1 Important Factors that affect the Vapour Pressure

Two important factors that determine the vapour pressure of a liquid are the following:

1. Nature of the Liquid If the intermolecular forces of attraction in the liquid are weak, the molecules can easily leave the liquid and come into the vapour phase and hence the vapour pressure is higher for example, the vapour pressures of ether, acetone, benzene, etc., are higher than that of water at the same temperature. This is shown in Fig. 4.10. Acetic acid gives lower pressure than water as the former has greater intermolecular forces caused by hydrogen bonding.

2. Effect of Temperature As the temperature of liquid is increased, the number of molecules with higher kinetic energies increases. Hence, the vapour pressure of the liquid increases. This is again evident from each curve in Fig. 4.10.

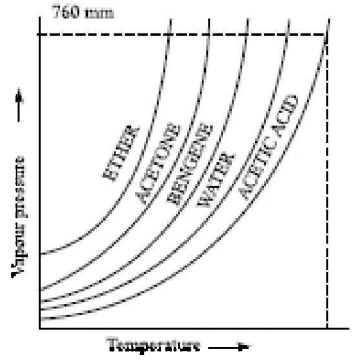


Fig. 4.10 *Vapour pressure-temperature curves for some liquids.*

(a) Boiling Point of a Liquid ***The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the boiling point of the liquid.*** For example, boiling point of water is 100°C. The boiling point for any liquid is obtained from the vapour pressure temperatures curves, as shown for acetic acid in Fig. 4.10. If the atmospheric pressure is 760 mm, the boiling point is called ***normal boiling point.***

Essentially, if the external pressure is higher, more heat will be required to make the vapour pressure equal to the external pressure and hence higher will be the boiling point. Similarly, if the external pressure is decreased, the boiling point is lowered. This is the reason that a liquid boils at a lower temperature on the top of a mountain (where pressure is low) than on the seashore.

(b) Heat of Vaporisation (ΔHv) of a Liquid After the liquid starts boiling, the extra heat supplied to the liquid is used up not in increasing the temperature of the liquid but to overcome the intermolecular forces of attraction existing in the liquid and thus changing the liquid into vapour. Hence, the temperature remains constant till whole of the liquid charges into vapour. ***The amount of heat required to change one mole of the liquid into its vapour at the boiling point is called the heat of vaporisation of the liquid.***

Quite clearly, greater the intermolecular forces of attraction present in a liquid, greater is the heat of vaporisation. For example, the heat of vaporisation of water is more than that of ether, acetone or benzene.

4.2.2 Relationship between Entities

1. Relationship between Boiling Point and Critical Temperature (Guldberg's Rule) Guld-berg gave the following general relationship between the normal boiling point (T_b) and the critical temperature (T_c) of the liquids:

$$T_b = \frac{2}{3} T_c \qquad (4.1)$$

i.e. normal boiling points of the liquids are nearly two third of their critical temperatures when both are expressed on the absolute scale.

2. Relationship between Boiling Point and Heat of Vaporisation (Trouton's Rule) Trou-ton observed the following generalisation about liquids which are not associated and which do not have too high boiling points:

$$\frac{\Delta H_v}{T_b} \approx 21 \text{ cal mol}^{-1} \text{ K}^{-1} \text{ or } \frac{\Delta H_v}{T_b} = 88 \text{ J mol}^{-1} \text{ K}^{-1} \quad (4.2)$$

where ΔH_v is in calories and T_b is in degrees absolute. This is known as ***Trouton's rule.***

Example 1 *The boiling point of carbon tetrachloride is 77°C. Estimate its molar heat of vaporisation assuming Trouton 's rule.*

Solution :$T_b = 77 + 273 = 350$ K

$$\frac{\Delta H_v}{T_b} = 88 \text{ J mol}^{-1} \text{ K}^{-1}, \text{ substituting for } T_b$$

$$\frac{\Delta H_v}{350 \text{ K}} = 88 \text{ J mol}^{-1} \text{ K}^{-1} \text{ or } \Delta H_v = (350 \text{ K})(88 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$= 30.8 \text{ kJ mol}^{-1}$$

4.2.3 Determination of Vapour Pressure of a Liquid

1. Static (Isoteniscope) Method It is a convenient and accurate method which can be used to measure the vapour pressure over a range of temperatures. The apparatus is shown in Fig 4.11. The main part of the apparatus is the isoteniscope which comprises a bulb *B* and *U*-shaped portion of the tube *C*. The bulb *B* is nearly half filled with the liquid under investigation and the same liquid is placed in the *U*-shaped portion with its level about 2-3 cm below that in the bulb. The isoteniscope is placed in the thermostat *A* whose temperature can be noted from the thermometer *T*. The isoteniscope is then connected to the rest of the apparatus which comprises a barometric tube *D* and a big bottle *E* as shown in Fig. 4.11. The bottle *E* can be connected to the atmosphere or to the vacuum pump as described:

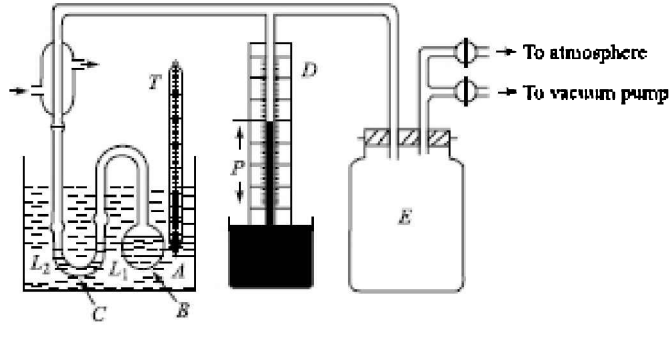


Fig. 4.11 *Isoteniscope method for measurement of vapour pressure.*

The experiment is carried out as under:

(a) The bottle E is connected to the vacuum pump and the apparatus is evacuated till the liquid boils vigorously in the bulb B. This expels all air from the isoteniscope BC. The level of the liquid in the limb L_2 stands higher than in the limb L_1.

(b) The temperature of the thermostat is now adjusted to the desired value and air is admitted slowly into the apparatus by connecting the bottle E to the atmosphere till the levels of the liquid in both the limbs L_1 and L_2 are equal. Under these conditions, the pressure in both the limbs L_1 and L_2 will be equal. Pressure in the limb L_1 is the vapour pressure whereas pressure in the limb L_2 is equal to the pressure in the rest of the apparatus and is equal to atmospheric pressure minus the height of the mercury column in the tube D. Hence, this difference gives the vapour pressure of the liquid at the temperature of the thermostat.

2. Dynamic Method This method is based upon the principle that a liquid boils at the temperature at which the vapour pressure becomes equal to the external pressure over the liquid. Thus, by fixing the external pressure over the liquid at different values, the boiling point of the liquid is determined at each external pressure. Suppose the boiling points are t_1, t_2 t_3, etc., at the external pressure P_1, P_2, P_3, etc. respectively. Then obviously the pressures P_1, P_2 P_3, etc., will be the vapour pressures at the temperatures t_1, t_2, t_3, etc., respectively. By plotting the pressures against the corresponding temperatures for any particular liquid, a curve of the type shown in Fig. 4.10 is obtained. From this curve, the vapour pressure at any temperature can be found.

4.3 SURFACE TENSION OF A LIQUID

Molecules of the liquid at the surface experience a different situation than those in the interior of the liquid. For example, a molecule lying inside the liquid is surrounded by other molecules and is attracted equally in all directions (Fig. 4.12). Hence, the net force of attraction acting on the molecule is zero. But a molecule lying at the surface is attracted downwards by the molecules lying in the bulk of the liquid. Thus, a molecule lying at the surface experiences a net inward attraction. As a result of this inward pull on all molecules lying at the surface, the surface behaves as if it were under tension. This property of liquids is called ***surface tension.*** The surface tension of a liquid is defined as the force acting at right angles to the surface along one centimetre length of the surface. Thus, the units of surface tension are dynes per cm (or newtons per metre, i.e. Nm^{-1} in the SI System).

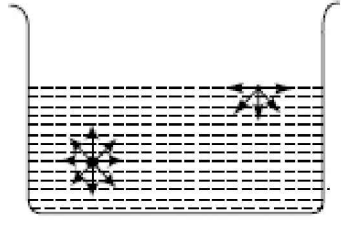


Fig. 4.12 *Surface tension*

1. Floating a Paper Clip on Water The *adjoining figure (Fig. 4.13) shows* a small piece of paper with a paper clip seated on it. The paper helps to keep the clip flat on the water surface. Slowly push the edge of the paper beneath the water with the help of a pencil as shown. The paper will go down but the clip shall remain afloat because of the surface tension of water

Why is a Drop of Liquid Spherical?

As a result of the inward pull on the molecules at the surface, the surface of the liquid tends to contract to the smallest possible area for a given volume of the liquid. It is for this reason that the drops of a liquid are spherical because for a given volume, a sphere has minimum surface area.

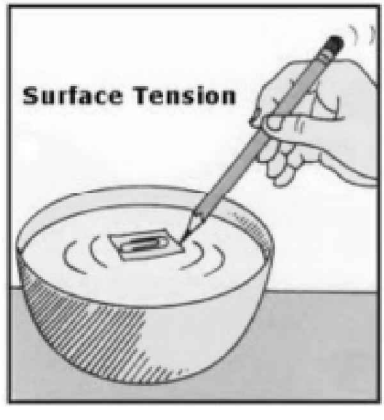


Fig. 4.13 *Surface tension experiments*

4.3.1 Surface Energy

The concept of surface energy can be understood as follows: To increase the area of surface, some work has to be done against the inward pull. Consider a soap solution film contained in a rectangular wire frame *ABCD* in which the side *CD* is movable (Fig. 4.14). In order to extend the surface area of the film, the movable wire has to be pulled from position *CD* to position *EF*. Thus, some work has to be done against surface tension.

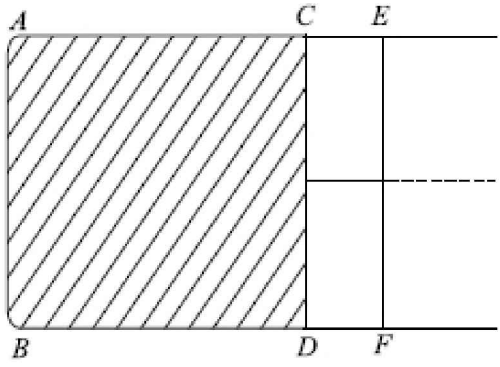


Fig. 4.14 *Concept of surface energy*

The work in ergs required to be done to increase or extend the surface area by 1 sq. cm is called surface energy. The unit of energy is, therefore, ergs per sq.cm (or joules per sq. metre J m^{-2} SI system).

In terms of dimensions,

$$\text{Surface energy} = \text{Work per sq. cm.} = (\text{Force} \times \text{Length})$$

$$= \frac{\text{dynes} \times \text{cm}}{\text{cm}^2} = \text{dyne cm}^{-1} \tag{4.3}$$

These units are the same as those of surface tension. Thus, the surface energy is same as surface tension.

4.3.2 Liquid Rises in a Capillary Tube

When one end of a capillary tube is put into a liquid that wets glass, the liquid rises into the capillary tube to a certain height. This rise is clearly due to the inward pull of surface which pushes the liquid into the capillary tube (Fig. 4.15).

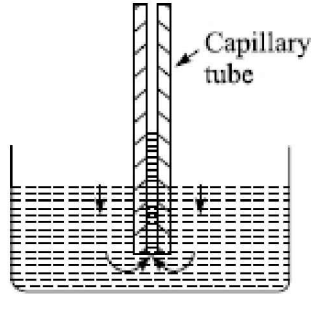


Fig. 4.15 *Rise of a liquid in a capillary tube*

In case of liquids which do not wet glass, e.g. mercury, the level inside the capillary falls below the level outside. Further whereas the upper surface of a liquid that wets glass is concave, that of mercury is convex. Such a surface is called ***meniscus*** (Greek: a

little moon). The angle which the curved surface (i.e. meniscus) makes with the wall of the tube is called ***contact angle*** (Fig. 4.16).

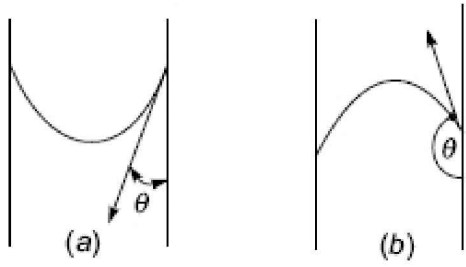


Fig. 4.16 *Contact angle fora liquid*
(a) that wets glass
(b) that does not wet glass.

1. Adhesion and Cohesion We introduce here the terms cohesion and adhesion. Cohesion refers to the intermolecular attraction between the molecules in a liquid while adhesion means attraction between the liquid and walls of the capillary. When adhesion is greater than the cohesion, the liquid is said to wet the wall of the glass. This happens with water and many other polar liquids. On the contrary, if cohesion is greater than adhesion, the liquid does not wet the glass. It happens so in the case of mercury, In mercury, the cohesive forces are much more due to metallic bonding. Thus, while water drops spread on a glass surface because of greater adhesion, the mercury drop takes a semispherical shape on the glass surface because of greater cohesion.

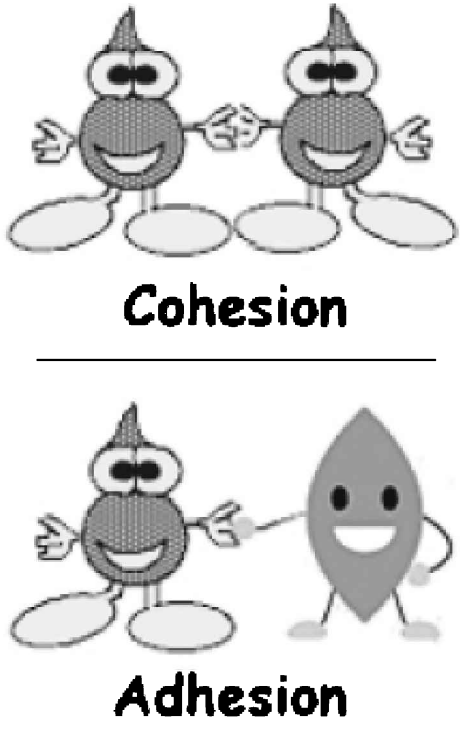


Fig. 4.17 (a) *Symbolic representation of cohesion and adhesion*

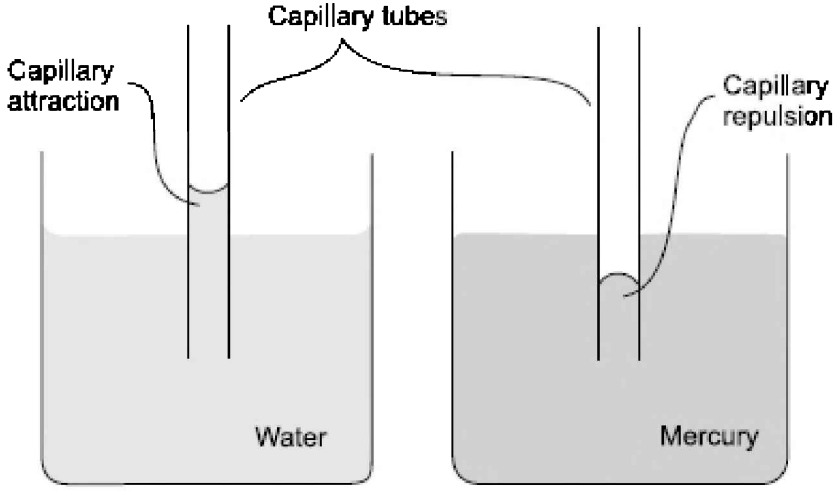


Fig. 4.17(b) *Capillary action with water and mercury*

2. Interfacial Tension If two immiscible or partially miscible liquids are taken in a

vessel, the surface tension acting along their surface of separation, i.e. along the interface, is called the interface tension. Its value is generally intermediate between the surface tension of the two liquids but sometimes it is less than both. This is due to the fact that at the interface, the molecules of one liquid are attracted by the molecules of the other.

As a matter of fact, the surface tension of a liquid is also an interfacial tension, the two phases involved being the liquid and the vapour above it.

4.3.3 Surface Active Agents

Substances like soaps, detergents and surfactants when added to water, even in a small amount, decrease the surface tension of water to a considerable extent. ***Such substances which lower the surface tension of water are called surface active agents.*** It is for this reason that soap acts as a ***detergent,*** For example, if grease is sticking on the surface of a cloth, water because of high surface tension does not wet the grease and hence grease is not removed by water alone. However, if soap is added to water, it lowers the interfacial tension between water and grease. As a result, the grease mixes into the water (soap solution) and hence is removed from the surface of the cloth.

4.3.4 Effect of Temperature on Surface Tension

The surface tension of a liquid generally decreases with increase in temperature and becomes zero at the critical temperature. The decrease in surface tension with increase in temperature is essentially due to the fact that the kinetic energy of the molecules increases and, therefore, intermolecular attraction decreases. An important relationship between temperature and surface tension as given by Eotvos is:

$$\gamma\left(\frac{M}{D}\right)^{2/3} = k(t_c - t) \tag{4.4}$$

where M = molecular mass of the liquid
D = density of the liquid at temperature
t_c = critical temperature of the liquid
γ = surface tension (or surface energy) of the liquid at temperature t°C
k = a constant

4.3.5 Ramsay and Shield's Equation

As the surface tension always vanishes at 6° above the critical temperature, Ramsay and Shields gave the following equation for the temperature dependence of surface tension.

$$r = (M/d)^{2/3} = k(t_c - t - 6) \tag{4.5}$$

Katayama Equation Katayama suggested a more correct equation, viz.

$$4\gamma\left(\frac{M}{D-d}\right)^{2/3} = K(t_c - t) \tag{4.6}$$

where d is density of the vapour at temperature t. In this equation, $\gamma = 0$ when $t = t_c$

4.4 DETERMINATION OF SURFACE TENSION

A number of methods are used for determination of surface tension of a liquid. Some of them are described as under.

4.4.1 Determining Capillary Rise Method for Surface Tension of a Liquid

The pinciple of the method is discussed as follows:

Suppose one end of a capillary tube is put into a liquid which wets glass. Then the force of surface tension pushes the liquid into the capillary to a certain height (as shown in Fig. 4.18) till the force of surface tension acting upwards balances the weight of the liquid column acting downwards.

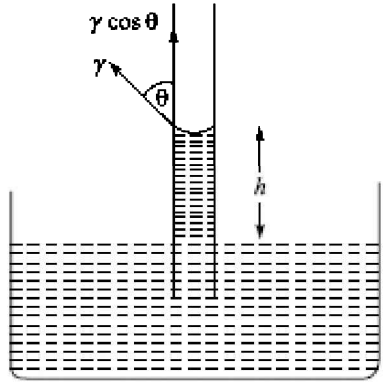


Fig. 4.18 *Capillary-rise method for measuring surface tension.*

Suppose height to which liquid rises in the capillary $= h$ cm
density of the liquid $= d$ g/ml
inner radius of the capillary $= r$ cm
surface tension of the liquid $= \gamma$ dynes/cm
and contact angle $= \theta$

The component of surface tension acting in the vertical direction $= \gamma \cos \theta$

$\therefore$ force of surface tension acting upwards all along the circumference $= 2\pi r.\gamma \cos \theta$

Weight of the liquid acting downwards $= \pi r^2 hdg$

where g is acceleration due to gravity, and $\pi r^2 h$ is the volume of the liquid column

Hence, at equilibrium

$$2\pi r.\gamma \cos\theta = \pi r^2 hdg$$

or

$$\gamma = \frac{rhdg}{2\cos\theta}$$

For most of the liquids which wet glass,

$$\theta = 0$$

so that

$$\cos\theta = 1$$

Hence,

$$\boxed{\gamma = \frac{rhdg}{2}} \qquad (4.7)$$

Thus, the only two parameters that need to be measured are the inner radius *(r,* of the capillary tube and the height *(h)* to which the liquid rises.

Example 2 *At 20°C, toluene rises 1.95 cm in a capillary tube of 0.3412 mm radius. Calculate the surface tension of toluene. The density of toluene at 20°C is 0.866 g per cc.*

Solution: Surface tension is given by the relation

$$\gamma = \frac{rhdg}{2}$$

$r = 0.3412$ mm
$h = 1.95$ cm
$d = 0.866$ g per cc
$g = 981$ cm s^{-2}

Substituting the values in the equation above

$$\gamma = \frac{0.03412 \times 1.95 \times 0.866 \times 981}{2} = 28.26 \text{ dynes cm}^{-1}$$

Example 3 *Consider two liquids A and B such that A has half the surface tension and twice the density of B. If liquid A rises to a height of 3.0 cm in a capillary, what will be the height to which liquid B rises in the same capillary?*

Solution:

$$\gamma = \frac{r h d g}{2}$$

For two liquids A and B, we have $\gamma_A = \frac{r h_A d_A g}{2}$ and $\gamma_B = \frac{r h_B d_B g}{2}$

Dividing the two equations, we get

$$\frac{\gamma_A}{\gamma_B} = \frac{h_A d_A}{h_B d_B}$$

Substituting the data into this equation, we get

$$\frac{1}{2} = \frac{(3\,\text{cm}) \times 2}{h_B} \text{ or } hB = (3\text{ cm}) \times 2 \times 2 = 12\text{ cm}$$

Example 4 *A plant has a capillary radius of0.003 mm. The density of the sap (liquid) in the plant is 1.2 g cm^{-3} and its surface tension is 70 dynes cm^{-1}. Calculate the height to which the plant can grow assuming that surface tension alone is responsible for the rise of the sap in the plant.*

Solution: Applying the relation

$$h = \frac{2\gamma}{r d g}, \text{ Substituting the data, we have}$$

$$h = \frac{2 \times (70\,\text{dynes cm}^{-1})}{(0.0003\,\text{cm})\,(1.2\,\text{g cm}^{-3})\,(981\,\text{cm s}^{-2})} = 396.4\text{ dynes s}^2\text{ g}^{-1}$$
$$= 396.4\text{ cm}$$

PROBLEMS FOR PRACTICE

1. The surface tension of water at 20°C is 72.8 dynes cm^{-1}. Calculate the minimum amount of work needed to increase the surface of water from 2.0 to 5.0 cm^2 at this temperatures

[Ans. 281.4 ergs]

2. Calculate the height to which water will rise in a glass capillary if the radius of the tube is 0.02 cm. The surface tension of water is 72.8 dynes cm^{-1}.

[Ans. 7.42 cm]

3. Calculate the surface tension of a liquid which rises to a height of 1 cm in a capillary tube of radius 0.50 mm. The density or the liquid is 1.5 g cm $^{-3}$

[Ans. 36.7 dynes cm^{-1}]

4.4.2 Drop Weight Method for the Determination of Surface Tension of a Liquid using a Stalgmometer

The principle of this method is that the weight of a drop falling slowly out of a capillary held vertically is directly proportional to its surface tension. Thus, for two liquids, the drops of which fall almost at the same rate out of the same capillary,

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \tag{4.8}$$

where γ_1 and m_1 are respectively the surface tension and weight of each drop of the first liquid, and γ_2 and m_2 are the corresponding values for the second liquid. Thus, knowing the surface tension of one of the liquids, that of the other can be determined.

The apparatus used for the determination of surface tension is called a ***stalgmometer*** and is shown in Fig 4.19. It consists of three parts, a glass tube as the upper portion, a bulb in the middle and a capillary tube as the lower portion. The lowest point of the capillary is flattened to help formation of spherical drops and smooth flow of liquid. There is an etched mark *M* on the glass tube portion.

The following steps are involved in the procedure.

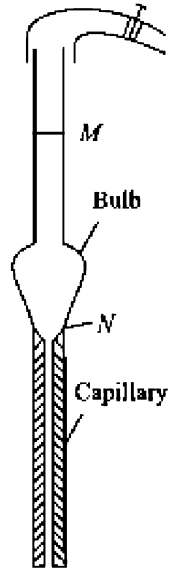


Fig. 4.19 *Stalgmometer*

1. The stalgmometer is clamped vertically in a clamp stand and a rubber tube with a pinch cook attached to the upper portion.
2. Distilled water is sucked into the apparatus and then the pressure adjusted with the help of pinch cook to about 15–20 drops per minute.
3. 10 drops of water are allowed to fall into a clean weighing bottle which has already been weighed when empty. The weight of the weighing bottle along with the drops is

taken.

4. The apparatus is now rinsed with acetone and then allowed to dry.
5. Now, the experimental liquid is sucked into the stalgmometer, the rate of fall of drops adjusted as before and 10 drops of the liquid taken into the empty weighing bottle and the bottle weighed.

Calculations

Suppose weight of empty bottle $= w_1$ g

Weight of bottle + 10 drops of water $= w_2$ g

Weight of bottle + 10 drops of liquid $= w_3$ g

Weight of 10 drops of water $= (w_2 - w_1)$ g

Weight of 10 drops of liquid $= (w_3 - w_1)$ g

If γ_w is surface tension of water then the surface tension of the experimental liquid, γ_1, is given by

$$\frac{\gamma_1}{\gamma_w} = \frac{w_3 - w_1}{w_2 - w_1}, \quad \text{or} \quad \gamma_1 = \frac{w_3 - w_1}{w_2 - w_1} \times \gamma_w \tag{4.9}$$

Knowing γ_w, γ_1 can be calculated.

4.4.3 Drop Number Method for Determination of Surface Tension

It is more convenient to count the number of drops formed from a certain volume of the liquid than to take the weight of a drop of a liquid. Therefore, the experiment may be carried out in an alternative manner as follows:

Suppose the number of drops formed from V mL of a liquid = n

Then weight of one drop of the liquid

$$= \frac{V \times d}{n} \tag{4.10}$$

where d is the density of the liquid. Thus, if from the same volume (say ∪ mL) of the two liquids, the number of drops formed are n_1, n_2 and d_1, d_2 are their respective densities then

$$\frac{\gamma_1}{\gamma_w} = \frac{m_1}{m_2} = \frac{\frac{V \times d_1}{n_1}}{\frac{V \times d_2}{n_2}} = \frac{n_2 \times d_1}{n_1 \times d_2} \tag{4.11}$$

Thus, knowing the number of drops (n_1 and n_2) formed from the same volume of two liquids, their densities (d_1 and d_2) and the surface tension of one them, that of the other can be calculated.

In the procedure, the apparatus is cleaned and clamped vertically. Distilled water is first sucked into the apparatus up to mark *M*. The number of drops, while water flows from *M* to the mark *N* is noted. The apparatus is rinsed with acetone and dried. The experimental liquid is now sucked in up to the mark *M* and the number of drops formed, while the liquid flows from *M* to *N* is counted. The result is then calculated using the formula derived above.

4.4.4 Nouy Torsion Balance Method for Measurement of Surface Tension

The method is based upon the principle that ***the force required to take out a horizontal platinum ring dipping just below the surface of a liquid is directly proportional to the surface tension of the liquid.*** The platinum ring used is usually of about 4 cm diameter and the liquid is usually taken in a watch glass. The force required is measured either by attaching the platinum ring to one end of the beam of a sensitive balance and placing weights on the other side or by using a special balance called ***torsion balance*** (Fig. 4.20). In this balance, the platinum ring is attached to one end of the beam and the other end of the beam is fixed to a wire which can be given a torsion by suitable device. The amount of torsion just sufficient to take out the ring can be recorded on a circular scale attached to one end of the wire as shown in Fig. 4.20. The experiment is first performed with water and then with the experimental liquid.

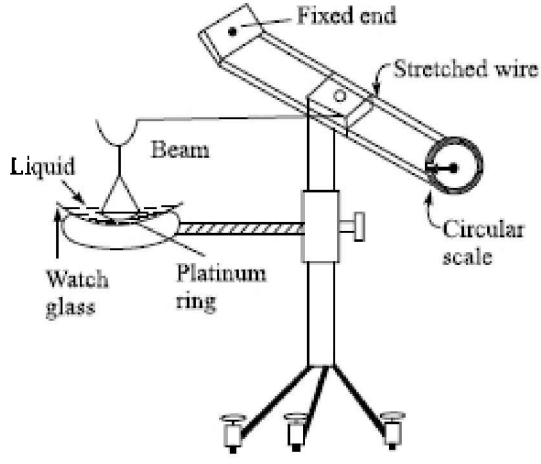


Fig. 4.20 *Torsion balance*

Suppose the torsion angles are θ_1 and θ_2 and their surface tensions are γ_1 and γ_2 respectively.

Then
$$\frac{\gamma_1}{\gamma_2} = \frac{\theta_1}{\theta_2} \tag{4.12}$$

Thus, knowing the surface tension of water, that of the experimental liquid can be found.

4.5 PARACHOR

Parachor is a quantity that is defined by the following relationship between surface tension and density:

$$\frac{\gamma^{1/4}}{D-d} = C \qquad \ldots(4.13)$$

where

γ = surface tension of the liquid
D = density of the liquid
d = density of the vapour at the same temperature
C = a constant, independent of temperature

Multiplying both sides of Eq. (4.13) with the molecular weight *(M)* of the liquid, we get

$$\frac{M\gamma^{1/4}}{D-d} = MC = [P] \qquad \ldots(4.14)$$

The constant $[P]$ thus obtained is called

At ordinary temperature, d is very small in comparison to D and hence can be neglected in the denominator. Hence, Eq. (4.14) becomes

$$\frac{M\gamma^{1/4}}{D} = [P] \qquad \ldots(4.15)$$

Putting $\frac{M}{D} = V$, the molar volume of the liquid, Eq. (4.15) become

$$V \times r^{1/4} = [P]$$

In this equation, if $\gamma = 1$ then

$$[P] = V \qquad (4.16)$$

Hence, ***parachor of a liquid is the volume of the liquid at a temperature at which the surface tension of the liquid is unity.***

4.5.1 Additive Property and Constitutive Property

1. Additive Property The additive property of a molecule is defined as that property, the total value of which is the sum of the values of its constituent atoms. Parachor offers an example of such a property. Thus, each atom has a definite value of parachor and the total parachor value of a simple molecule (not containing any multiple bond or a ring, etc.) is the sum of the parachor values of the constituent atoms. The parachor values associated with the atoms ate called atomic parachors.

2. Constitutive Property A constitutive property of a molecule is defined as that property which depends upon the constitution of the molecule, i.e. the arrangement of atoms within the molecule. In case of parachor, it is found that the total parachor value of a molecule containing some multiple bond or a closed ring, etc., depends not only

upon the atomic parachors but also upon the multiple bonds or rings present. The parachor values associated with structure of the molecule, i.e. the multiple bonds, closed rings, etc., are called **structural parachors.**

Values of some atomic and structural parachors are given in Table 4.1 below:

Table 4.1 Some atomic and structural parachors

Atomic Parachors		Structural Parachors	
Atom	Parachor	Structure	Parachor
C	4.8	Single bond	0.0
H	17.1	Double bond	23.2
O	20.0	Triple bond	46.6
Cl	53.8	3-membered ring	16.7
Br	68.0	4-membered ring	11.6
I	90.0	5-membered ring	8.5
N	12.5	6-membered ring	6.1
P	37.7	Co-ordinate bond	−1.6
S	48.5	O_2 in esters	60.0

Example 5 *Establish the structure of benzene based on parachor values.*

Solution: The structure of benzene is confirmed by the parachor values as follows:

Kekule's structure for benzene (C_6H_6) is 

Calculated value of parachor for benzene is (using values from Table 4.1)

$$= 6\,[P]_C + 6\,[P]_H + 3\,[P]_{\text{Double bond}} + [P]_{\text{6-ring}}$$
$$= (6 \times 4.8) + (4 \times 17.1) + (3 \times 23.2) + (6.1)$$
$$= 207.1$$

Density of benzene at 20°C, *(D)* = 0.878 g/ml
Surface tension of benzene at 20°C, (γ) = 29.3 dynes/cm
Molecular weight of benzene (C_6H_6) = 78

$$\therefore \text{ Experimental value of parachor, } (P) = \frac{M\gamma^{1/4}}{D}$$

$$= \frac{78 \times (29.3)^{1/4}}{0.878} = \mathbf{206.7}$$

Thus, the experimental value is in close agreement with the calculated value. Hence, Kekule's structure is confirmed.

Example 6 *How high will a liquid rise in a capillary tube of 0.1 mm diameter if its density be 1.3 g cm^{-3} and surface tension is 65 dynes cm^{-1}? (g = 980 cm s^{-2})*

Solution: Diameter of the capillary ($2r$) = 0.1 mm = 0.01 cm
$\therefore$ Radius r = 0.005 cm
Density of the liquid (d) = 1.3 g cm^{-3}
Surface tension of the liquid (γ) = 65 dynes cm^{-1}
The formula for the rise of liquid in the capillary is

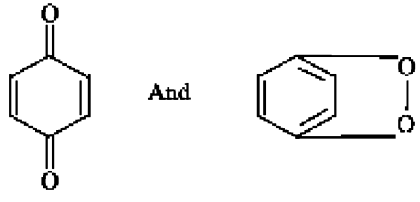
$$\gamma = \frac{r h d g}{2}$$

$$h = \frac{2\gamma}{rdg}$$

$$= \frac{2 \times 65}{0.005 \times 1.3 \times 980} = \mathbf{20.41\ cm}$$

Example 7 *Establish the structure of quinone based upon parachor values.*

Solution: The following two structures are possible, the molecular formula for quinone being $C_6H_4O_2$.



I II

Parachor of quinone according to structure I (using values from Table 4.1)

$$= 6[P]_C + 4[P]_H + 2[P]_O + 4[P]_{\text{Double bond}} + [P]_{\text{6-ring}}$$
$$= (6 \times 4.8) + (4 \times 17.1) + (2 \times 20.0) + (4 \times 23.2) + 6.1$$
$$= \mathbf{236.1}$$

Parachor of quinone according to structure II (using value from Table 4.1)

$$= 6[P]_C + 4[P]_H + 2[P]_O + 3[P]_{\text{Double bond}} + 2[P]_{\text{6-ring}}$$

($\because$ there are two 6-membered rings in II)

$$= (6 \times 4.8) + (4 \times 17.1) + (2 \times 20.0) + (3 \times 23.2) + (2 \times 6.1)$$
$$= \mathbf{219.0}$$

Observed value of parachor for quinone (from experiment) = **236.8**
This value is close to the value calculated for the structure I.
Hence, I must be the correct structure for quinone.

Example 8 *The density of acetone at 20°C is 0.7910 g/ml. Calculate the surface tension of acetone, given that the parachor values of C, H, O and double bond are 7.2, 16.2, 20.0 and 23.2 respectively.*

Solution: Density of acetone at 20°C, (D) = 0.791 g/ml
Parachor values:

$$[P]_C = 7.2$$
$$[P]_H = 16.2$$
$$[P]_O = 20.0$$
$$[P]_{\text{Double bond}} = 23.2$$

$$\therefore \text{ Parachor for acetone } (CH_3-\overset{\overset{O}{\|}}{C}-CH_3) = 3\,[P]_C + 6\,[P]_H + [P]_O + [P]_{\text{double bond}}$$
$$= (3 \times 7.2) + (6 \times 16.2) + 20.0 + 23.2$$
$$= 162$$

Molecular weight of acetone (M) = 58
Surface tension is related to parachor according to the formula

$$\frac{M\gamma^{1/4}}{D} = [P]$$

$$\therefore \quad \gamma^{1/4} = \frac{[P]D}{M}$$

or

$$\gamma = \left[\frac{[P]D}{M}\right]^4$$

Substituting the value for $[P]$, D and M,

$$\gamma = \left[\frac{162 \times 0.791}{58}\right]^4$$
$$= \mathbf{23.83\ dynes/cm}$$

Example 9 *The parachors of ethane and propane are 110.5 and 150.8 respectively. What values of parachor do you expect for hexane?*

Solution:

$$
\begin{aligned}
[P]\ C_2H_6 &= 110.5 \\
[P]\ C_3H_8 &= 150.8 \\
[P]\ CH_2 &= [P]\ C_3H_8 - [P]\ C_2H_6 \\
&= 150.8 - 110.5 = 40.3 \\
[P]\ C_6H_{14} &= [P]\ C_3H_8 + 3[P]\ CH_2 \\
&= 150.8 + 3 \times 40.3 = 271.7
\end{aligned}
$$

4.6 VISCOSITY

Consider a liquid flowing through a narrow tube, Fig 4.21. All parts of the liquid do not move through the tube with the same velocity. Imagine the liquid to be made up of a large number of thin cylindrical layers. The layer which is in contact with the walls of the tube is almost stationary.

As we move from the walls towards the centre of the tube, the velocity of the cylindrical layers increases progressively It is maximum at the centre. Conversely, we may say that as we move from the centre towards the walls, the velocity of the layers shows a decrease. In other words, every layer offers some resistance or friction to the layer immediately below it. ***This force of friction which one part of the liquid offers to another part of the liquid in called viscosity.***

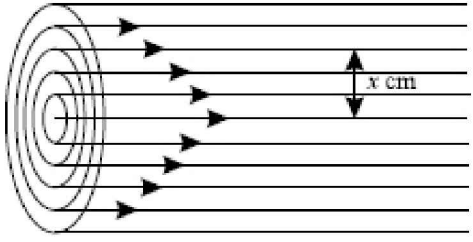


Fig. 4.21 *Flow of a liquid through a narrow tube.*

It has been found that the force of attraction (f) between two cylindrical layers, each having area A sq. cm. separated by a distance x cm, and having a velocity difference of u cm/s, is given by

$$f \propto Av/x$$

or
$$f = \eta \frac{Av}{x} \text{ or } \eta = \frac{fx}{Av} \qquad (4.17)$$

where η is a constant known as **coefficient of viscosity.**

If x =1 cm, A = 1 sq. cm and v = 1 cm/s then

$$\eta = f$$

Hence, ***the coefficient of viscosity may be defined as the force of friction (in dynes)***

required to maintain a velocity difference of 1 cm/s between two parallel layers, 1 cm apart and each having an area of 1 sq. cm.

Units of η are

$$\frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm s}^{-1}} = \text{dynes cm}^{-2}$$

For simplicity, the unit of *n*, viz. dynes cm^{-2}, is called poise (*P*). Smaller units of decipoise (*dP*) and centipoise (*cP*) are also used.

In SI units,

$$\eta = \frac{\text{Newton}}{\text{metre}^2} \times \frac{\text{metre}}{\text{metre/second}}$$

$$= \text{Newton second metre}^{-2}$$

$$\eta = \text{Ns m}^{-2} = \text{kg m}^{-1}\ \text{s}^{-1}$$

The unit of viscosity is SI system is Ns m^{-2} or kg m^{-1} s^{-1}

It can be shown that 1 poise = 10^{-1} kg m^{-1} s^{-1}

Dynes s cm^{-2} = g × cm s^{-2} = (10^{-3} kg) (10^{-2} m)$^{-1}$ s^{-1}

$$= 10^{-3}\ \text{kg} \times 10^{2}\ \text{m}^{-1}\ \text{s}^{-1} = \frac{1}{10}\ \text{kg m}^{-1}\ \text{s}^{-1}$$

Fluidity Reciprocal of viscosity is fluidity, represented by ϕ Thus, $\phi = \frac{1}{\eta}$ unit of fluidity is poise^{-1}.

4.6.1 Viscosity Change of a Liquid with Change in Temperature

With increase of temperature, the kinetic energy of the molecules of a liquid increases. Hence, the liquid starts flowing faster. In other words, the ***viscosity of a liquid decreases with increase in temperature.*** It has been found that the decrease takes place to the extent of 2% per degree rise of temperature.

Arrhenius gave the following relationship between viscosity and temperature.

$$\eta = Ae^{B/RT}$$

where *A* and *B* are the constants for the liquid and *T* is the absolute temperature. The above equation may be written as

$$\log \eta = \log A + \frac{B}{RT}$$

or

$$\log \eta = A' + \frac{B'}{T} \qquad (4.18)$$

Thus, the plot of log η vs $\frac{1}{T}$ is a straight line.

Reynolds Number The flow of a liquid through a pipe of radius r is associated with a number called Reynold number, N_R. It is mathematically related as

$$N_R = \frac{2R\bar{v}d}{\eta} \tag{4.19}$$

In this equation, $\bar{v}$ is average bulk velocity of the liquid, d is the density and η is the coefficient of viscosity. If N_R is greater than 4000, the flow is turbulent and if it is less than 2100, the flow is laminar.

In a laminar flow, a velocity profile given by the following equation

$$\bar{v} = \frac{\Delta P(R^2 - r^2)}{4\eta l} \tag{4.20}$$

is observed in a pipe when ΔP is the pressure drop over a length of l and r is distance of the axis of the pipe of radius R.

The volume of the liquid flowing in time t through a pipe of radius R is given by

$$V = \frac{\pi R^4 (\Delta P)t}{8\eta l} \tag{4.21}$$

Example 10 *Consider the flow of water through a horizontal pipe with R = 3.2 cm and* $\bar{v}$ *= 3 cm* s^{-1}*. If* η *= 1.008 cP at 20°C and d = 0.9994 g* cm^{-3}*, calculate the Reynolds number. Tell whether the flow is turbulent or laminar.*

Solution: Apply the relation $N_R = \frac{2R\bar{v}d}{\eta}$

Substituting the data into the equation,

$$N_R = \frac{2(3.2\times10^{-2}\,\text{m})(3\times10^{-2}\,\text{m s}^{-1})(0.9994\times10^{-3}\times10^{6}\,\text{kg m}^{-3})}{(1.008\times10^{-2}\,\text{Poise})(10^{-1}\,\text{kg m}^{-1}\text{s}^{-1}\text{Poise}^{-1})}$$
$$= 1903$$

Since the value of N_R is below 2100, the flow is laminar.

4.6.2 Poiseulle's Equation and Determination of Viscosity of a Liquid

Poiseulle gave a relation between viscosity of a liquid flowing through a capillary tube and volume of the liquid, pressure of the liquid, radius and length of the tube and the time taken for the flow which is given as under:

$$\eta = \frac{\pi pr^4 t}{8lV}\ \text{(Poiseulle's equation)} \tag{4.22}$$

where

V = volume of the liquid flowing through the capillary in time t

P = pressure head r = radius of the capillary tube
r = radius of the capillary tube
l = length of the tube though which the liquid flows.

It is quite cumbersome to determine experimatally the values of p, r, l and V. Hence, it may not be practical to use Poiseulle's equation for the determination of viscosity of a liquid.

Viscosity is generally determined w.r.t. water. This value of called ***relative viscosity.*** We note down the time for flow of water from the point M to the point M' on the viscometer (see Fig. 4.22). We repeat the experiment with the unknown liquid. Let t_1 and t_{H_2O} be the times for the flow of liquid and water in the same viscometer. As the viscometer is the same, the value of r, l and V will remain the same. We can write the Poiseulle equation for the liquid and water as under.

$$\eta_l = \frac{\pi P_l r^4 t_l}{8 l V} \tag{4.23}$$

$$\eta_{H_2O} = \frac{\pi P_{H_2O} r^4 t_{H_2O}}{8 l V} \tag{4.24}$$

Divide Eq. (4.23) by Eq. (4.24),

$$\frac{\eta_l}{\eta_{H_2O}} = \frac{P_l t_l}{P_{H_2O} t_{H_2O}} \tag{4.25}$$

Pressure is proportional to the density. Thus, $P_l \propto d_l$ and $P_{H_2O} \propto d_{H_2O}$ Therefore, Eq. (4.25) is reduced to

$$\frac{\eta_l}{\eta_{H_2O}} = \frac{d_l t_l}{d_{H_2O} t_{H_2O}} \tag{4.26}$$

t_1 and t_{H_2O} are determined from the experiment. Substituting the values of d_l d_{H_2O} and η_{H_2O} we can find out η_l, that is the viscosity of the liquid.

4.6.3 Ostwald's Viscometer Method for Determination of Viscosity of a Liquid

The apparatus used for the measurement of relative viscosities is called a ***viscometer.*** The simplest viscometer is the one given by Ostwald and is called Ostwalds's viscometer. It is shown in Fig. 4.22. It consists of a bulb B, to which is sealed a tube above and a capillary below. There is a mark M on the tube and a mark M' just above the capillary as shown. The lower end of the capillary is sealed to a bigger bulb C and a wider tube CD.

The following steps are involved in the determination of viscosity.

1. The apparatus is first washed with chromic acid and then thorougly with water. It is then clamped vertically and a rubber tube is attached to the end A.
2. A definite volume of water is introduced into the bulb C through the end D.
3. Through the rubber tube attached to the end A, distilled water is sucked up into the bulb B so that the level of water is a little above the mark M. The water is then

allowed to flow back and the time taken for the water to flow from the mark *M* to *M'* is noted.

4. The apparatus is then dried and the experiment is repeated as above taking the same volume of the experimental liquid. The result is then calculated using the formula as given below:

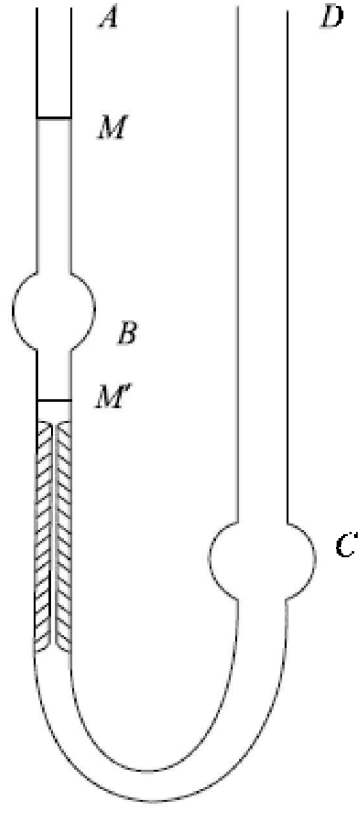


Fig. 4.22 *Ostwald's viscometer.*

$$\frac{\eta_l}{\eta_{H_2O}} = \frac{d_l t_l}{d_{H_2O} t_{H_2O}} \tag{4.27}$$

where

η_l = coefficient of viscosity of liquid
η_{H_2O} = coefficient of viscosity of water
d_l = density of liquid
d_{H_2O} = density of water
t_l = time of flow with the liquid
t_{H_2O} = time of flow with the water

Knowing the values of all other terms, η_l can be calculated.

Example 11 *Why do we use the same viscometer for the liquid and water during the experimental determination of viscosity by Ostwald viscometer?*

Solution: For determination of viscosity of the liquid by Ostwald viscometer, we use the equation

$$\frac{\eta_l}{\eta_{H_2O}} = \frac{d_l\, t_l}{d_{H_2O}\, t_{H_2O}}$$

This equation is derived using Poiseuille's equation

$$\eta = \frac{\pi\, P r^4 t}{8\, l V}$$

We have assumed that the values of r, l and V remain the same. This can happen when the Ostwald viscometer remains the same measurement with liquid and water.

4.6.4 Relationship Between Viscosity and Chemical Constitution

The following correlation has been observed between viscosity and chemical constitution.

1. In a homologous series, the viscosity increases as we go up a series and the increase per CH_2 group is almost constant.
2. In compounds involving chain isomerism, the *n*-isomers have generally greater viscosity than branched chain isomers.
3. In compounds involving geometrical isomerism, trans-isomers have higher value of viscosity than the corresponding cis isomers.

According to ***Dunstan's rule,*** for non-associated or normal liquids, the following equation holds

$$\frac{d}{M}\eta \times 10^6 \approx 40 \text{ to } 80 \qquad (4.28)$$

where

d = density of the liquid

η = coefficient of viscosity

M = molecular mass

For associated liquids, the value is much greater than 80.

4.7 RHEOCHOR

The following relation exists between rheochor [R], molecular mass density and coefficient of viscosity of the liquid.

$$[R] = \frac{M}{D}(\eta)^{1/8} \tag{4.29}$$

where M, D and η are the molecular mass, density and coefficient of viscosity of the liquid respectively.

Thus, if

$$\eta = 1$$

Then
$$[R] = \frac{M}{D} = V, \text{ molar volume} \tag{4.30}$$

Hence, ***rheochor may be defined as the molar volume of the liquid at a temperature at which its coefficient of viscosity is unity.***

Molecular Mass of Polymers using Coefficient of Viscosity If the viscosity of a solution is η at concentration c, and the viscosity of pure solvent is η_o then the specific viscosity of a solution is defined by the relationship

$$\frac{\eta - \eta_o}{\eta_o} = \eta_{sp} \tag{4.31}$$

The plot of $\frac{\eta_{sp}}{c}$ vs c is found to be linear. The value of $\frac{\eta_{sp}}{c}$ obtained by extrapolating the plot to zero concentration given what is called ***intrinsic viscosity,*** [η]. It is found to be related to the average molecular mass of the polymers, $\overline{M}$, by the equation

$$[\eta] = k\,\overline{M}^{a} \tag{4.32}$$

where k and a are constants for a given type of polymer and a solvent. The values of these constants are found by first performing the experiments with two samples of the given polymer whose molecular masses have already been found by some other method.

Example 12 *The waterflow time for an Ostwald viscometer is 59.2 seconds at 25°C. If 46.2 seconds are required for the same volume of ethyl benzene (density = 0.867 g cm^{-3}) to flow through the capillary, calculate its absolute viscosity at 25°C, that of water being 0.00895 poise at the same temperature.*

Solution:

For water, $t_1 = 59.2$ seconds

$\eta_1 = 0.00895$ poise

$d_1 = 1.0$ g/cc

For ethyl benzene, $t_2 = 46.2$ seconds

$d_2 = 0.867$ g/cc

$\eta_2 = ?$

Substituting the values in the formula,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

$$\eta_2 = \frac{\eta_1 \times d_2 \times t_2}{d_1 t_1}$$

$$= \frac{0.00895 \times 0.867 \times 46.2}{1 \times 59.2}$$

$$= \mathbf{0.00606 \text{ poise}}$$

Example 13 *At 20°C, the density ofwater is 0.9983 g/mL and its viscosity is 0.010087 poise. How do these figures indicate that water is an associated liquid?*

Solution: Here, we are given that

$d = 0.9983$ g/mL

$\eta = 0.010087$ poise

For H_2O,

$M = 18$

According to Dunstan's rule, $\frac{d}{M}\eta \times 10^6$ for normal liquids is from 40 to 60.

In this case, $$\frac{d}{M}\eta \times 10^6 = \frac{0.9983}{18} \times 0.010087 \times 10^6$$

$$= \mathbf{559.4}$$

which is much greater than 80. Hence, water is an associated liquid.

4.8 REFRACTIVE INDEX

When a ray of light travels from one medium to another, it undergoes a change in direction, As shown in Fig. 4.23. the phenomenon is called ***refraction.*** If a ray of light travels from air or vacuum to a more dense medium (i.e., any liquid or solid) then the ratio of the sine of the angle of incidence, *i*, to the sine of the angle of refraction, *r*, is constant depending upon the nature of the medium. This constant is called the ***refractive index*** of the medium. It is usually represented by μ. Thus,

$$\mu = \frac{\sin i}{\sin r} \tag{4.33}$$

This is called ***Snell's law.*** The value of refractive index is also found to depend upon the wavelength of the light used and the temperature. These are usually specified as subscripts and superscripts respectively. Thus, $\mu_D^{20^\circ}$ indicates a refractive index taken at 20°C with light corresponding to yellow *D* line of the sodium spectrum obtained from a sodium vapour lamp.

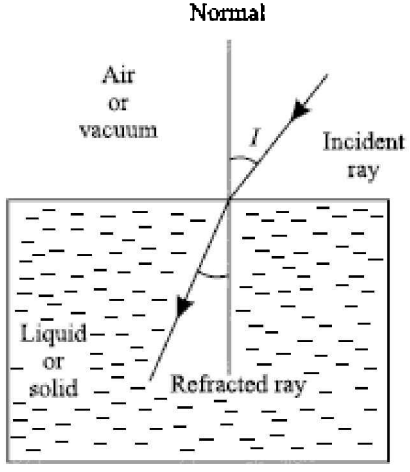


Fig 4.23 *Refraction of light from air to a more dense medium*

Alternatively, ***the refractive index of a medium is defined as the ratio of the velocity of light in vacuum to the velocity of light in the medium, i.e.***

$$\mu = \frac{\text{Velocity of light in vacuum}}{\text{Velocity of light in the meduim}}$$

Any type of wave can be refracted, as refraction is a change in direction. After refraction, the wave has the same frequency, but a different speed, wavelength and direction. When a ray propagates from one medium to an optically dense medium, the ray refracts towards the normal. Conversely, a ray propagating from one medium to an optically less dense medium is refracted away from the normal. A swimming pool seems shallower (less deep) than it actually is, a spoon appears bent when a part of it is in water and your legs look shorter when immersed in it. All these effects are a consequence of refraction of light.

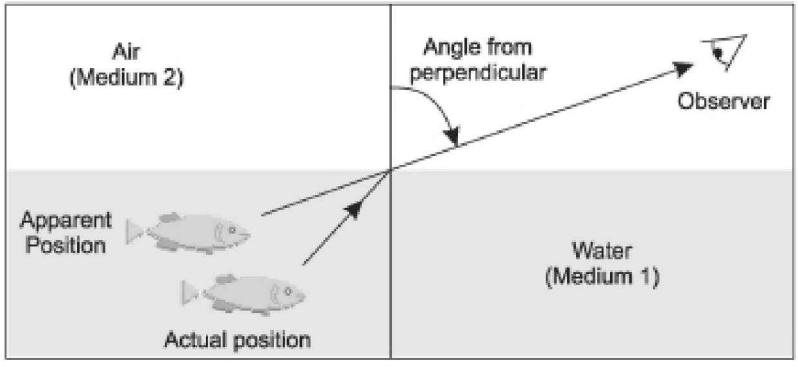


Fig. 4.24 *Effects of refraction of light*

4.8.1 Refractometer and its Types

The instrument used for measurement of refractive index is called a ***refractometer.*** The two most common refractometers are:

1. Pulfrich refractometer
2. Abbe's refractometer

We shall describe in detail Abbe's refratometer only.

The principle of Abbe's refractometer is explained in Fig. 4.25. The actual design of the instrument as shown in Fig. 4.27. It consists of two thin layers of right-angled prisms *P* and *Q* with their hypotenuse liquid faces together. These can be clamped together with a clamp *X* in a metal box hinged at Y The box is attached to an arm *R* with the help of which the prism system can be rotated and the value of refractive index can be read directly on the circular scale fixed at the top of the arm *R.* The hypotenuse face of the lower prism *(P)* is ground whereas that of the upper prism *(Q)* is polished. A drop of the liquid is placed on the hypotenuse face of the prism *P* which spreads between the two faces when the two prisms are fixed together. The light from a suitable source (say an electric bulb) is then reflected by the mirror *M* onto the liquid layer. On striking the ground surface of the prism *P*, the light gets diffused in all directions. Thus, the rays are incident to the polished face of the prism *Q* at angles less than 90° (in the liquid medium) and at angles greater than 90° (in the prism *Q).* The rays incident at angles greater than 90° undergo total internal reflection within the prism *Q* and do not come out of the prism *Q*. The rays incident at angles less than 90° undergo refraction and come out of the prism *Q* in the form of a bright band of light. To observe the edge of the bright band corresponding to the 'grazing incidence', a telescope is fixed above the prism system and the box containing the prism system is rotated till the edge of the bright band coincides with the crosswire of the telescope. This setting corresponds to the refracted ray, refracted at the critical angle *e*. However, instead of measuring the angles, the circular scale is graduated directly for reading the refractive indices

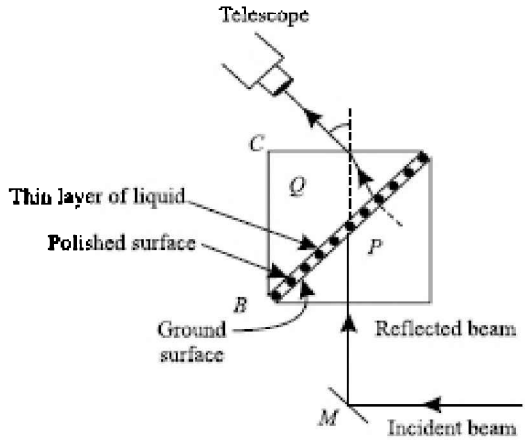


Fig. 4.25 *Principie of Abbe's refractometer*



Fig. 4.26 *Ernst Kari Abbe was a German physicist, optometrist and entrepreneur. He iaid the foundation of modern optics aiong with Otto Schott and Cari Zeiss.*

4.8.2 Specific Refractivity Molar Refractivity

1. Specific Refractivity It has been found that for any substance having refractive index n and density d at the same temperature, the following equation holds good for the particular substance and is independent of temperature.

$$r = \left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{1}{d} \tag{4.34}$$

The quantity r is called the specific refractivity or specific refraction of the

substance.

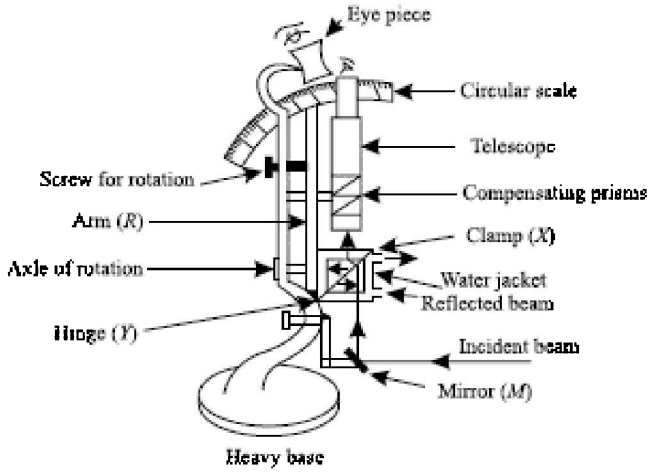


Fig. 4.27 *Design of the instrument (Abbe's refractrometer)*

2. Molar Refractivity Multiplying the specific refraction by the molecular mass M of the substance, we get what is known as molar refractivity or molar refraction R. Thus,

$$R_m = r \times M = \left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{M}{d} \tag{4.35}$$

The above formula is applicable to gases, liquids and solids. To determine the molar refractivity of a solid, it is dissolved in a suitable solvent and the refractive index n and density d of the solution are measured. The molar refractivity R_s of the solution is then given by the formula

$$R_s = \left[\frac{n^2 - 1}{n^2 + 2}\right]\left(\frac{N_1 M_1 + N_2 M_2}{d}\right) \tag{4.36}$$

where N_1 and N_2 are mole fractions of the solvent and solute respectively and M_1 and M_2 are their molecular masses. But the total molar refractivity of the solution is the sum of the contributions made up the solute (solid) and the solvent.

Hence,

$$R_s = N_1 R_1 + N_2 R_2 \tag{4.37}$$

where R_1 is the molar refractivity of the solvent and R_2, that of the solid. Thus, knowing R_1, R_2 can be calculated.

4.8.3 Role of Molar Refractivity in Determination of Structure of Compounds

Molar refractivity has been found to be additive as well as constitutive. The additive property is supported again by the facts that (i) the difference in the molar refractivity of

the successive members of a homologous series is nearly constant, and (ii) the isomeric compounds with similar structures (e.g., iso-propyl alcohol and *n*-propyl alcohol) are found to have nearly same value of the molar refractivity.

Similarly, the constitutive nature is supported by the fact that in case of compounds containing double bond, triple bond or a closed ring, etc., the observed value of molar refractivity is higher than that obtained by simply adding the atomic refractivities. However, while calculating the molar refractivity, the following two points are noteworthy.

1. The atomic refractivity of oxygen atom is different in alcohols, ethers and ketones.
2. When a compound contains more than one double and triple bonds, the molar refractivity depends not only on the number of double or triple bonds, but also on their relative position in the molecule. When the double bonds or triple bonds are present in a conjugated position, e.g. –CH = CH – CH = CH–, the molar refractivity is higher than the calculated value. This is known as ***optical exaltation.***

   Thus, for hexatriene,

$$CH_2 = CH - CH = CH - CH = CH_2$$

Refractivities for C and H are 2.418 and 1.1 respectively. Refractivity for carbon-carbon double bond is 1.733.

$$\begin{aligned} \text{Calculated value of } [R] &= 28.52 \\ \text{Experimental value of } [R] &= 30.58 \\ \text{Optical exalation} &= 30.58 - 28.52 = 2.06 \end{aligned}$$

Example 14 *Calculate the molar refraction of acetic acid (CH_3COOH) at the temperature at which its density is 1.046 g/cm^3. The experimentally observed value of refractive index at this temperature is 1.3715.*

Solution: Here, we are given

$$d = 1.046 \text{ g/cm}^3$$
$$N = 1.3715$$

Molecular mass of CH_3COOH is $M = 60$
Substituting these value in the formula,

$$R_m = \left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{M}{d}$$

$$R_m = \frac{(1.3715)^2 - 1}{(1.3715)^2 + 2} \cdot \frac{60}{1.046}$$

$$= \mathbf{13.021\ cm^{-3}\ mol^{-1}}$$

Example 15 *Density of acetic acid at 25°C is 1.046 gm/mL. Calculate the refractive*

index of acetic acid. Values of R_m (molecular refractivity) for C = 2.42, H = 1.10, O in OH = 1.50, O in CO = 2.21

Solution:

Step 1 To Calculate the value of R_m for CH_3COOH

Here, we are given

$$R_C = 2.42, \quad R_H = 1.10$$

$$R_o \text{ in } -OH = 1.50, \quad R_o \text{ in } > CO = 2.21$$

$$\begin{aligned} R_m \text{ for } \quad CH_3 - C - OH &= 2R_C + 4R_H + R_o \text{ in } 3 - OH + R_o \text{ in } > CO \\ &= 2 \times 2.42 + 4 \times 1.10 + 1.50 + 2.21 \\ &= \mathbf{12.95 \text{ cm}^3 \text{ mol}^{-1}} \end{aligned}$$

Step 2 To calculate the value of *n*

Also we are given *d* = 1.046 g/mL. Molar mass of CH_3COOH (*M*) = 60

Substituting these values in the formula,

$$R_m = \left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{M}{d}$$

We get

$$12.95 = \left[\frac{n^2 - 1}{n^2 + 2}\right]\frac{60}{1.046}$$

or

$$\frac{n^2 - 1}{n^2 + 2} = 0.2258$$

$$n^2 - 1 = 0.2258\, n^2 + 0.4516$$

or

$$0.7742\, n^2 = 1.4516$$

$$n^2 = \frac{1.4516}{0.7742} = 1.8753$$

$$\boldsymbol{n = 1.369}$$

Example 16 *A substance having the formula C_3H_6O might be either acetone* $\left[\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\! C = O\right]$ *or allyl alcohol ($CH_2 = CH - CH_2 - OH$). Determine which substance it actually is if its molar refractivity is found to be 16.974 by experiment. Given that refractivities for C = 2.418. H = 1.100, O (Carbonyl) = 2.211, O (hydroxyl) = 1.525, C = C double bond = 1.733.*

Solution: Theoretical molar refractivities of the two compounds are calculated below:

Acetone	Allyl alcohol
3 Carbons = 3 × 2.418 = 72	3 Carbons = 7.254
6 Hydrogens = 6 × 1.100 = 6.600	6 Hydrogens = 6.600
1 Carbonyl oxygen = 2.211	1 Double bond (C = C)
Total: 16.065	1 Hydrogen oxygen = 1.525
	Total = 17.112

As the experimental value is close to the calculated value for allyl alcohol, the compound must be allyl alcohol.

PROBLEM FOR PRACTICE

1. The refractive index of *C* Cl_4 at 20°C is 1.4573. If its density at the given temperature is 1.595 g cm^{-3}, calculate the molar refraction

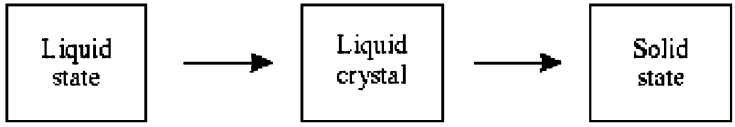
[Ans. 26.51]

4.9 LIQUID CRYSTALS

A large number of organic compounds with long chain molecules such as cholesteryl acetate (CH_3 $COOC_{27}$ H_{45}), cholesteryl benzoate (C_6H_5 $COOC_{27}$ H_{45}) acid and ammonium oleate (C_{17} H_{33} $COONH_4$) on heating melt sharply to give a milky (turbid) liquid which on further heating becomes clear again at a definite temperature.

The liquid crystal state is intermediate between the liquid state and the solid state. Molecules in a liquid have random arrangement and are able to move past each other but they have an ordered arrangement and are in fixed positions in the solid state. Thus, the liquid crystals have the fluidity of a liquid and optical properties of solid crystals.

On cooling the clear liquid (melt) the reverse changes take place exactly at the same temperatures. The turbid liquids thus obtained are found to be ***anisotropic,*** a property possessed by crystalline substances. An anisotropic substance shows different physical properties in difference directions. These turbid liquids are called ***liquid crystals***.



However, it is found that the molecules of a liquid crystal do not have the arrangement like that of a crystal lattice. Moreover, they behave like true liquids, e.g. they possess surface tension and have the property to flow; hence, in place of 'liquid crystals', certain other names have been proposed such an ***anisotropic liquids*** or ***para crystals.*** The best name for the substances in this state is ***mesomorphic state.*** However, in spite of all this, the name 'liquid crystals' is still frequently used.

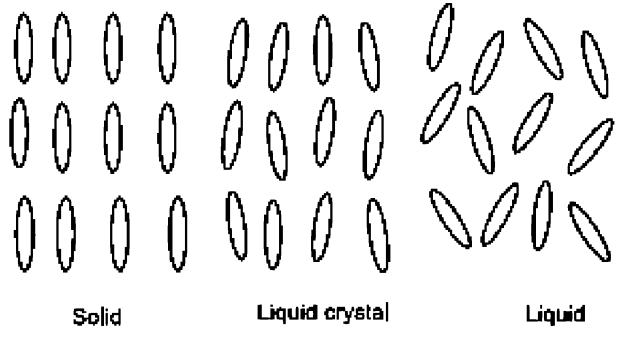


Fig. 4. 28 *Solids, liquied crystais and liquids*

Substances showing this type of property have long-chain organic molecules and have sp^2 hybridised carbon atoms. Also length of the molecule is much greater than the width. Such a substance also contains rings in the structure.

Cholestertyl benzoate ($C_6H_5COO_{27}H_{45}$) was amongst the first solids discovered in 1888 with the characteristic property. It fuses sharply at 145°C to give a turbid liquid which on further heating changes suddenly to a clear liquid at 178°C. The above changes are reversed on cooling.

An essential requirement for mesomorphism (liquid crystal state) to occur is that the molecule should be anisotropic in shape, like a rod or a disc. Proteins and fats also get changed into this state before digestion and are thus easily assimilated into the body. Thus, this state plays an important role in nutritional science.

For a solid showing mesomorphic behaviour, the phase changes involved in the conversion of an ordinary solid into liquid and gaseous state are represented by

$$\text{Solid} \rightleftarrows \text{Liquid crystal} \rightleftarrows \text{Liquid} \rightleftarrows \text{Vapour}$$

Pressure-temperature curve for such phase transformation is represented in Fig. 4.29.

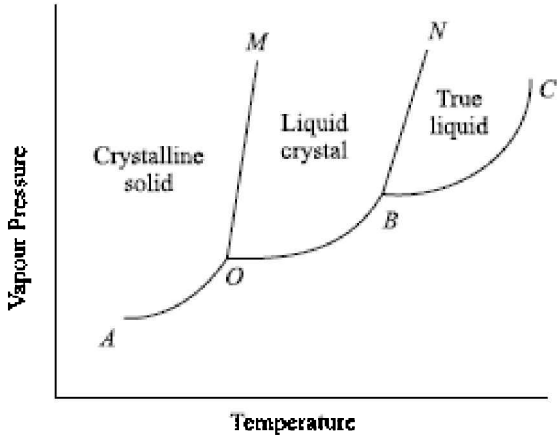


Fig. 4.29 *V.P-temperature curves fora substance undergoing mesomorphic change*

Thermography The phase changes observed on heating a crystalline substance showing mesomorphic behaviour may be expressed in the form of temperature-time graph shown in Fig 4.30. This is known as thermography.

The 1991 Physics Nobel Prize was awarded to the French physicist P.G de Gennes for his contribution to liquid crystals and polymers.

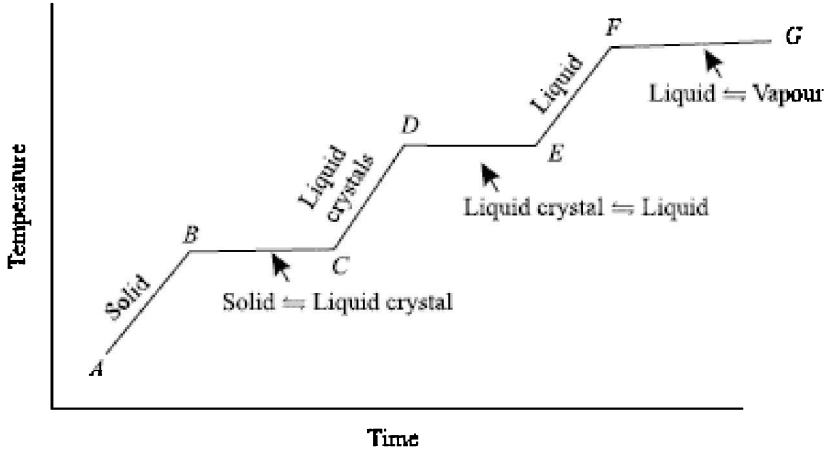


Fig. 4.30 *Thermographic behaviour of a solid showing mesomorphism*

4.9.1 Different Kinds of Liquid Crystals

Liquid crystals are of the following three types:

1. Smectic Liquid Crystals. The smectic liquid crystals have restricted mobility. They flow in layers as if different sheets are gliding over one another. The distribution of velocity in different layers is different from that found in a true liquid. The concept of viscosity is, therefore, not applicable to the liquid crystals of this type. When spread over a clean glass surfaces, they form a series of terraces or strata, as shown in Fig. 4.31. The edges of these terraces often show a series of fine lines even in ordinary light, though more so in polarised light.

Smectic liquid crystals also give *X*-ray diffraction patterns like solid crystals but it is in one direction only. Thus, smectic phase has a complex internal structure.

When viewed in polarised light, smectic phases appear to have a fanlike appearance. They are always
uniaxial and are not affected by a magnetic field. Ethyl-*p*-azoxy benzoate and ethyl *p*-azoxy cinnamate are some examples of this class of liquid crystals.

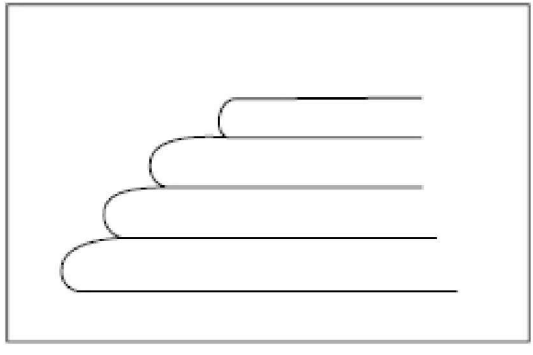


Fig. 4.31 *Layer structure of smectic liquid crystals*

2. Nematic Liquid Crystals Nematic liquid crystals show almost normal flow behaviour of liquids. They flow more readily than the smectic liquid crystals Their flow is Newtonian and the concept of viscosity is applicable to their flow. Their viscosity, however, is rather low as compared to that of liquids. The nematic phase has liquidlike character and yet being turbid and anisotropic, they are unlike true liquids. This type is, therefore, regarded less truely anisotropic than the smectic type.

In polarised light, substances in nematic phase appear to have threadlike structures. They are uniaxial like smetic substances but unlike the latter, they are affected by a strong magnetic field. Thus, when viewed in the direction of the lines of force of a magnetic field, the turbid liquid appears quite clear. If the magnetic field is cut off, the liquid appears turbid again. *p*-Azoxy anisole and *p*-azoxy phenetole are some examples of this typed of liquid crystals.

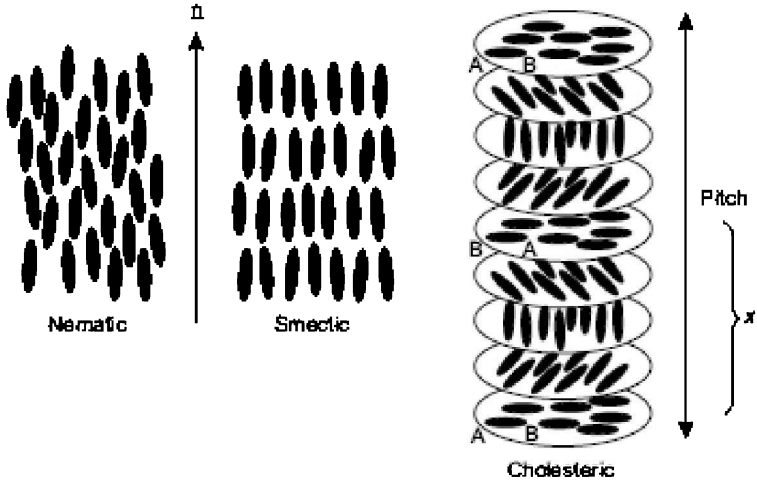
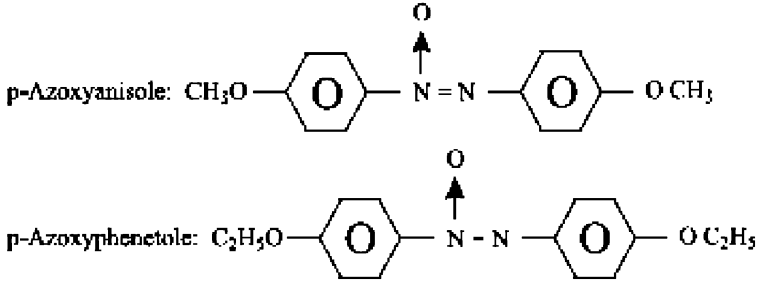


Fig. 4.32 *Three types of liquid crystals*

3. Cholesteric Liquid Crystals Certain optically active compounds show many characteristics of nematic behaviour but at the same time, they show strong colour effects in polarised light. This indicates that they have a layer structure like smectic liquid crystals. But they differ from smectic liquid crystals in leaving much thicker layers which are of the order of 500 to 5000 molecules thick. Such liquid crystals having some nematic and some smectic characteristics called **cholesteric liquid crystals.** (Fig. 4.32)



The first substance in which this type of mesomorphism was detected was cholesteryl benzoate. Its transition point is 178°C. l-Cholesteryl formate is another example of this type of liquid crystals.

4.9.2 Swarm Theory of Liquid Crystals

The best explanation for turbidity is provided by the 'Swarm Theory' proposed by Bose. According to this theory, since mesomorphic behaviour is shown by substances having long chains, their force rotation is restricted and they tend to arrange themselves in parallel formations. In this way, a number of groups or 'swarms' are obtained. The molecules in any one swarm are parallel to one another but may not be parallel to those

present in another swarm (Fig. 4.33). Each swarm consisting of several molecules, arranged parallel to one another, is taken as a small crystal Thus, a turbid liquid is viewed as consisting of a series of small 'crystals' distributed at random in the body of the liquid. Lehmann actually found that each particular swarm appears as a ***transparent liquid crystal*** under a microscope. The turbidity of the liquid crystals is due to the ***scattering of light at the boundaries between the various swarms.*** The effect is similar to that observed when a *transparent substance like glass is finely powered. Each piece is transparent but when huddled together the mass appears somewhat opaque.* As the temperature of the liquid crystals is raised, the molecular motion increases and an interchange between the swarms occurs. The swarms become smaller and smaller with rise in temperature and ultimately at a certain temperature, the swarms become smaller than half the wavelength of light. They are then too small to scatter light. turbidity now disappears and the liquid becomes clear. The double refraction and other anisotropic properties due to orientation of molecules within the swarms disappear. The liquid becomes singly refracting and isotropic. This temperature is the melting point of the substance. The arrangement of molecules in an isotropic liquid is depicted in Fig. 4.34.

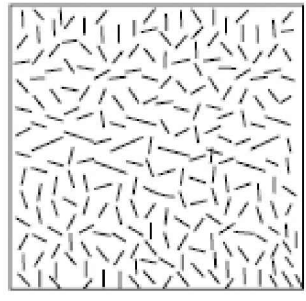


Fig. 4.33 *Arrangement of molecules in isotropic liquids*

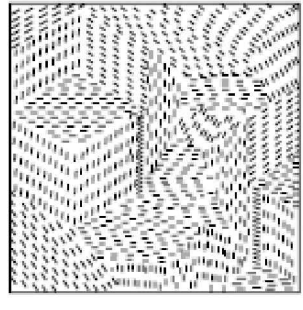


Fig. 4.34 *Arrangement of molecules in anisotropic liquids*

S. Chandrasekhar, a physicist at the Indian Institute of Science, Bangalore, has made important contribution to the field of liquid crystals.

4.9.3 Applications of Liquid Crystals

1. Liquid crystals have found applications in many fields. ***Liquid Crystal Display (LCD)*** in calculators, watches, laptop computers are possible because polarised light can be transmitted through liquid crystals in one phase but not transmitted through another. Polarised light is oduced by passing ordinary light through a filter that allows only the light waves oscillating in one particular phase to pass through. When the current is on, the liquid crystal molecules are aligned and polarised light cannot pass through. When the current is off, the molecules are not aligned and light can pass through.
2. Liquid crystals can also be used in thermometers, to determine temperature, and in rings to determine the mood of a person the spacing between crystal layers depends upon the temperature and wavelength of light reflected by the crystal on this spacing. The colour reflected by the liquid crystal will change with temperature and this colour can be used to indicate the temperature of the body or any other substance to which the liquid crystal is exposed.

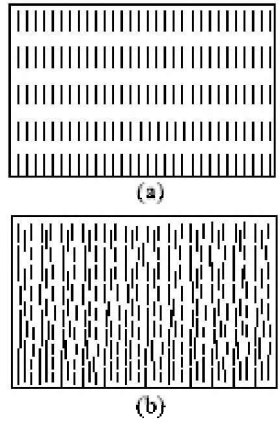


Fig. 4.35 *Molecular arrangement in (a) smectic state, and (b) nematic state in liquid crystals*

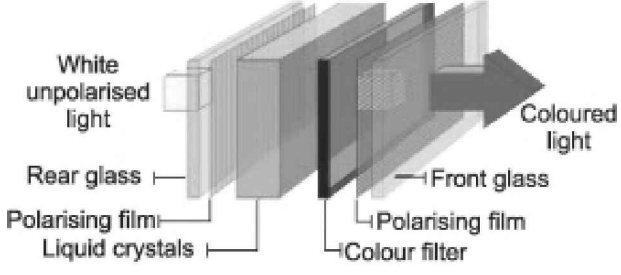


Fig. 4.36 *Liquid crystal display*

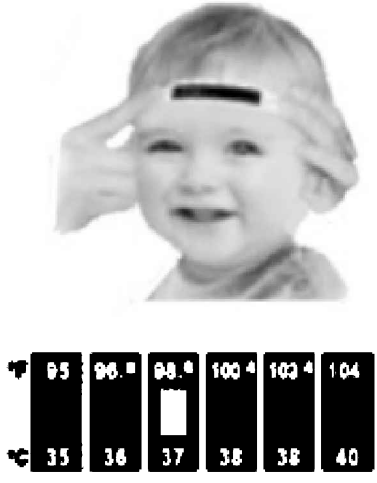


Fig. 4.37 *LCD thermometer*

A liquid crystal display is a flat panel display, electronic visual display or video display that uses the light-modulating properties of liquid crystals. Liquid crystals do not emit light directly.

SUMMARY

1. A liquid may be defined as a collection of molecules held close to one another but showing random motion through the intervening empty spaces.
2. *Dipole-dipole* interactions occur in polar molecules, e.g. in the molecules of HCl.
3. *London forces* occur between nonpolar molecules. In nonpolar molecules, the electrons may shift to one side of the molecules at a particular instance making one side positive and the other side negative, thus creating a dipole.
4. *Hydrogen bonding* occurs in molecules containing hydrogen and an electronegative atom like O, N, F, covalently bonded. In the case of water, O of one molecule is attracted by H of second molecule and a weak bond is created, which is called hydrogen bond.
5. The phenomenon of high-energy molecules leaving the liquid phase and moving into the vapour phase is called *evaporation*. Transference of molecules from the vapour phase to the liquid phase is called condensation.
6. Nature of the liquid and temperature influence vapour pressure. The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the boiling point of the liquid.
7. The amount of heat required to change one mole of the liquid into its vapour at the boiling point is called the *heat of vaporisation* of the liquid.
8. *Guldberg's rule* $T_b = 2T_c/3$, where T_b and T_c are the boiling point and critical

temperature respectively.

9. Trouton's rule, $\Delta H_v/T_b = 21$, where ΔH_v is in calories and T_b is in degrees absolute.
10. *Surface tension* of a liquid is defined as the force acting at right angles to the surface along one cm length of the surface. Surface tension of a liquid can be determined by capillary rise method, drop weight and drop number methods using a stalgmometer and Nuoy torsion balance method.
11. *Parachor* of a liquid is the molar volume of the liquid at a temperature at which the surface tension of the liquid is unity.
12. *Coefficient of viscosity* may be defined as the force of friction (in dynes) required to maintain a velocity difference of 1 cm/s between two parallel layers 1 cm apart and each having an area of one sq. cm.
13. Refractive index of a medium is defined as the ratio of the velocity of light in vacuum to the velocity of light in the medium.
14. Molar refractivity or molar refraction R_m is given by

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{d}$$

where M is the molecular mass and d is the density of the liquid.

15. A liquid crystal has structure between that of a liquid and a solid.
16. Three different kinds of liquid crystals are smectic, nematic and cholesteric liquid crystals. Liquid crystals find applications in LCDs, watches, calculators and laptop computers. They are also used as thermometers.

EXERCISES

Based on Different University Papers

1. Objective Questions

(A) Fill in the Blanks

1. The unit of viscosity is _____
2. Surface tension _____ with increase of temperature.
3. The formula to calculate dipole moment is _____
4. Dispole moment of *p*-dichlorobenzene is _____
5. The temperature, at which, the vapour of a liquid is _____ pressure, is called its boiling point.
6. The equation to calculate parachor is _____
7. In a trans isomer the dipole moment is _____

8. Viscosity of a liquid _____ with increase of atomic mass.
9. Parachor can be used to assess the _____ of a liquid compound.
10. The formula to calculate rheochor is _____

(B) Multiple-Choice Questions

1. Water boils at lower temperature on high altitudes because

(a) atmospheric pressure is low there

(b) atmospheric pressure is high there

(c) water is weakly hydrogen bonded there

(d) water in pure form is found there

2. If η_1 and η_2 are coefficients of viscosity of two liquids, d_1 and d_2 are their densities and t_1 and t_2 are their flow times in an Ostwald's viscometer then

(a) $\frac{\eta_1}{\eta_2} = \frac{d_1 t_2}{d_2 t_1}$

(b) $\frac{\eta_1}{\eta_2} = \frac{d_2 t_2}{d_1 t_1}$

(c) $\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$

(d) $\frac{\eta_1}{\eta_2} = \frac{d_2 t_1}{d_1 t_2}$

3. When a student was given a viscometer, the liquid was sucked with difficulty; the liquid may be:

(a) benzene

(b) toluene

(c) water

(d) glycerine

4. The rise of a liquid in capillary tube is due to

(a) viscosity

(b) osmosis

(c) diffusion

(d) surface tension

5. Which is correct for parachor?

(a) $\frac{M}{D} \cdot \gamma^{1/8}$

(b) $\frac{M}{D} \cdot \gamma^{1/2}$

(c) $\frac{M}{D} \cdot \gamma^{1/6}$

(d) $\frac{M}{D} \cdot \gamma^{1/4}$

6. Which of the following statements is wrong?

(a) Evaporation is a spontaneous process.

(b) Evaporation is a surface phenomenon.

(c) Vapour pressure decreases with increase of temperature.

(d) The vapour pressure of a solution is always less than the vapour pressure of the pure solvent.

7. Mark the statement which is correct:

(a) Surface tension of a liquid increases with temperature.

(b) Addition of chemicals reduces the surface tension of a liquid.

(c) Stalgmometer is used for measuring viscosity of the liquid.

(d) Viscosity of a liquid does not depend on intermolecular forces.

8. Normal boiling point of a liquid is that temperature at which vapour pressure of the liquid is equal to

(a) zero

(b) 380 mm of Hg

(c) 760 mm of Hg

(d) 100 mm of Hg

9. The viscosity of which liquid is highest?

(a) Water

(b) Glycol

(c) Acetone

(d) Ethanol

10. With increase in temperature, the fluidity of liquids:

(a) increases

(b) decreases

(c) remains constant

(d) may increase or decrease

11. Which of the following expressions regarding the unit of coefficient of viscosity is not true?

(a) dyne cm^{-2} sec

(b) dyne cm $^{-2}$ sec^{-1}

(c) Nm^{-2} s

(d) 1 poise = l0^{-1} Nm^{-2} s

12. Unit of surface tension is

(a) dyne cm

(b) dyne cm^{-1}

(c) dyne cm^{-2}

(d) none

13. Association of molecules in water is due to

(a) covalent bonding

(b) hydrogen bonding

(c) ionic bonding

(d) van der Waals forces

14. With the increasing molecular mass of a liquid, the viscosity

(a) decreases

(b) increases

(c) is not affected

(d) none of above

15. The boiling points of water, ethanol and diethyl ether are 100°C and 78.5°C and 34.6°C respectively. The intermolecular forces will be in the order:

(a) water > ethanol > diethyl ether

(b) ethanol > water > diethyl ether

(c) diethyl ether > ethanol > water

16. Parachor is a property which is

(a) additive-cum-constitutive

(b) colligative

(c) additive

(d) none

17. For any liquid, the number of drops formed per unit volume depends on

(a) viscosity

(b) surface tension

(c) pressure

(d) none

18. Which of the following is a colligative property?

(a) Molecular weight
(b) Osmotic pressure
(c) Parachor
(d) Surface tension

19. Parachors of two liquids can be compared by
(a) their molar volumes
(b) their molecular masses
(c) their atomic numbers
(d) their vapour pressure

20. The molecular viscosity of a liquid is given by
(a) viscosity × mol. wt.
(b) viscosity × molar volume
(c) viscosity × molar surface
(d) none

Answers

(A) Fill in the Blanks

1. Poise
2. decrease
3. $\mu = e \times d$
4. Smaller
5. Atmospheric
6. $[\mathrm{P}] = \frac{M}{D} \cdot \gamma^{1/4}$
7. Zero
8. Increases
9. Structure
10. $[\mathrm{R}] = \frac{M}{d}[\eta]^{1/8}$

(B) Multiple-Choice Questions

1. (a)
2. (c)
3. (d)

4. (d)
5. (d)
6. (b)
7. (b)
8. (c)
9. (b)
10. (a)
11. (b)
12. (b)
13. (b)
14. (b)
15. (a)
16. (a)
17. (b)
18. (b)
19. (a)
20. (c)

SHORT-ANSWER QUESTIONS

1. What is meant by free volume of a liquid?
2. State and explain Trouton's law.
3. Define the terms: *refractive index, specific refraction.*
5. Illustrate using figures the difference between molecular structures of a gas, a liquid and a solid.
6. Explain dipole-dipole interactions and London forces in liquids.
7. Differentiate between adhesion and cohesion giving examples
8. What is Poiseulle's equation? What is its utility?
9. What is the relation between viscosity and chemical constitution?
10. What are different kinds of liquid crystals? Explain, in brief, one of them.
11. What is thermography as applied to liquid crystals? Explain with the help of a diagram.
12. How do we obtain the molecular mass of polymers from viscosity measurement?

GENERAL QUESTIONS

1. What is the meant by vapour pressure of a liquid? How will you account for it?
2. How does surface tension vary with temperature? Describe Eotvos equation.
3. Describe the drop weight method for the determination of surface tension of a given liquid.
4. Define surface tension. Describe one method for determining the surface tension of a liquid.
5. Define the terms *refraction, specific refraction, molar refraction.* How is refractive index measured experimentally?
6. (a) "What do you understand by viscosity, coefficient of viscosity and fluidity? How is fluidity related to viscosity? What are the units of viscosity?

   (b) What is the effect of temperature on viscosity?

   (c) Describe one method for the determination of viscosity of a given liquid.

   (d) At 293 K, the density of acetone is 0.291 g/cc and its viscosity is 3.29 millipoise. Explain these figures which indicates that acetone is an associated liquid.
7. What is rheochor? How is it related with viscosity of liquid?
8. In what way does knowledge of surface tension help in deciding chemical constitution of the liquid?
9. Justify: *The term mesomorphic state is also used to describe liquid crystals.*
10. Differentiate clearly between smectic liquid crystals and nematic liquid crystals.
11. Explain the term *parachor*. Discuss its utility in the elucidation of structure of molecules.
12. (a) Define surface tension. What is the surface tension of a liquid at its critical temperature?

    (b) Calculate the molar refraction of acetic acid at temperature at which its density is 1.046 g/cc. The experimentally observed value of refractive index at this temperature is 1.3715.

    (c) Explain the term *viscosity* and *viscosity coefficient.* What are the units of viscosity coefficient?

    (d) Give the relationship between boiling point and heat of vaporisation of a liquid.
13. (a) How is boiling point of a liquid related to its vapour pressure?

    (b) The normal boiling point of benzene is 353.3 K. Assuming Trouton's rule, estimate the boiling point of benzene at a pressure of i00 mm.
14. Define coefficient of viscosity. How does it vary with temperature?
15. Explain swarm theory of liquid crystals briefly.
16. Describe a method to determine the viscosity of a liquid. In what units is the viscosity of a liquid measured?
17. (a) What are additive and constitutive properties?

    (b) How is molar refraction used to determine the chemical constitution of an organic compound?

18. (a) Discuss Ostwald's viscometer for measuring the viscosity of a liquid.

    (b) Explain the following terms:

    (i) Vapour pressure of a liquid

    (ii) Fluidity

    (iii) Surface tension

    (iv) Parachor

    (v) Specific and molar refraction

    (c) The coefficient of viscosity of two liquid's at 300 K are 1.4×10^{-3} kg m^{-1} s^{-1} and 1.6×10^{-3} kg m^{-1} s^{-1} and their densities at the same temperature are 8×10^{2} and 10×10^{2} kg m^{-3} respectively. If the time of flow in the Ostwald's viscometer for the first liquid is 100 seconds, calculate the time flow for the second liquid.

19. What is meant by surface tension of liquid? How is it measured experimentally?

20. What do you know by the term *refractive index?*

21. What are cholestic liquid crystals? What are their uses?

22. Differentiate between surface tension and surface energy. How are they related to each other?

23. Name different types of liquid crystals and briefly explain each type and give their uses.

24. Describe the gas saturation method for the determination of vapour pressure of a liquid.

25. When a capillary is dipped is mercury, the mercury level in the capillary is lower than the surface of the free liquid. How do you account for it.

26. What do you understand by the term "association of a liquid? The viscosity of a liquid is 2.04 centipoise at 20°C. Its density is 1.2. Is the liquid associated?

27. What is meant by Reynolds number? What is its significance?



The Solid State

5

LEARNING OBJECTIVES

- Classify solids into different types and compare their properties
- Understand the meaning of isotropy
- Understand ionic, molecular, covalent and metallic crystals
- Define the terms *space lattice* and *unit cells* and know their different types
- Follow the structures of NaCl, CsCl, ZnS and CaF_2
- Know the packing of particles in a crystal of three dimensions
- Differentiate between body-centred and face-centred cubic crystals
- Understand tetrahedral and octahedral voids
- Calculate the number of atoms in simple cubic, FCC and BCC unit cells.
- Derive a relationship between atomic radius and edge length in crystals and the relation between density and edge length of the cube.
- Follow the laws of crystallography and terms used therein and follow different symmetry elements
- Know about weiss and Miller indices
- Understand point groups and space groups
- Investigate the internal structure of a solid by *X*-ray diffraction using Bragg's equation
- Understand powder method and Luae method for structure determination of solid

5.1 INTRODUCTION

Some of the characteristic properties of solids include definite mass, volume and shape; short intermolecular distance, strong intermolecular forces and incompressibility and rigidity. The constituent particles of a solid, namely atoms, molecules or ions, have fixed positions and can only oscillate about their mean positions. For our day-to-day needs, we use more of solids than liquids and gases. Properties of a solid depend upon the nature of constituent particles and the binding forces between them. The correlation between the structure and properties helps in developing new solid materials with desired prop erties. We have been able to discover biodegradable polymass for packaging, magnetic and electric materials, and high-temperature superconductors making use of this correlation.

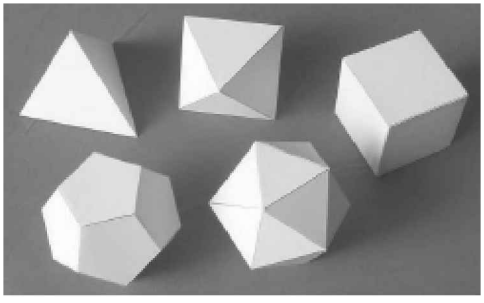


Fig. 5.1 *Solid shapes*

5.2 TYPES OF SILIDS

Solids may be broadly classified into two types.

(a) Crystalline Solids If various ions, atoms and molecules constituting the solid are arranged in definite geometric pattern within the solid, it is called a crystalline solid. All solid elements and compounds exist in this form.

(b) Amorphous Solids A solid is known as amorphous if the constituent particles of the substance are not arranged in any regular fashion. Glass, pitch and polymers of high molecular mass appear in this category. Amorphous solids are not accepted as ***true solids.*** They are regarded as supercooled liquids of high viscosity.

Points of Difference between Crystalline and Amorphous Solids

The points of difference between the two solids are given as under:

(a) Arrangement of Particles The constituent atoms or ions are arranged in a definite pattern in crystalline solids whereas there is no regular pattern of arrangement of particles in amorphous solids.

(b) Melting Point Crystalline solids melt sharply at their melting points while amorphous solids melt gradually over a range of temperature.

(c) Isotropy and Anisotropy Properties like refractive index and electrical conductivity are identical in all directions in the case of amorphous substances. This property, also shown by gases and liquids, is called ***isotropy*** and substances showing this property are called ***isotropic.*** On the other hand, in the case of crystalline substances, the properties mentioned above have different values in different directions. This behaviour is called ***anisotropy*** and the substances exhibiting this behaviour are called ***anisotropic solids.*** Thus, whereas amorphous substances are isotropic in nature, crystalline substances are anisotropic. The anisotropy exhibited by crystalline substances is obviously due to the reason that we come across different particles in different directions (Fig. 5.2).

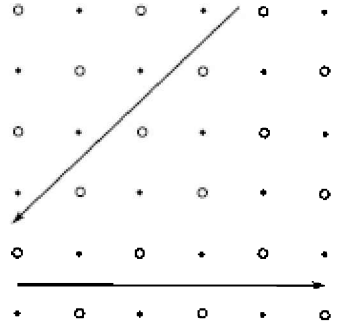


Fig. 5.2 *Anisotropy exhibited by crystalline substances*

(d) Regular and Irregular Cuts A crystalline solid on being cut with a sharp-edged knife gives a clean cleavage, whereas an amorphous solid breaks irregularly as shown in Fig. 5.3.

(i) A crystalline solid gives a clean cut.

(ii) An amorphous solid gives an irregular cut.

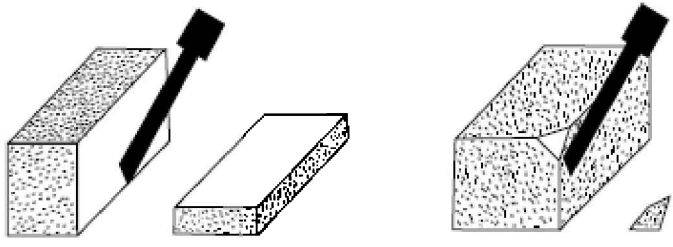


Fig. 5.3 *Cutting of solids*

5.3 TYPES OF CRYSTALS

1. Ionic Crystals In these crystals, the constituent particles occupying the lattice points are the positive and negative ions. These ions are held together by the strong electrostatic forces of attraction. Some of the important characteristics of these crystals are as follows:

(a) Because of strong electrostatic forces of attraction among the ions, they have high melting and boiling points.

(b) They are good conductors of electricity in the molten state and in solution.

(c) They are soluble in polar solvents but insoluble in nonpolar solvents.

(d) Because of strong electrostatic forces of attraction, the ions are closely packed and hence the ionic crystals are hard. However, they are brittle because on applying force, their arrangement pattern is disturbed. Sodium chloride crystal is a common example of this type of solid.

2. Molecular Crystals The constituent particles occupying the lattice points, in this case are the molecules. The intermolecular forces holding the molecules together in the crystal lattice are the weak van der Waals forces. In the case of polar molecules (e.g. HCl, H_2O, HN_3, etc.), these van der Waals forces are the **dipole-dipole attractions** as shown in Fig. 5.4(a). In case of nonpolar molecules (eg. H_2, Cl_2, CH_4, etc.) the van der Waals forces are the London dispersion forces.

These forces are assumed to arise due to momentary dipole produced as a result of distortion of the electron cloud of one molecule which produces an induced dipole in the other molecule as shown in Fig. 5.4(b).

The main characteristics of the molecular crystals are given as under:

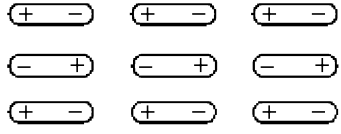


Fig. 5.4(a) *Dipole-dipole attraction in molecular crystals*

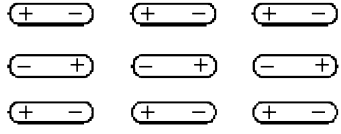


Fig. 5.4(b) *London dispersion force in the molecular of hydrogen*

(a) As the van der Waals forces are much weaker than the electrostatic forces existing in ionic crystals, the molecular crystals are soft and have low melting and boiling points.

(b) They do not conduct electricity in the solid or liquid state or in solution as there are no ions present. Electricity is conducted with the help of ions which are missing in this case.

(c) They are less soluble in water and more soluble in nonpolar solvents.

(d) As dipole-dipole attractions are stronger than London forces, polar molecular crystals generally have higher melting points and boiling points than crystals of nonpolar molecules of ***comparable molecular size and shape.***

3. Network or Covalent Crystals In these crystals, the lattice points are occupied by atoms which are linked together by a network of covalent bonds to form a giant molecule. A common example of the crystals of this type is that of diamond in which the carbon atoms are linked together by cova-lent bonds to give a three-dimensional structure as shown in Fig. 5.5.

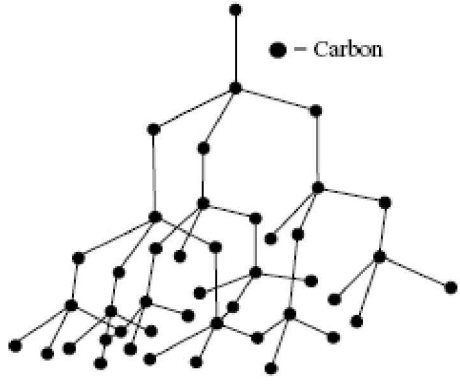


Fig. 5.5 *Structure of diamond*

Substances of this type show high melting point, high boiling point and are extremely hard because of the large number of covalent bonds that have to be broken to destroy the crystal structure. Further, they are nonconductors of electricity.

4. Metallic Crystals These crystals consist of positively. charged metals ions (kernels) occupying the lattice points which are held together by the metallic bond. The metallic bond arises due to the presence of mobile electrons.

These mobile electrons undergo simultaneous attractions by · Electrons a number of positive ions and hence the ions are held together (Fig. 5.6).

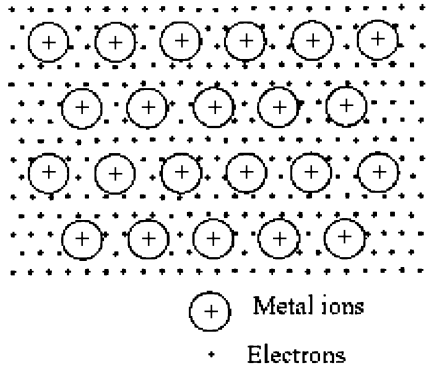


Fig. 5.6 *Metallic crystal*

The position of the positive ions can be changed without destroying the crystal, because of the uniform charge distribution provided by the free moving electrons. Thus, metallic crystals can be easily deformed. That is why the metals are ***malleable*** and ***ductile.*** The other properties of metals like lustre, thermal and electrical conductivity can be explained on the basis of the free-moving electrons. Also, as the positive ions are closely packed in the crystal lattice, most of the metals possess ***high melting point*** and ***high densities.***

5.4 SPACE LATTICE AND UNIT CELL OF A CRYSTAL

It is found that the particles constituting a crystalline substance are arranged in a regular fashion within the crystal in the three-dimensional space. For example, the arrangement of particles (represented by black dots) for a cubic crystal is shown in Fig. 6.

The regular arrangement of ions, atoms or molecules constituting the crystal in the three-dimensional space within the crystal is called the space lattice.

If a big-size crystal is broken again and again, ultimately a stage is reached when we get the smallest possible crystal. If it is broken further, it will break to give the constituent particles, i.e. ions, atoms or molecules. For example, if a big cubic crystal is broken, the smallest crystal obtained will be a small cube, as represented by shaded volume in Fig. 5.7. This small cubic crystal has all the elements of symmetry as possessed by the big cubic crystal. Evidently, the complete lattice has been obtained by repetition of this smallest unit in different directions.

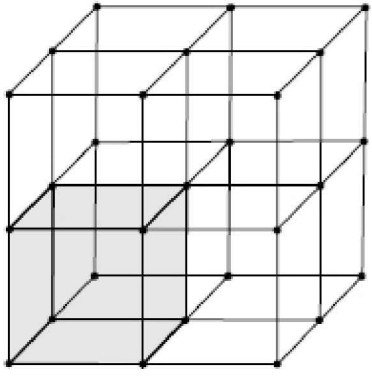


Fig. 5.7 *Space lattice and unit cell*

The smallest portion of the complete space lattice, which when repeated over and again in different directions, produces the complete space lattice is called the unit cell (shown as shaded in Fig. 5.7).

5.4.1 Different Types of Unit Cells (Crystal Systems)

Unit cells can be divided into four types:

(a) Simple Unit Cell This type of unit cell is produced when the particles are present only at the corners of the unit cell.

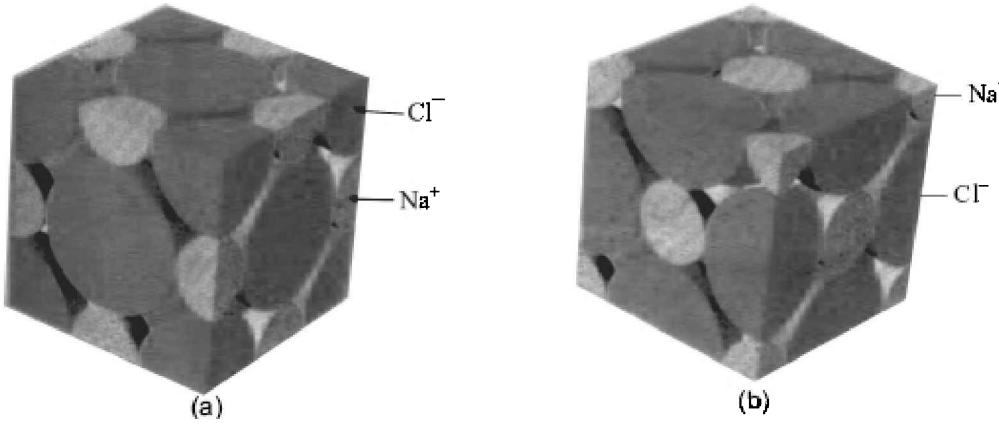


Fig. 5.8 *The unit cell of an ionic compound can be defined either by (a) the positions of anions, or (b) the positions of cations*

The simple unit cell is also called *primitive unit cell.*

(b) Face-centred Unit Cell If the particles are located at the centre of each face in addition to the corners, a ***face-centred unit cell*** is obtained.

(c) End-face-centred Unit Cell If the particles are located at the centre of two opposite faces in addition to the corners, an ***end-face-centred unit cell*** is obtained.

(d) Body-centred Unit Cell If the particles are present at the centre of the cell in addition to the corners, a ***body-centred unit cell*** is produced.

Different unit cells are shown in Fig. 5.9.

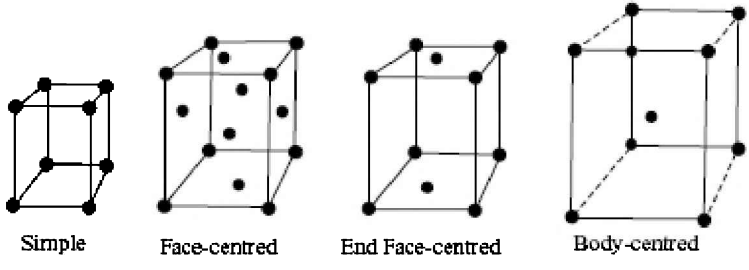


Fig. 5.9 *Types of unit cells*

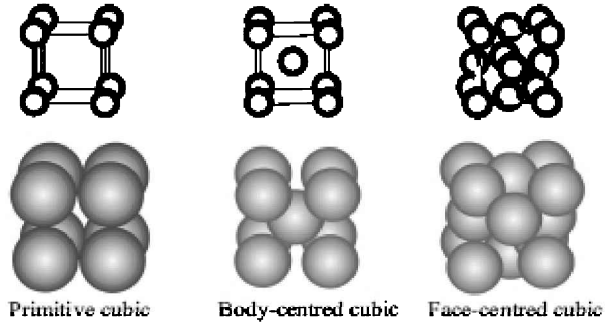


Fig. 5.10 *Three types of cubic cells. The top view makes it easier to see the locations of the lattice points but the bottom view is more realistic, with the spheres touching one another*

Co-ordination Number In solid-state chemistry, we represent constituent particles by spheres.

The number of spheres which are in direct contact with a particular sphere is called co-ordination number of that sphere (constituent particle).

In case of an ionic solid, the co-ordination number of a particular ion is the number of oppositely charged ions surrounding that particular ion.

5.4.2 Structure of Sodium Chloride (NaCl)

NaCl has the structure as shown in Fig. 5.11.

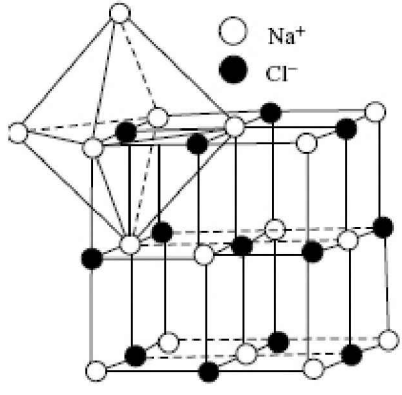


Fig. 5.11 *Structure of sodium chloride*

1. It has a face-centred cube (FCC) lattice. Na^+ ions are present at the corners and face centres while Cl^- ions are present at the body centre and edge centres. It can also be vice-versa.
2. Every sodium ion is surrounded by six Cl^- ions, one above, one below, one on the left, one on the right, one in front and one at the back. Similarly, every chloride ion is surrounded by six sodium ions. We express it by saying that the sodium ions as well as chloride ions have co-ordination number equal to 6. Co-ordination number is the number of atoms or ions immediately around a particular atom or ion. This structure has the co-ordination number 6 :

6.

3. If we look carefully at the structure of sodium chloride, we shall find that there are 4 units of sodium and chloride ions each in a unit cell:

This can be understood as follows:

The unit cell of an ionic compound can be defined either by (a) the position of anions, or (b) by the position of cations. NaCl adopts a face-centred cubic arrangement as shown. Note the positions of the ions within the unit cell. Both the Na^+ ions and the Cl^- ions adapt face-centred cubic arrangement. Look at the Fig. 5.11. It is defined as FCC by the positioning of Na^+ ions.

Contribution of spheres (Na^+) at the eight corners of the cube $= \frac{1}{8} \times 8 = 1$

Contribution of six spheres (Na^+ ions) at the six faces of the cube $= \frac{1}{2} \times 6 = 3$

Total Na^+ ions in the unit cell = 1 + 3 = 4

Coming to Cl^- ions, there are Cl^- ions at the centre of each edge and one Cl^- ion at the centre of the cube. Contribution of an edge sphere to the unit cell is one-fourth (there are 12 edges).

hence, contribution of spheres to Cl^- ions to the unit cell $= \left(\frac{1}{4} \times 12\right) + 1 = 4$

Thus, there are four Na^+ ions and four Cl^- ions in a unit cell. Sodium bromide, sodium iodide, silver chloride and magnesium oxide also possess sodium-chloride –type structure, i.e. FCC lattice.

5.4.3 Structure of Cesium Chloride (CsCl)

Cesium chloride has the structure as shown in Fig. 5.12. The eight corners of the cube are occupied by Cl^-.

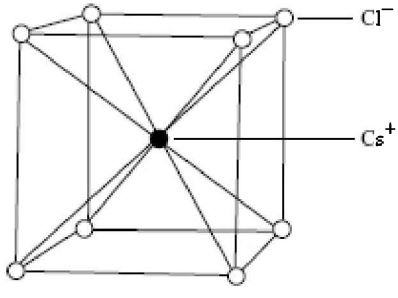


Fig. 5.12 *Structure of cesium chloride*

It is a common mistake to consider the CsCl structure as body centred cubic. We need to remember that the lattice points used to describe a unit cell must all be identical. In this case, they are all Cl ions. It is a simple cubic unit cell.

The contribution of Cl^- ions per unit cell is $\frac{1}{8} \times 8 = 1$

It can be seen from the figure that the number of chloride ions surrounding a particular cesium ion is 8. Similarly, the number of cesium ions surrounding a particular chloride ions

would be 8. Hence, the co-ordination number of chloride as well as cesium is 8. The number of ions of Cs and Cl per unit is one. Other substances showing this type of structure are cesium bromide and thalium chloride.

5.4.4 Structure of Zinc Blende (ZnS)

Zinc sulphide also exists in FCC (face-centred cubic) structure. Here, the co-ordination number of Zn^{2+} as well as S^{2-} ions is 4. Thus, every Zn^{2+} is surrounded by 4 S^{2-} ions and every S^{2-} ion is surrounded by 4 Zn^{2+} ions. Copper chloride and mercuric sulphide also exist in this structure.

A unit cell representation of zinc-blende-type structure is shown in Fig. 5.13. The sulphide ions are present at the corners and at the centre of each face of the cube. Zn^{2+} ions occupy alternate tetrahedral sites.

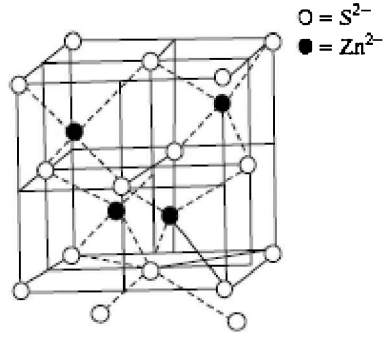


Fig. 5.13 *Structure of zinc blende*

5.4.5 Structures of Calcium Fluoride (CaF_2) and Na_20

1. Structure of CaF_2 In CaF_2, the fluoride ion is surrounded by four calcium ions and each calcium ion is surrounded by eight fluoride ions. Strontium fluoride, also possesses this structure.

The unit cell is represented in Fig. 5.14. Ca^{2+} ions form CCP type of arrangement. Thus, Ca^{2+} ions are present at all the corners and at the centre of each face of the cube. Fluoride ions occupy all the tetrahedral sites.

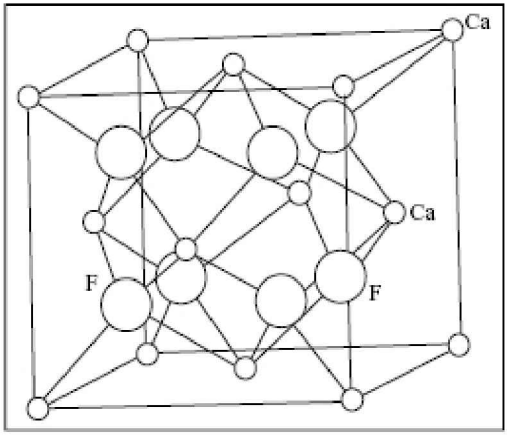


Fig. 5.14 *Structure of CaF_2. (fluorite structure)*

2. Structure of Na_20 (Antifluorite Structure) In Na_2O, each oxide ion is surrounded by eight sodium ions and each sodium ion, by four oxide ions. It has 4 : 8 co-ordination.

Table 5.1 gives the features and co-ordination numbers of different types of crystal structures.

Table 5.1 *Characteristics of different typeof structures*

Structure Type		Characteristics with Examples	Co-ordination Number
1.	NaCl	It is FCC structure. The two ions interpenetrate each other in sodium halides: AgCl, MgO.	$Na^+ = 6$ $Cl^- = 6$
2.	CsCl	Cs+ at the body centre of a cube of Cl^- ions or viceversa: CsCl, CsBr.	$Cs^+ = 8$ $Cl^- = 8$
3.	ZnS	FCC arrangement of both ions ZnS, CuCl, HgS.	$Zn^{2+} = 4$ $S^{2-} = 4$

5.4.6 Effect of Temperature and Pressure on Crystal Lattice

It is observed that substances undergo changes in their structure when temperature and pressure are changed. As a general rule, high pressure favours greater co-ordination number and high temperature favours lower co-ordination number. For example, when sodium chloride is subjected to high pressure, it transforms to body-centred cubic structure of cesium chloride. Thus, the co-ordination number is increased from 6 : 6 to 8 : 8. On the other hand, if we heat CsCl to a high temperature of 760 K, it converts to the structure of sodium chloride.

NaCl structure (6:6 Co-ordination) ⇌ (Pressure / Heat) CsCl structure (8:8 Co-ordination)

5.5 PACKING OF PARTICLES IN A CRYSTAL

Considering the particles as spheres of equal size, we can visualize the formation of a solid as shown in Fig. 5.15.

1. One-Dimensional Packing We can arrange the spheres in a row, [see Fig. 5.15(a)] such that they touch one another. This is to utilize the space economically and to account for the high density of the solids.

2. Two-dimensional Packing Then we can place another row of spheres by the sides of the first row. This can be done in two ways. One way is depicted in Fig. 5.15(B). The second method is shown in Fig. 5.15(C). The first type [Fig. 5.15(B)] is called square close packing and the second type [Fig. 5.15(C)] is called hexagonal close packing.

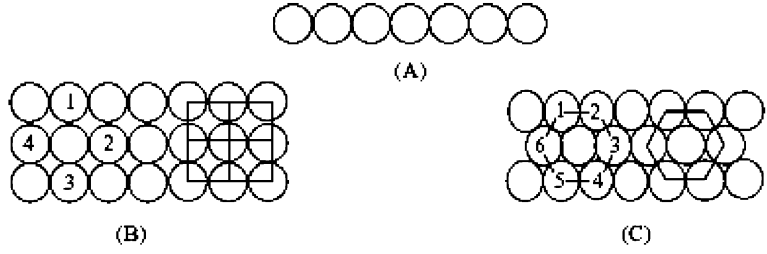


Fig. 5.15 *Packing of spheres for efficient use of space. (A) Edge formation (B) Square close packing (C) Hexagonal close packing*

In square close packing, a sphere is surrounded by four spheres in the plane whereas in hexagonal close packing, a sphere is surrounded by six spheres in the plane. Thus, empty space in square close packing is more as compared to the hexagonal close packing. In other words, hexagonal close packing is more dense than square close packing.

3. Three-Dimensional Packing Now let us form a second layer of spheres on the first layer in hexagonal close packing (see Fig. 5.16).

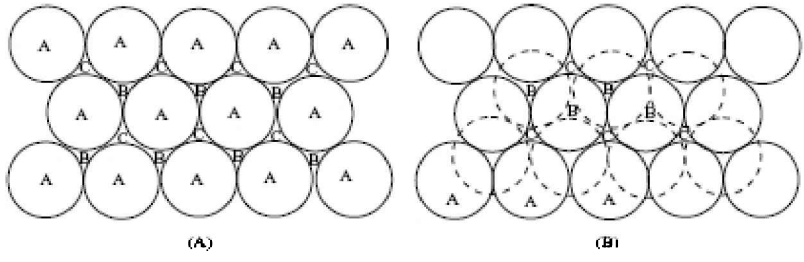


Fig. 5.16 *(a) Hexagonal closed packed layer (b) Formation of the second layer*

Spheres in the first layer are named A. There are voids in between them. These voids are C

voids and B voids as indicated in Fig. 5.16(a). We could place the spheres of the second layer on the first layer in such a way that every sphere in the second layer lies vertically over the sphere in the first layer. But this would not be an efficient packing as this would leave lots of gaps between them.

So let us place the spheres in the second layer over the voids B in the first layer as shown in Fig. 5.16(b). It will then not be possible to place spheres over the voids C because of space limitation. Now in the second layer of spheres, there are B' voids and C´ voids. In fact, C´ voids of the second layer lie over the C voids of the first layer.

Let us now place a third layer of spheres over the second layer. There are two possibilities. Either we place spheres on B' voids or on C' voids. If we place the spheres on the B' voids in the third layer, these spheres in fact would be seated over the spheres of the first layer. This arrangement would be ABABAB... arrangement. This type of packing is called ***hexagonal close packing.***

If we place the spheres in the third layer over the C' voids then the sphere in the third layer will neither be seated over the spheres in the first layer nor the second layer. This will give rise to ABC, ABC, ABC... arrangement because the spheres in the fourth, fifth and sixth layers will lie over first second and third layers respectively. This type of packing is called ***cubic close packing.*** This is similar to face-centred cubic system. Three-dimensional views of hexagonal and cubic close packing lattices are shown in Fig. 5.17.

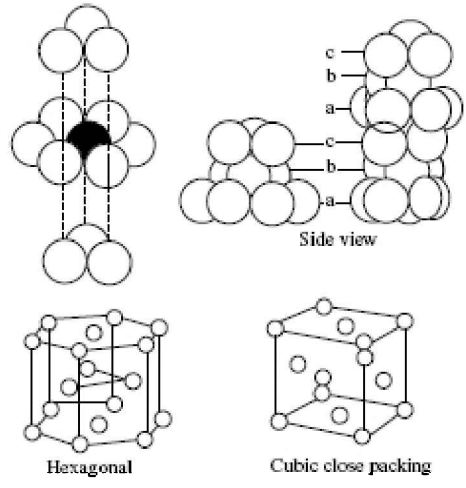


Fig. 5.17 *Three-dimensional view of hexagonal and cubic close packed lattices*

5.5.1 Body-Centred Cubic BCC Arrangement

This is a deviation from the close packing. If the spheres of the first layer are loosened up, we obtain body-centred cubic structure. Each sphere in the second layer is in contact with four spheres of the first layer (see Fig. 5.18).

The spheres in the second layer have the same packing as those in the first layer. The spheres in the third layer, having the same packing will be lying exactly over the corresponding spheres in the first layer. Thus, every sphere will be in contact with 8 spheres, four of the layer above and four of the layer below it. The coordination number is thus 8. Alkali metals like Li, Na, K, etc., crystallize in BCC structure. The structure is less closely packed than the CCP and HCP structures and the empty space is about 32%.

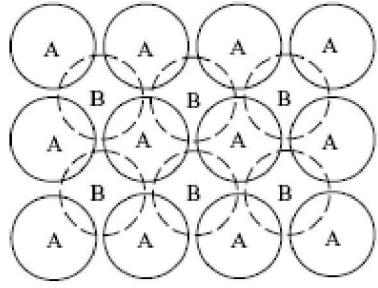


Fig. 5.18 *Body-centred cubic packing*

5.5.2 Tetrahedral and Octahedral Voids

A void or empty space in a lattice which is surrounded by four spheres is called a tetrahedral void. For example, the voids B in Fig. 5.16 are tetrahedral voids because they are surrounded by four spheres, three in the first layer and the fourth in the second layer.

A void which is surrounded by six spheres, is called the ***octahedral void.*** The voids C in Fig. 5.16 are octahedral voids because they are surrounded by six spheres, three in the first layer and three in the second layer. These voids are shown in Fig. 5.19.

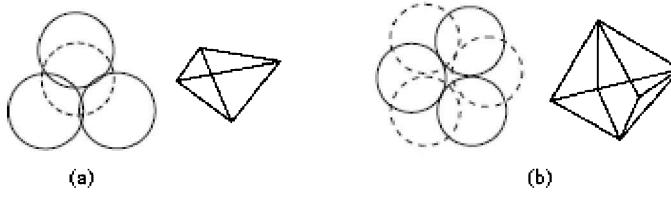


Fig. 5.19 *Two types of voids: (a) Tetrahedral (b) Octahedral*

Example 1 *Ferric oxide crystallizes in hexagonal close packed arrays of oxide ions with two out of every three octahedral holes occupied by ferric ions. Describe the formula offerric oxide.*

Solution

$$\text{Let the number of } O^{2-} \text{ ions in the packing} = N$$

$$\text{Number of octahedral voids} = N$$

$$\text{Voids occupied by } Fe^{3+} = \frac{2N}{3}$$

$$\text{Ratio of } Fe^{3+} : O^{2-} = \frac{2N}{3} : N$$

$$= 2 : 3$$

Hence, the formula of ferric oxide is Fe_2O_3

5.5.3 Co-ordination Number in HCP and CCP

Every sphere in either HCP or CCP has 12 spheres directly touching it, 6 in its own layer, 3 in the layer below it and 3 in the layer above it. Thus, the co-ordination number of a sphere in HCP or CCP is 12. In other types of crystals, co-ordination numbers of 4, 6, 8 are quite common.

Some general observations that have been made in the study of crystals:

1. Noble gases and most metals crystallize in closed packed structures.
2. A large number of ionic compounds crystallize in structures which are related to close packed structures. Here, one of the ions forms the close packed structures and the other ion goes into voids.
3. If in a compound of the general formula AB, the B ions form the close packed structure then A ions will occupy all the octahedral voids or half the tetrahedral voids.
4. In a compound of the type A_2B, all the tetrahedral sites will be occupied by A ions.
5. In NaCl, Cl^- forms the CCP structure and Na^+ occupies the octahedral voids. In ZnS, S^{2-} forms the CCP structures with Zn^{2+} occupying alternate tetrahedral voids. In CaF_2, it is the Ca^{2+} which forms the CCP lattice and F^- occupies all the tetrahedral voids.
6. In the packing of oxides of ion, viz. FeO and Fe_2O_3, FeO has the NaCl structure. Thus, Fe^{2+} should occupy the octahedral voids. But this oxide has stoichiometry with a formula $Fe_{0.95}O$. In converting two thirds of Fe^{2+} in FeO into Fe^{3+}, we get FeO, Fe_2O_3 or Fe_3O_4. In Fe_2O_4, all the Fe^{2+} are in octahedral voids and Fe^{3+} are equally distributed between octahedral and tetrahedral voids. $MgFe_2O_4$ also has a similar structure.
7. $MgAl_2O_4$ and $ZnFe_2O_4$ (ferrites) form spinal structure. Mg^{2+} in the former and Zn^{2+} in the latter (divalent ions) are in tetrahedral voids and Al^{3+} and Fe^{3+} are in octahedral voids. These spiral-type compounds are important magnetic materials used in memory loops in computers.

5.6 RADIUS RATIO

In a solid, the co-ordination number of an ion depends upon the radius ratio. In ionic solids, radius ratio is defined as ***the ratio of the radius of the cation to the radius of the anion.***

$$\text{Radius ratio} = \frac{\text{Radius of cation } (r^+)}{\text{Radius of anion } (r^-)} \tag{5.1}$$

It is observed that greater the radius ratio, greater is the co-ordination number of the ions. This can be understood as the ions have a tendency to get surrounded by maximum number of ions of opposite charge. Thus, in NaCl, the Na^+ ion has co-ordination number 6, while in CsCl, the Cs^+ ion which is bigger than Na^+ ion has a co-ordination number 8. A bigger cation has a greater surface area and thus will have a tendency to get surrounded by a larger number of anions.

Table 5.2 below gives the relation between the radius ratio and co-ordination number.

Table 5.2 *Limiting radius ratio*

Radius Ratio	Co-ordination No.	Arrangement
1.0-0.732	8	Cubic

0.732-0.414	6	Octahedral
0.414-0.225	4	Tetrahedral
0.225-0.155	3	Triangular

We may visualize the above results as follows:
If the anions are touching one another and also the cation together, it leads to stable arrangement. The stable arrangement for triangular structure will be as shown in Fig. 5.20(a). If the cation becomes bigger in size, the anion will no longer be touching one another, leading to instability [Fig. 5.20(b)]. To counter this, they will transform into tetrahedral arrangement [Fig. 5.20(c)]. So that anions continue to touch one another and also the cation is in contact with all the three anions. Let us start from the octahedral arrangement. If the cation becomes smaller (radius ratio decrease), the arrangement changes to tet-rahedral in order to maintain close contact between the anions and between the anions and the cations.

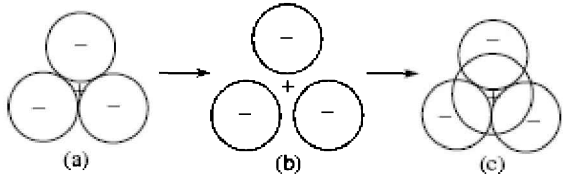


Fig. 5.20 *The stable planar triangular arrangement changing to tetrahedral arrangement as r*/r- increases*

On the other hand, if the cation becomes bigger (radius ratio increase), the structure changes to BCC (co-ordination number 8) again to maintain close contact between the anions and between anions and cations. This is illustrated in Fig. 5.21.

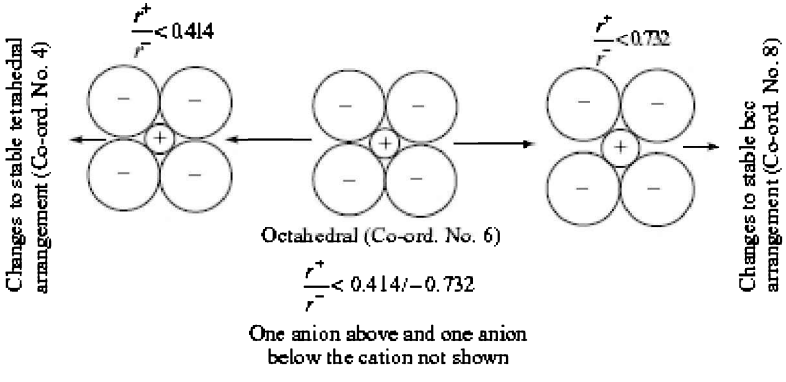


Fig. 5.21 *Effect of radius ratio on co-ordination number*

Example 2 *A solid AB has the NaCl structure. If the radius of the cation A is 100 pm, what is the radius of the anion B?*

Solution: Since the solid has NaCl structure, the co-ordination number of A and B each is 6. This is possible when the radius ratio is in the range 0.414 – 0.732.

Thus, $$\frac{\text{Radius of cation}}{\text{Radius of anion}} = 0.414 \text{ to } 0.732$$

Or $$\text{Radius of anion} = \frac{\text{Radius of cation}}{0.414 \text{ to } 0.732}$$

$$= 241.6 \text{ to } 133.0 \text{ pm} = 133.6 \text{ to } 241.6 \text{ pm}$$

Example 3 *The radius of the cation in a solid measures 33 pm and the anion measures 70 pm. Predict the co-ordination number of cation and structure of solid.*

Solution:

$$\text{Radius of cation } (r^+) = 30 \text{ pm}$$

$$\text{Radius of anion } (r^-) = 70 \text{ pm}$$

$$\text{Radius of ratio } (r^+/r^-) = \frac{30}{70} = 0.471 \text{ pm}$$

As the value lies in the range 0.732 – 0.414, the co-ordination number of the cation is 6 and octahedral arrangement is predicted.

5.7 NUMBER OF ATOMS IN A UNIT CELL FOR SIMPLE CUBIC, FCC AND BCC STRUCTURES

The following points are to be kept in mind while calculating the number of atoms in a unit cell.

(a) Each corner atom in a cube is shared between eight unit cells. Therefore, a corner atom contributes 1/8 to each unit cell.

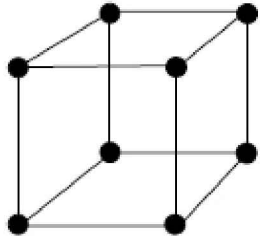
(b) An atom on the face of a unit cell is shared by two unit cells. Thus, a face atom contributes ½ to each unit cell.

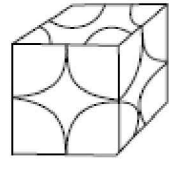
(c) An atom on the edge of a cube is shared by four unit cells. Hence, an edge atom contributes ¼ to each unit cell.

(d) An atom inside a cube belongs to that cube only. Hence, that atom contributes fully to that unit cell.

We shall calculate separately the number of atoms in simple, face-centred and body-centred cubic-structures.

1. Number of Atoms in Unit Cell of Simple Cubic In this type of structure, the atom (or ions or molecules) are situated only at the corners of a cube (Fig. 22). Each corner atom contributes 1/8 to a unit cell.





1/8 Atom

Fig. 5.22 *Simple cubic arrangement and the number ofatoms in unit cell*

Contribution of 1 corner atom = 1/8
Contribution of 8 corner atoms = 1/8 × 8 = 1
Hence, the number of atoms per unit cell in a simple cubic structure is 1.

2. Number of Atoms in a Unit Cell of FCC In a face-centred cubic, there are 8 atoms at the 8 corners of the cubic and 6 atoms at the centre of 6 faces of the cube (Fig. 5.23)

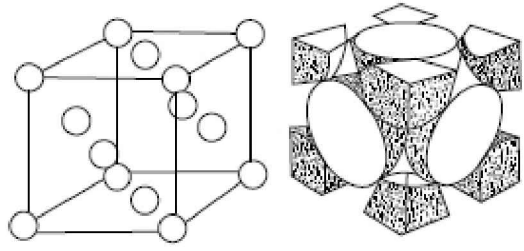


Fig. 5.23 *Face-centered cubic arrangement*

Contribution of 1 corner atom = $\frac{1}{8}$

Contribution of 8 corner atoms = $\frac{1}{8} \times 8 = 1$

Contribution of 1 face atom = $\frac{1}{2}$

Contribution of 6 face atoms = $6 \times \frac{1}{2} = 3$

∴ Total number of atoms in unit cell of FCC = 1 + 3 = 4

3. No. of Atoms in a Unit Cell of BCC In body-centred cubic structure, there are 8 atoms at the corners and one atom at the centre of the body of the cube (Fig. 5.24).

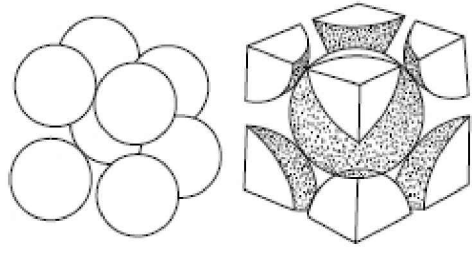


Fig. 5.24 *Body-centred cubic arrangement*

Contribution of 1 corner atom = $\frac{1}{8}$

Contribution of 8 corner atoms = $\frac{1}{8} \times 8 = 1$

Contribution of 1 central atom = 1

Thus, total number of atoms in a unit cell of body-centred cubic = 1 + 1 = 2

Example 4 *A cubic solid is made up of two elements P and Q. Atoms Q are present at the corner of cube and atoms P at the body centre. What is the formula of the compound? What are the co-ordination numbers of P and Q?*

Solution:

Number of atoms of Q (at the corner) in unit cell = $\frac{1}{8} \times 8 = 1$

Number of atoms of P (at body centre) in unit cell = 1

Hence, the formula of the compound is PQ. Co-ordination numbers of P and Q each = 8.

Example 5 *A compound formed by elements X and Y crystallizes in the cubic structure. Xatoms are situated at the corners and Y atoms are at the centre offaces. What is the formula of the compound?*

Solution. There are 8 atoms of X at 8 corners and 6 atoms of Y at the centre of six faces of the face centred cubic.

$$\text{Contribution of 1 corner atom} = \frac{1}{8}$$

$$\text{Contribution of 8 corner atoms} = \frac{1}{8} \times 8 = 1$$

$$\text{Contribution of 1 face centred atom} = \frac{1}{2}$$

$$\text{Contribution of 6 face centred atoms} = 6 \times \frac{1}{2} = 3$$

Thus, there is 1 atom of X and 3 atoms of Y per unit cell.

Hence, the formula of the compound is XY_3.

5.7.1 Relation between Atomic Radius (r) and the Edge Length (a) in Crystals

Table 5.3 *The following relations between rand a forvarious structures.*

Structure	Relation
Simple cubic	$r = \frac{a}{2}$
Body-centred	$r = \frac{\sqrt{3}}{4} a = 0.433\, a$

Face-centred	$r = \frac{a}{2\sqrt{2}} 0.3535\, a$

The relation between r and a can be obtained as under (see Fig. 5.25).

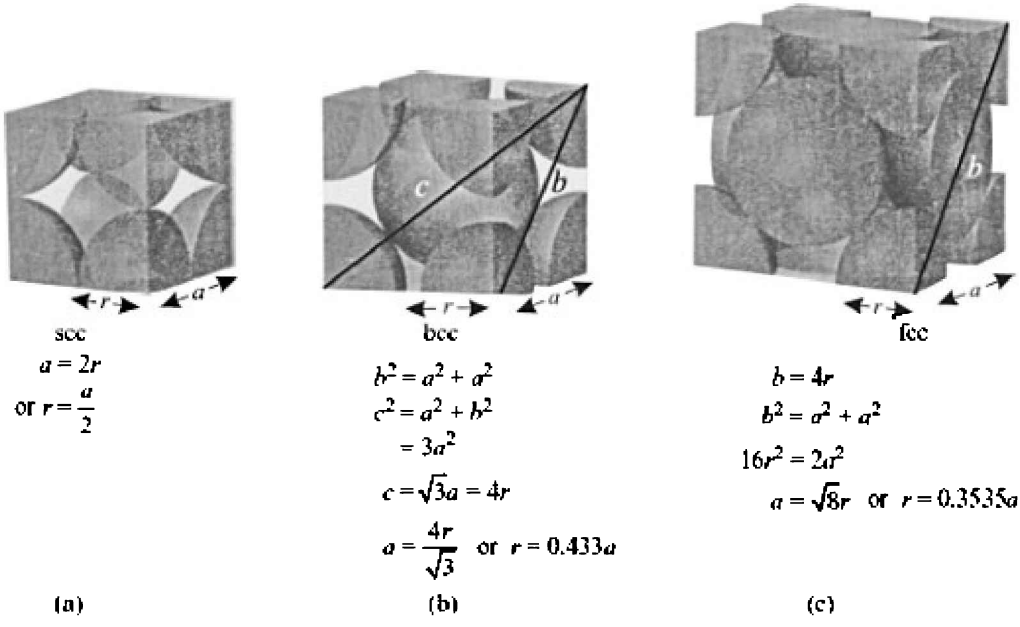


Fig. 5.25 The *relationship between the edge length (a) and radius (r) of atoms in the (a) simple cubic cell, (b) body-centred cubic cell, and (c) face-centred cubic cell*

Example 6 *CsCl has a simple cubic arrangement and its unit cell edge length is 400pm. Calculate the interionic distance in CsCl.*

Solution: Figure 5.26 shows the arrangement of CsCl. Open circles represent Cl^- and solid circle, Cs+. Half of the distance *CE* is the interior distance

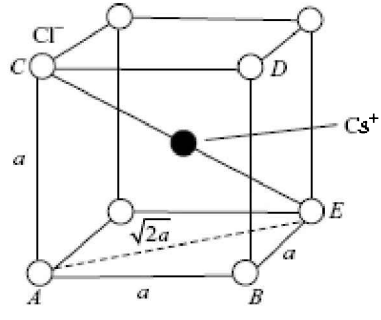


Fig. 5.26 *Structure of CsCl*

$$AE = \sqrt{a^2 + a^2} = \sqrt{2}\, a$$

$$CE = \sqrt{2a^2 + a^2} = \sqrt{3}\, a$$

$$\sqrt{3} \times 400$$

$$\text{Interior distance} \quad \frac{1}{2} \times \sqrt{3} \times 400 \quad 346.4 \text{ pm}$$

Example 7 *Calculate packing efficiency in CCP structure.*

Solution: A CCP structure is, in fact, a face-centred cubic structure. For a face-centred cubic,

$$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\, r \quad \text{or} \quad r = \frac{a}{2\sqrt{2}}$$

$$\text{Packing efficiency} = \frac{\text{Volume occupied by four spheres in unit cell}}{\text{Total volume of the unit cell}} \times 100\ \%$$

$$= \frac{4 \times \frac{4}{3}\pi r^3 \times 100}{(2\sqrt{2}\, r)^3}\ \% = \frac{(16/3)\,\pi r^3 \times 100}{16\sqrt{2}\, r^3}\ \% = 74\ \%$$

Example 8 *Tungsten crystallizes in a body-centred cubic unit cell. If the edge of the unit cell is 316.5 pm, what is the radius of the tungsten atom?*

Solution: For FCC structure,

$$r = \frac{\sqrt{3}}{4} a \quad \text{Given } a = 316.5 \text{ pm}$$

Substituting the value of a in the equation above, we have

$$r = \frac{\sqrt{3}}{4} \times 316.5 = \mathbf{137.04\ pm}$$

Example 9 *Aluminium crystallizes in an FCC structure. Atomic radius of the metal is 125pm. What is the length of the side of the unit cell of the metal?*

Solution: For FCC structure,

$$r = \frac{a}{2\sqrt{2}} \text{ or } a = 2\sqrt{2}\, r$$

Given $r = 125$ pm

$\therefore$ $a = 2\sqrt{2} \times 125 \text{ pm} = 2 \times 1.4142 \times 125 \text{ pm} = 353.55 \text{ pm}$

PROBLEMS FOR PRACTICE

1. Gold (atomic radius = 0.144 nm) crystallizes in a face-centred unit cell. What is the length of the side of the cell?

[Ans. a = 0.407 nm]

2. KF has CCP structure. Calculate the radius of unit cell if the side of the cube or edge length is 400 pm. How many F^- ions and octahedral voids are there in this unit cell?

[Ans. r = 141.4 pm, there are 4 F^- ions and 4 octahedral voids]

3. Silver crystallizes with face-centred cubic unit cell. Each side of the unit cells has a length of 409 pm. What is the radius of an atom of silver? (Assume that each face atom is touching the four corner atoms.)

[Ans. r = 144.6 pm]

5.7.2 Relation between the Density and Edge Length of a Cube

If we know the structure of the solid then it is possible to calculate the density, provided we know the cell parameters, i.e. length of the cube.

$$\text{Let the length of edge of the cube} = a \text{ pm} = a \times 10^{-10} \text{ cm}$$

$$\text{The volume of the cube} = (\text{Edge})^3 = (a \times 10^{-10})^3 = a^3 \times 10^{-30} \text{ cm}^3$$

$$\text{Density of the unit cell} = \frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}} \quad \ldots (5.2)$$

But mass of unit cell = Number of atoms in the unit cell × Mass of each atom

If we represent the number of atoms in the unit cell by Z and mass of each atom m. Then

$$\text{Mass of unit cell} = Z \times m \quad \ldots (5.3)$$

Also,

Mass of each atom,

$$m = \frac{\text{Atomic mass}}{\text{Avogadro's no.}} \quad \ldots (5.4)$$

Substituting the value of m from Eq. (5.4) in Eq. (5.3),

$$\text{Mass of unit cell} = Z \times \frac{\text{Atomic mass}}{6.023 \times 10^{23}} \quad \ldots (5.5)$$

Substituting the value of mass of unit cell from Eq. (5.5) in Eq. (5.2)

$$\text{Density of the unit cell of the solid} = \frac{Z \times \text{atomic mass}}{6.023 \times 10^{23} \times a^3 \times 10^{-30}} \text{ g/cm}^3$$

Example 10 *An element (atomic mass = 60 a.m.u.) having face-centred cubic unit cell has a density of 6.23 gcm*$^{-3}$*. Calculate the edge length of the unit cell.*

Solution: Use the relation between density and edge length (a):

$$\text{Density} = \frac{Z \times \text{atomic mass}}{6.02 \times 10^{23} \times a^3 \times 10^{-30}} \text{ g/cm}^3$$

(a has the units of picometre pm.)

$$a^3 = \frac{Z \times \text{atomic mass}}{6.023 \times 10^{23} \times 10^{-30} \times \text{density}} \text{ cm}^3$$

For a face-centred cubic, $Z = 4$

Substitute the values in the above equation

$$a^3 = \frac{4 \times 60}{6.023 \times 10^{-7} \times \text{density}} = \frac{4 \times 60}{6.023 \times 10^{-7} \times 6.23}$$

or $$a^3 = 63.96 \times 10^6$$

$$a = 4 \times 10^2 \text{ pm}$$

$= 400$ pm or 400×10^{-10} cm or 4×10^{-8} cm or $4\ A^\circ$

Example 11 *Unit cell of an element (atomic mass = 108 u and density = 10.5 g cm^{-3}) has an edge length of409pm. Deduce the type of crystal lattice. $N_A = 6.02 \times 10^{23}$ mot^{-1}.*

Solution: The following data are provided:

$Z = ?$ $M = 108$ u, $d = 10.5$ g cm^{-3}, $a = 409$ pm, $N_A = 6.02 \times 10^{23}$ mol^{-1}

Applying the relation $d = \frac{Z \times M}{a^3 \times N_A}$

or $Z = \frac{d \times a^3 \times N_A}{M}$, Substituting the values, we get

$$Z = \frac{10.5 g \text{ cm}^{-3} \times (409)^3 \times (10^{-10})^3 \text{ cm}^3 \times 6.02 \times 10^{23} \text{ mol}^{-1}}{108}$$

$= 4$ (1 pm = 1×10^{-10} cm)

As the density is in gcm^{-3}, we must convert pm into cm.

A value of **4** suggests that the element occurs in **FCC** structure.

Example 12 *In an ionic compound, the anion (N^-) forms cubic close type of packing, while the cation M^+ ions occupy one third of tetrahedral voids. Deduce the empirical formula of the compound and the coordination number of (M^+) ions.*

Solution:

$$\text{Number of } N^- \text{ ions per unit cell } = \frac{1}{8} \times 8 = 1$$

$$\text{Number of } M^+ \text{ ions. } = \frac{1}{3} \times 2 = \frac{2}{3}$$

Empirical formula = $M_{2/3} N_1$ or $M_2 N_3$

Coordination number of $M^+ = 4$

Example 13 *Analysis shows that a metal oxide has the empirical formula $M_{0.98}\ O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal.*

Solution: The *formula $M_{0.98}\ O_{1.00}$ suggests that if out of 100 metal ions, two are missing, these two missing ions would have carried a charge of +4 units. This charge is balanced by the presence of 4 M^{3+} ions*

$$\text{Thus, number of } M^{2+} \text{ ions} = 98 - 4 = 94$$

$$\text{Percentage of } M^{3+} \text{ ions} = \frac{4}{98} \times 100 = 4.08$$

$$\text{Percentage of } M^{2+} \text{ ions} = 95.92$$

Example 14 *Iron has a body-centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro number (Atomic mass of Fe = 55.845 u)*

Solution: Apply the following relation $N = \frac{Z \times M}{d \times a^3}$

As it has FCC structure, $Z = 2$

Substituting the values in the above relation, we have

$$N = \frac{2 \times 55.845}{(286.65)^3 \times 10^{-30} \times 7.874} = 6.02 \times 10^{23}$$

Example 15 *Silver crystallizes with a face-centred cubic lattice. The length of the unit cell is found to be 4.077 × 10^{-8} cm. Calculate the atomic radius and density of silver. (Atomic mass of Ag = 108 u, Avogadro number = 6.022 × 10^{23} mot^{-1})*

Solution: The following data is provided:

$a = 4.077 \times 10^{-8}$ cm, $Z = 4$, $M = 108$ g mol^{-1}, $N = 6.022 \times 10^{23}$

Apply the relation $d = \frac{Z \times M}{a^3 \times N}$

Substituting the values, we have

$$d = \frac{4 \times 108}{(4.077 \times 10^{-8})^3 \times 6.022 \times 10^{23}} = 6.22 \text{ g } 10^3$$

To calculate atomic radius, use the relation

$$R = \frac{a}{2\sqrt{2}} \text{ (For FCC)}$$

Substituting the value of a, we have

$$R = \frac{4.077 \times 10^{-8}}{2\sqrt{2}} = 1.44 \times 10^{-8} \text{ cm}$$

PROBLEMS FOR PRACTICE

1. Copper crystallizes with face-centred cubic unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal (At. Mass of copper = 63.55 u and Avogadro number =

$6.02 \times 10^{23}\ mol^{-1}$)

[Ans. Density = 8.95 g cm^{-3}]

2. An element with molar mass 2.7×10^{-2} kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^{3} kg m^{-3}, what is the natures of the cubic unit cell?

[Ans. $Z = 4$, face centred cubic]

3. Niobium crystallizes in body-centred cubic structure. If the density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass of 93 u.

[Ans. $r = 143.1$ pm]

5.8 FUNDAMENTAL LAWS OF CRYSTALLOGRAPHY

The branch of science which deals with the study of geometry, properties and structure of crystals and crystalline substances is known as ***crystallography.*** Three fundamental laws of crystallography are

1. The law of constancy of interfacial angles
2. The law of rationality of indices
3. The law of symmetry

Some Terms used in Crystallography

• Face The plane surfaces of a crystals are called the faces of the crystal.

• Edge The line along which the two adjacent faces of a crystal intersect is called the edge.

• Form A set of similar faces of a crystal is called a form.

• Zone Faces are found to occur in sets, which meet in parallel edges or would meet in parallel edges if the planes of the faces were extended. Such a set of faces is known as zone.

• Crystal Habit The external shape of the crystal is called crystal habit.

• Interfacial Angle The angle between the adjacent faces of a crystal is called interfacial angle. If we represent the number of faces by F, the number of interfacial angles by C and the number of edges by E then the following relation holds:

$$F + C = E + 2$$

5.8.1 Law of Constancy of Interfacial Angles

The crystals of a substance are obtained by cooling the liquid (or the melt) or the solution of that substance. The size of the crystals depends upon the rate of cooling. If cooling is carried out slowly, crystals of large size are obtained because the particles (viz. ions, atoms or molecules) get sufficient time to arrange themselves in proper positions. Similarly, it has been observed that the shape of the crystals of a substance also depends upon the conditions under which the crystallization takes place, i.e. the absence or presence of any other substance, etc. Shapes of the crystals of a particular substance are shown in Fig. 5.27.

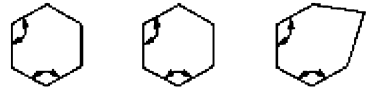


Fig. 5.27 *Shapes of crystal (crystal habits) of a particular substance*

However, in spite of the different sizes and shapes of the crystal of the same substance, it is observed that ***the angles between the corresponding faces, called the interfacial angles of the crystals of a particular substance are always the same. This is called law of constancy of interfacial angles.*** The instrument used for the measurement of interfacial angles is called a ***goniometer.***

5.8.2 Symmetry Elements of a Crystal

The symmetry element is a geometrical entity such as a plane, a line or a point with respect to which one or more symmetry operations may be carried out.

Symmetry operation means movement of the body in such a way that after the movement has been carried out, every point of the body coincides exactly or is in coincidence with equivalent points of the body in the original orientation. This movement is called ***symmetry operation.***

For example, when a molecule *XYX* is rotated in the plane of paper about an axis passing through the centre of *Y* through 180°, the new orientation has exactly the same appearance as the original one. In this case, the symmetry element is axis of rotation and the symmetry operation is rotation (Fig. 5.28).

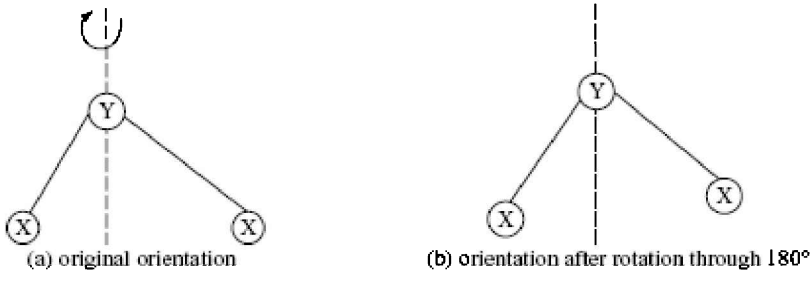


Fig. 5.28 *Symmetry orientation*

The symmetry properties can be expressed with the help of symmetry operations. Different symmetry elements of a crystal are described as under:

1. Centre of Symmetry It is defined as an imaginary point within the crystal such that any line passing through this point intersects the opposite faces of the crystal at equal distances. The centre of symmetry is also called the *centre of inversion* because if the crystal or the molecule is inverted through the centre of symmetry, it gives results equivalent to the original and hence is indistinguishable from the original one. For example, the centre of inversion represented by solid dots of a few molecules are shown in Fig. 5.29.

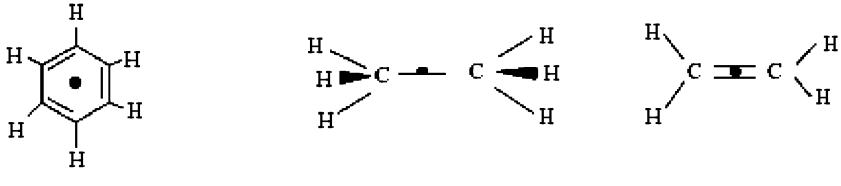


Fig. 5.29 *Centres of inversion of a few molecules*

2. Plane of Symmetry It is defined as an imaginary plane passing through the crystal such that it divides the crystal into two parts in such a way that one part is the mirror image of the

other.

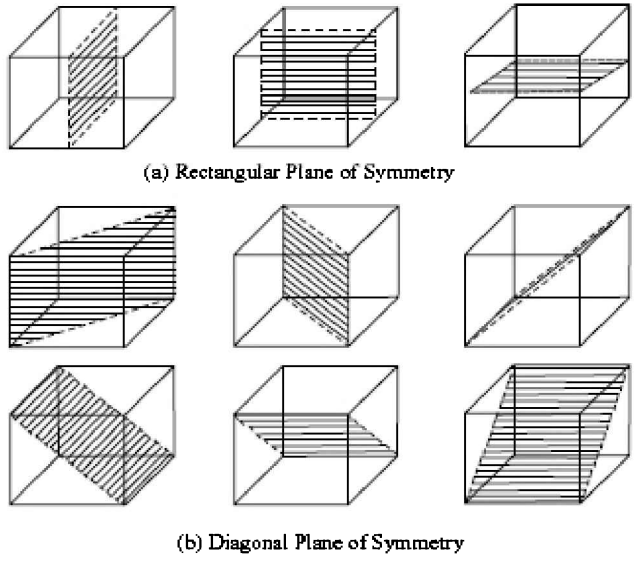


Fig. 5.30 *Planes of symmetry of a cube*

This plane is called mirror plane, i.e. the plane may be regarded as mirror through which the two halves of the object are reflected.

Planes of symmetry of a cube may be represented as shown in (Fig. 5.30).

There are nine planes of symmetry in a cube, six are diagonal planes and three, rectangular planes.

3. Rotation Axis of Symmetry The rotation axis of symmetry, or simple called the axis of symmetry, is defined as the imaginary line passing through the crystal such that when the crystal is rotated about this line, exactly similar appearance occurs more than once in one complete revolution, i.e. in a rotation through 360°. If a similar appearance occurs twice in one complete revolution (i.e. after every 180°), the axis is called **two-fold axis** of symmetry or a diad axis. Similarly, the other possibilities found for similar appearance in one complete revolution are three, four or six times (i.e. after rotation through 120°, 90° or 60°). The corresponding axes are called threefold (triad), fourfold (tetrad) and sixfold (hexad) axes of symmetry.

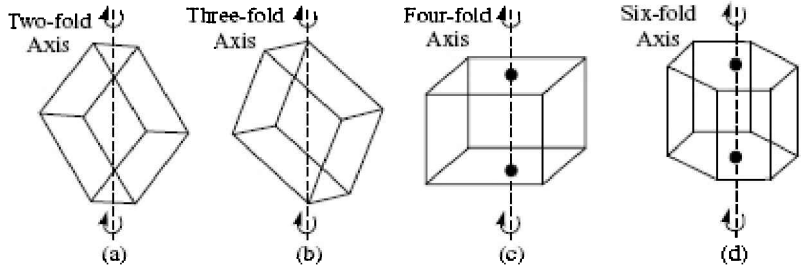


Fig. 5.31 *Different axes of symmetry*

In general, if the crystal presents the same appearance *n* times after rotation through 360°, it is called *n*-fold axis of symmetry (Fig. 5.31)

It may be noted that only 2-fold, 3-fold, 4-fold and 6-fold axes of symmetry are possible. 5-fold, 7-fold, 8-fold or higher fold axes of symmetry are not possible because it is not possible to get compact structure with these shapes as some space is always left vacant. On the other hand, it is possible to get compact structure of crystals with 2-fold, 3-fold, 4-fold and 6-fold axes of symmetry. The rotation about these axes gives identical appearance of various configurations.

4. Rotation-Reflection Axis of Symmetry When the rotation of a molecule or a crystal about an *n*-fold axis of proper rotation is followed by reflection through a plane perpendicular to the axis, the axis is called an *n*-fold rotation-reflection axis (Fig. 5.32). The new configuration obtained is not congruent, but enantiomorphous.

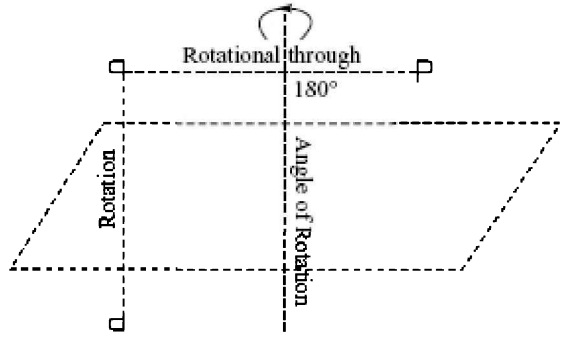


Fig. 5.32 *Rotation followed by reflection of the letter P*

Rotation-Inversion Axis of Symmetry When the rotation of a molecule or a crystal is followed by inversion through the centre of symmetry, the axis is called an n-fold rotation-inversion axis (Fig. 5.33). The new configuration obtained is not congruent but is enautiomorphous, as in the above case.

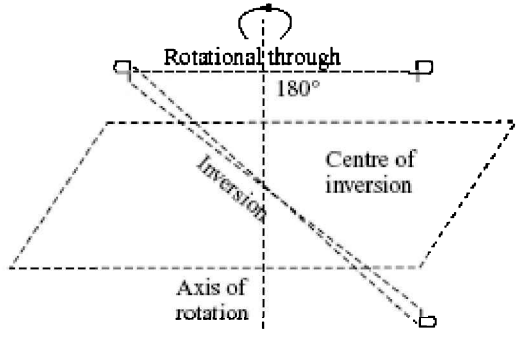


Fig. 5.33 *Rotation followed by inversion through the centre of inversion of the letter P*

5.8.3 Proper Rotation and Improper Rotation

1. Rotations, which give rise to equivalent and congruent configurations, are called proper rotations. For example, rotation around axis of symmetry is ***proper rotation.***

2. Rotations which give rise to enontiomorphous but incongruent configurations are called ***improper rotations.*** For example, rotation around the axis of symmetry followed by reflection or inversion gives rise to improper rotation.

5.8.4 Planes and Axes of Symmetry in a Simple Cube

The crystals of a particular substance always possess the same elements of symmetry. This is called ***law of symmetry.*** A cubic crystal always possesses the following 23 different elements of symmetry

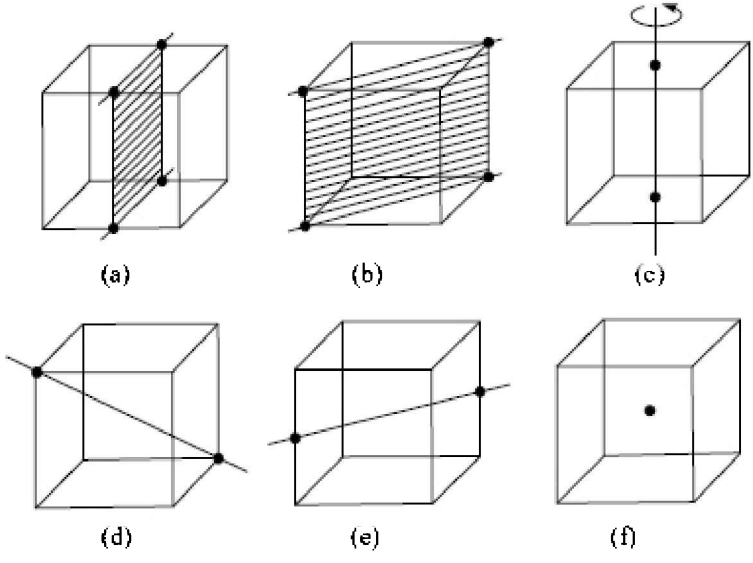


Fig. 5.34 *Elements of symmetry of a cube*

(a) Rectangular planes of symmetry = 3
(b) Diagonal plane of symmetry = 6
} = 9

(c) Four-fold axes of symmetry = 3
(d) Three-fold axes of symmetry = 4
(e) Two-fold axes of symmetry = 6
} = 13

6. Centre of symmetry (located at the centre of gravity of the cube) = 1

An example of each type of symmetry possessed by a cube is shown in Fig. 5.34.

5.8.5 Crystallographic Axes and Axial Ratio

1. Crystallographic Axes In order to describe the relative directions and orientations of the faces and also the planes present within the crystal, three suitable axes are chosen which meet at a point, say *O* (Fig. 5.35). These axes can be selected in a number of ways depending upon the symmetries of the crystals. The best choice is usually the lines, coinciding with or parallel to the edges between the principal faces. For example, in a cubic crystal, the best choice of the axes is

the three lines mutually at right angles to each other. The three lines thus selected meeting at a point are called crystal-lographic axes.

The angles between the axes opposite to the intercepts *a*, *b* and *c* are represented by α, β and γ respectively. These angles are the same as the inter-axial ratio. Facial angles of the axes chosen are the lines coinciding with or parallel to the edges of the principal faces of the crystal.

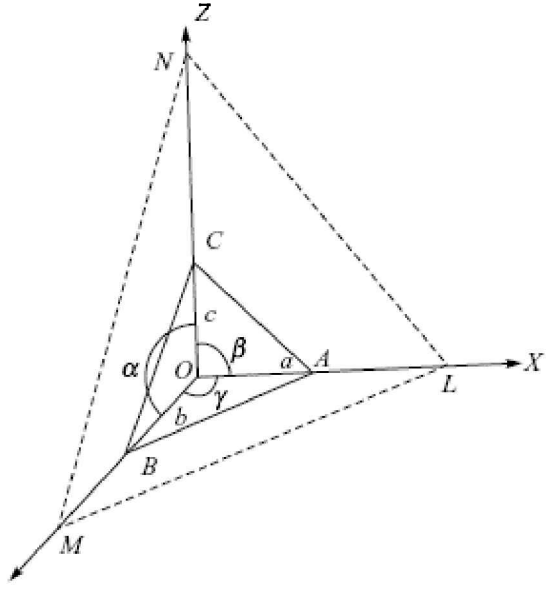


Fig. 5.35 *Crystallographic axes and axial ratio*

2. Axial Ratio To explain axial ratio, consider a plane called *unit plane* which meets the crystallographic axes. For example, suppose the three axes are represented by *OX*, *OY* and *OZ* and the unit plane *ABC* cuts these axes at *A*, *B* and *C*respectively making the intercepts $OA = a$, $OB = b$, $OC = c$. The ratio $a : b : c$ is called the axial ratio. Thus, the axial ratio may by defined as the ratio of the intercepts made by the unit plane on the crystallographic axes.

5.8.6 Law of Rational Indices

If the intercepts of any face of the crystal on the three axes are measured, the following generalization is observed which is called law of rational indices.

The intercepts made by any face of the crystal on the crystallographic axis are either:

1. same as those of the unit plane, or
2. simple whole number multiplies of those of the unit plane, or
3. One or two intercepts may be infinity, if the face is parallel to one or two axes, i.e. the face does not cut one or two axes.

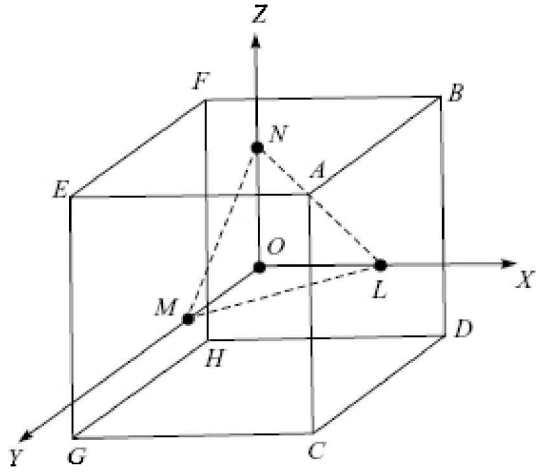


Fig. 5.36 *Intercepts made by the faces of a cube on the axes*

For example in Fig. 5.35, the intercepts made by the face *LMN* are 2*a*, 2*b* and 3*c* which are simple whole number multiples of those of the unit plane. Again consider the case of a cube. Suppose the origin *O* of the crystallographic axes lies at the centre of symmetry and the axes *OX*, *OY*, *OZ* are parallel to the edges as shown in Fig. 5.36. Suppose the axis *OX* cuts the face *ABCD* at the point *L*. Similarly, suppose the axes *OY* and *OZ* cut the faces at *M* and *N*. If *LMN* is taken as the unit plane, the intercepts made by the unit plane on the three axes are *OL*, *OM* and *ON*. The face *ABCD* cuts the *X*-axis at *L*, i.e. makes the same intercepts as that made by the unit plane but it does not cut the *Y* axis and *Z* axis at all, because these two axes are parallel to this face. In other words, the intercepts made by the face *ABCD* on the *Y*-axis and *Z*-axis are ***infinity.***

In general, if a face *PQR* makes intercepts *p*, *q* and *r* on the three axes and the intercepts made by the unit plane are *a*, *b*, *c* then we have $p = na$, $q = n'b$ and $r = n''c$ where *n*, *n'* and *n''* are simple whole numbers or some out of these may be ***infinity.***

Weiss Indices If a face makes intercepts na, *n'b* and *n"c* on the crystallographic axes, the face may be represented by (*n*, *n'*, *n"*). The numbers *n*, *n'*, *n"* thus used to represent a face are called Weiss indices.

5.9 MILLER INDICES

Miller indices are a set of integers (*h*, *k*, *l*) which are used to describe a given plane in a crystal. Suppose *n*, *n'* and *n"* are the coefficients of the intercepts of a given plane on the crystallographic axes. Reciprocal of the numbers *n*, *n'* and *n"* are taken and multiplied by the smallest number (i.e. LCM of denominators) so as to express all the reciprocals as integers. The integers thus obtained are called Miller indices. Thus, ***Miller indices may be defined as the reciprocals of the coefficients of the intercepts expressed as integers. Obviously, the Miller indices of a face are inversely proportional to the intercepts of that face on the crystallographic axes. Alternatively,*** the intercepts made by any crystal plane such as *DEF*, in Fig. 5.35, are usually expressed in terms of the intercepts of the unit plane (*a*, *b*, *c*) as follows:

$$OD = \frac{a}{h}, OE = \frac{b}{k} \text{ and } OF = \frac{c}{l}$$

Then the Miller indices of the plane are represented as (*hkl*).

The unit plane is represented as shown in Fig. 5.37(a) and any other plane of the crystal may be represented as shown in Fig. 5.37(b).

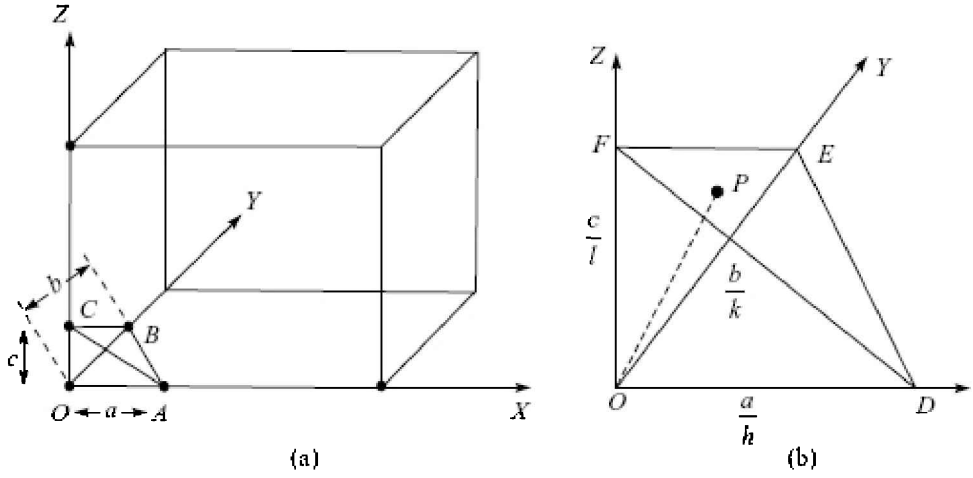


Fig. 5.37 *(a) Representing the unit plane ABC (b) Representing any other plane DEF*

The interplanar spacing d_{hkd} between the planes *hkl* in a cubic lattice is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{5.26}$$

where *a* is a side of the cube.

Examples of Miller Indices

1. In Fig. 5.36, the intercepts made by the face *LMN* are 2*a*, 2*b*, 2*c*. The reciprocals of the coefficient of *a*, *b*, *c* are $\frac{1}{2}, \frac{1}{2}, \frac{1}{3}$. LCM of 2, 2, 3 = 6. Multiplying the reciprocals by 6, we have 3, 3, 2. These are the Miller indices of the face *LMN* in Fig. 5.36. This face is represented as (332).
2. The intercepts made by the unit *ABC* [Fig. 5.37] plane are *a*, *b*, *c*. The coefficients of these intercepts are 1, 1, 1. Hence the unit plane is always represented as (111).
3. If some face does not cut some axis at all, the intercept on this axis is taken as infinity. For example, suppose a face makes intercepts 2*a* and 3*b* on the *X*-axis and *Y*-axis respectively and does not cut the *Z*-axis at all, the intercepts will be 2*a*, 3*b* and ∞ (or ∞ *c*). The reciprocals of the coefficients are $\frac{1}{2}, \frac{1}{3}, 0$. LCM of 2, 3 = 6. Multiplying by 6, the Miller indices will be 3, 2, 0, i.e. the face will be represented as (320). Similarly, if a face makes intercepts *a* on the *X*-axis and does not cut the *Y*-axis and *Z*-axis at all (see Fig. 5.36, face *ABCD*), its Miller indices will be 1, 0, 0 i.e. it will be represented as (100).
4. If some intercept made by a face is negative, i.e. the face is cut by the axis when extended in the opposite direction, it is represented by putting a bar over it. For example, in Fig. 5.36, the intercept made by the face *EFGH* on the *X*-axis is $-a$ and this face does not cut the *X*-axis

and Z-axis at all. Hence, this face is represented as (100).

5. *Miller Indices of the Faces of a Cube.* In Fig. 5.36, in which the origin of the crystallographic axes is the centre of symmetry of the cube, following the method as explained in (3) and (4) above, the various faces of the cube in terms of Miller indices may be represented as (100), (010), (001), ($\bar{1}$00), (0$\bar{1}$0) and (00$\bar{1}$).

5.9.1 Interplanar Distance in a Crystal System

It can be mathematically shown that interplanar distance d_{hkl} in a crystal is given by

$$\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \quad \ldots (5.7)$$

where h, k, l are the Miller indices and a, b, c are the dimensions of the cell.
For a **simple cubic** system $a = b = c$, the equation (5.7) reduces to

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (5.8)$$

For a ***tetragonal*** crystal system, $a = b \neq c$, we have

$$\frac{1}{(d_{hkl})^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (5.9)$$

For an ***orthorhombic*** crystal system $a \neq b \neq c$, thus we have

$$\frac{1}{(d_{hkl})^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (5.10)$$

Example 16 *Write Miller indices for any four faces of a cubic unit cell.*

Solution: Refer to Fig. 5.36

If O is taken as the origin of crystallographic axes, then Miller indices of

- Plane $ABCD$ are 100
- Plane $ACGE$ are 010
- Plane $ABFE$ are 001
- Plane $EFGH$ are $\bar{1}$00

Example 17 *Determine the interplanar spacing between the (221) planes of a cubic lattice of 4.5 A° (450 pm) length.*

Solution: In a cubic lattice, the interplanar spacing d_{221} is given by

$$d_{221} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \text{ Å}$$

$$= \frac{4.5}{(4 + 4 + 1)^{1/2}} \text{ Å} = 1.5 \text{ A°} = 150 \text{ pm}$$

Example 18 *An orthorhombic unit cell has dimensions a = 50 pm, b = 100 pm and c = 150 pm. Determine the interplanar distance between (123) planes.*

Solution:

$$\frac{1}{(d_{hkl})^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Substituting the values, we have

$$\frac{1}{(d_{123})^2} = \left(\frac{1}{50}\text{ pm}\right)^2 + \left(\frac{2}{100}\text{ pm}\right)^2 + \left(\frac{3}{150}\text{ pm}\right)^2 = 3 \times \left(\frac{1}{50}\text{ pm}\right)^2$$

or $$\left(\frac{1}{d_{123}}\right) = \frac{\sqrt{3}}{50\text{ pm}} \quad \text{or} \quad d_{123} = \frac{50\text{ pm}}{\sqrt{3}} = 29\text{ pm}$$

Example 19 *A crystal plane has intercepts on the three axes of the crystal in the ratio of* $\frac{3}{2} : 2 : 1$. *What are the Miller indices of the plane?*

Solution: The reciprocal of the ratio of intercepts are $\frac{2}{3} : \frac{1}{2} : 1$

Multiplying by the LCM of 3 and 2, i.e., 6,

$$4 : 3 : 6$$

The Miller indices of the plane are 436.

Example 20 *The Weiss indices of a planes are* $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. *What are the Miller indices?*

Solution: Miller indices are obtained by taking the reciprocal of Weiss indices and then by multiplying, if required, with a suitable number to obtain integral numbers.

Miller indices will be

$$\frac{1}{1/2}\frac{1}{1/2}\frac{1}{1/2} \quad \text{or} \quad 222$$

Example 21 *Find the Miller indices of the place that intersect the crystallographic axes at the distance a, 2b,* ∞ *c.*

Solution: Miller indices of the plane are

$$\frac{1}{1}, \frac{1}{2}, \frac{1}{\infty} \quad \text{or} \quad 210$$

Example 22 *The density of a metal is 0.53 g* cm^{-3} *and the spacing between (100) planes of the metal is 350 pm. Determine the crystal structure of the metal given that its molecular mass is 6.941 g* mol^{-1}.

Solution: Convert the data to SI units:

$$\text{Density} = 0.53\text{ g cm}^{-3} = 530\text{ kg m}^{-3}$$

For a simple cubic system,

$$d_{100} = \frac{a}{\sqrt{1^2+0^2+0^2}} = 350 \text{ pm} = 350 \times 10^{-12} \text{ m}$$

We have the relation

$$\text{Density} = \frac{Z \times \text{Atomic mass}}{\text{Avogardo No.} \times \text{Volume of the unit cell}}$$

or

$$Z = \frac{\text{Density} \times \text{Avogadro No} \times \text{Volume of unit cell}}{\text{Atomic mass}}$$

$$= \frac{(530 \text{ kg m}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})(350 \times 10^{-12} \text{ m})^3}{6.941 \times 10^{-3} \text{ kg mol}^{-\text{I}}} = 2$$

Note that interplanar distance in this case will also be the dimension of the unit cell.
The number of atoms per unit cell in FCC is 2.
Hence, the element has FCC crystal structure.

5.10 ISOMORPHISM AND POLYMORPHISM

Certain crystalline substances which have similar chemical composition (for example, sodium phosphate and sodium arsenate, i.e. Na_3PO_4 and Na_3AsO_4) are found to possess the same crystal shape. This phenomenon is called as ***isomorphism*** and the substances are said to be ***isomorphous.***

Again, there are certain substances which exist in more than one crystalline form which are formed under different conditions of temperature and pressure. This phenomenon is known as ***polymorphism.*** For example, carbon exists in two crystalline forms called graphite and diamond; Calcium carbonate exists in two crystalline forms called calcite and aragonite. The polymorphism exhibited by the elements is commonly called ***allotropy.***

5.10.1 Different Crystallographic Systems

Various crystallographic systems along with the axial characteristics and symmetry elements are given in the tabular form as shown below in Table 5.4.

Table 5.4 *Related information regarding crystallographic systems*

	System	Axial Characteristics	Maximum Symmetry	Examples
1.	Cubic	$\alpha = \beta = \gamma = 90°$ $a = b = c$	Plane = 9 Axis = 13 Plane = 5	NaCl, KCl, Alums, Diamonds

2.	Tetragonal	$\alpha = \beta = \gamma = 90°$ $a = b \neq c$	Axis = 5	Sn, Sn O_2, TiO_2
3.	Orthorhombic	$\alpha = \beta = \gamma = 90°$ $a \neq b \neq c$	Planes = 3 Axes = 3	KNO_3, K_2SO_4 $BaSO_4$, Pb CO_3 Rhombic sulphur
4.	Monoclinic	$\alpha = \gamma = 90° \neq \beta$ $a \neq b \neq c$	Plane = 1 Axis = 1	Na_2SO_4, $10H_2O$ $CaSO_4$, $2H_2O$ Monoclinic sulphur
5.	Triclinic	$\alpha \neq \beta \neq \gamma \neq 90°$ $a \neq b \neq c$	Planes = Nil Axes = Nil	$CuSO_4$. $5H_2O$ $K_2Cr_2O_7$,
6.	Rhombohedral or Trigonal	$\alpha = \beta = \gamma \neq 90°$ $a = b = c$	Planes = 7 Axes = 7	$NaNO_3$, ICl, As, Sb,Bi
7.	Hexagonal	$\alpha = \beta = 90$ $\gamma = 120°$ $a = b \neq c$	Planes = 7 Axes = 7	HgS, Ice, Graphite. Mg, Zn, Cd

Example 23 *Explain: We do not come across 5-fold, 7-fold, 8-fold or higher fold axis of rotation in crystals.*

Solution: We have only 2-fold, 3-fold, 4-fold and 6-fold axis of rotation and we do not have 5-fold, 7-fold, 8-fold or higher fold axis of rotation. This is due to the fact that the most essential requirement of a lattice is that it should be built up by the repetition of unit cells, the faces of each unit cell touching the faces of the surrounding unit cells without leaving any gap in between. Such a close packing is possible if an object has 2-fold, 3-fold, 4-fold or 6-fold axis of symmetry but is not possible in case an object has 5-fold, 7-fold, 8-fold or higher fold axis of symmetry. This is illustrated alongside for objects having 6-fold axis of symmetry and 5-fold axis of symmetry (Fig. 5.38). We find that a gap is created in a solid with 5-fold axis of symmetry.

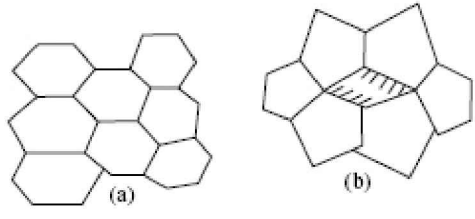


Fig 5.38 *(a) The close packing of hexagonal objects (b) A gap created in the packing of pentagonal objects*

Example 24 *Identify the crystal system to which some solids having the following dimensions for their unit cell belong. Give examples of the solids:*

(a) $a \neq b \neq c$ $\quad \alpha \neq \beta \neq \gamma \neq 90°$

(b) $a \neq b \neq c$ $\quad \alpha = \beta = \gamma = 90°$

Solution

(a) Solids having these characteristics are ***triclinic.*** Examples of this crystal system are $CuSO_4.5H_2O$ and $K_2Cr_2O_7$.

(b) Solids having these characteristics are ***orthorhombic*** or ***rhombic.*** Examples of this category of solids are KNO_3 and K_2SO_4.

5.10.2 Bravais Lattices

The detailed study of the internal structure by Bravais has shown that the points (particles) may be present not only at the corners of unit cells but also at the centre of the faces or within the body of the unit cells. This gives rise to different types of lattices corresponding to the seven crystallographic systems. These 14 types of lattices are called ***Bravais lattices.*** The description of these lattices is given in Table 5.5 and the shapes are shown in the figure ahead. The terms simple, face-centred (end-centred and body-centred) are explained as under:

1. **Simple:** When the points are present only at the corners of the unit cell.
2. **Face-centred:** When in addition to the points at the corners, there are points at the centre of each face of the unit cell.
3. **End-centred:** When there are points present at the centre of the end faces of the unit cell, in addition to points at the corners.
4. **Body centred:** When in addition to the points at the corners, there is one point present within the body of each unit cell.

Table 5.5 *Bravais lattices corresponding to different crystal systems*

	System	Crystal Systems Number of Bravais	Description of the Lattices
1.	Cubic	3	Simple, Face centred, Body-centred
2.	Tetragonal	2	Simple, Body-centred
3.	Orthorhombic or Rhombic	4	Simple, Face-centred, End-centred, Body-centred
4.	Monoclinic	2	Simple, End-centred
5.	Triclinic	1	Simple
6.	Rhombohedral or Trigonal	1	Simple
7.	Hexagonal	1	Simple

5.10.3 Number of Atoms Per Unit Cell

The number of points per unit cell *(N)* is given by the expression

$$N = \frac{N_c}{8} + \frac{N_f}{2} + N_i$$

where

N_c = number of points present on the corners of the unit cell

N_f = number of points present on the faces of the unit cell

N_i = number of point present in the interior of the unit cell

It may be understood that each point present on the corner is shared by 8 unit cells, each point present on the face is shared by two unit cells and the point present in the interior is shared by no other unit cell.

For any simple lattice $N = 8$, $N_f = 0$, $N_i = 0$, so that

$$N = \frac{8}{8} + 0 + 0 = 1$$

for a face-centred cubic lattice, $N_c = 8$, $N_f = 6$, $N_i = 0$ so that

$$N = \frac{8}{8} + \frac{6}{2} + 0 = 4$$

For a body-centred orthorhombic lattice, $Nc = 8$, $N_f = 0$ $N_i = 1$ so that

$$N = \frac{8}{8} + 0 + 1 = 2$$

For an end-centred monoclinic lattice, $N_c = 8$, $N_f = 2$, $N_i = 0$ so that

$$N = \frac{8}{8} + \frac{2}{2} + 0 = 2$$

5.11 POINT GROUPS AND SPACE GROUPS

Theoretically, there are 32 different ways of arranging the elements of symmetry about a point. These different arrangements are called ***point groups.*** However, in a complete space lattice, because of the regular repetition of the pattern in the three-dimensional space, two additional symmetry elements called ***glide planes*** and ***screw axes*** become possible. Because of these additional elements of symmetry, the number of arrangements possible for the elements of symmetry about a point of a space lattice becomes equal to 230. These 230 possible arrangements of the elements of symmetry about a lattice point are called ***space groups.*** (See Fig. 5.39)

Example 25 *A certain solid X (atomic mass 27) crystallizes in an FCC structure. If the density of X is 2.7 g cm^{-3}, what is the length of the edge?*

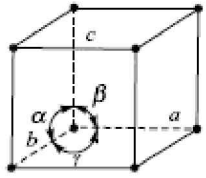
Solution: Mass of unit cell = No. of atoms in a unit cell × Atomic mass = $\frac{4 \times 27}{6.023 \times 10^{23}}$

$$\text{Volume of unit cell} = \frac{\text{Mass of unit cell}}{\text{Density of unit cell}} = \frac{4 \times 27}{6.023 \times 10^{23} \times 2.7}$$

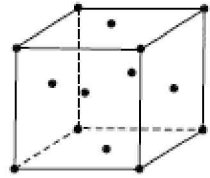
$$= 66.412 \times 10^{-24} \text{ cm}^3$$

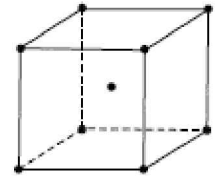
$$\text{Length of edge} = (\text{Volume of unit cell})^{1/3}$$

$$= (66.412 \times 10^{-24})^{1/3} = 4.05 \times 10^{-8} \text{ cm} = \mathbf{4.05\ Å}$$

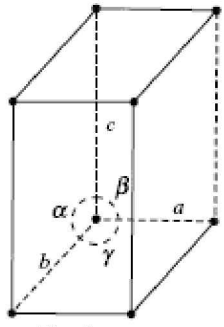


Simple

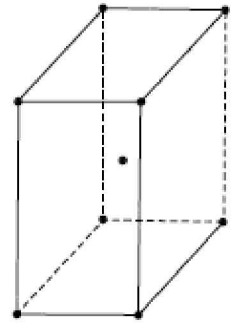

Face-Centred


Body-Centred

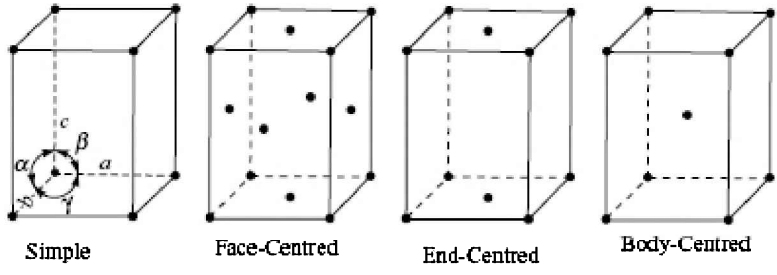
1. Cubic $\begin{Bmatrix} \alpha = \beta = \gamma = 90° \\ a = b = c \end{Bmatrix}$



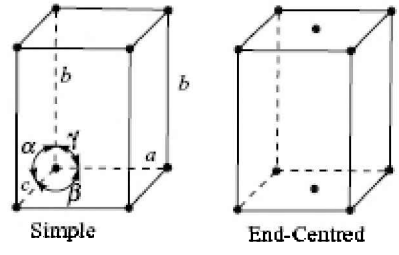
Simple


Body-Centred

2. Tetragonal $\begin{Bmatrix} \alpha = \beta = \gamma = 90° \\ a = b \neq c \end{Bmatrix}$



3. Orthorhombic $\begin{Bmatrix} \alpha = \beta = \gamma = 90° \\ a \neq b \neq c \end{Bmatrix}$



3. Orthorhombic $\begin{Bmatrix} \alpha = \gamma = 90° \neq \beta \\ a \neq b \neq c \end{Bmatrix}$

Fig. 5.39 *Point groups and space groups*

5.12 INVESTIGATION OF INTERNAL STRUCTURE OF A SOLID BYX-RAY DIFFRACTION

5.12.1 Bragg'sMethod

William Henry Bragg (1862-1942) and Sir William Lawrence Bragg (1890-1972), English physicists, father and son, both worked on X-ray crystallography. The younger Bragg formulated the fundamental equation for X-ray diffraction. The duo were jointly awarded the Nobel Prize in Physics in 1915.

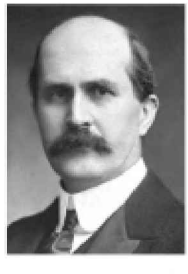


Fig. 5.40 *William Henry Bragg*



Fig. 5.41 *Sir William Lawrence Bragg*

When a beam of X-ray is passed through a crystal, and the impression is taken on a photographic plate, a pattern called diffraction pattern is obtained. By using this pattern, Bragg investigated the structure of crystals of NaCl, KCl, etc. Bragg devised a spectrometer for the measurement of intensity of X-ray beams. The diffraction pattern thus obtained can be used to study the crystal structure. The Bragg's method for study of the internal structure of crystals is based upon Bragg's equation, which may be derived as follows:

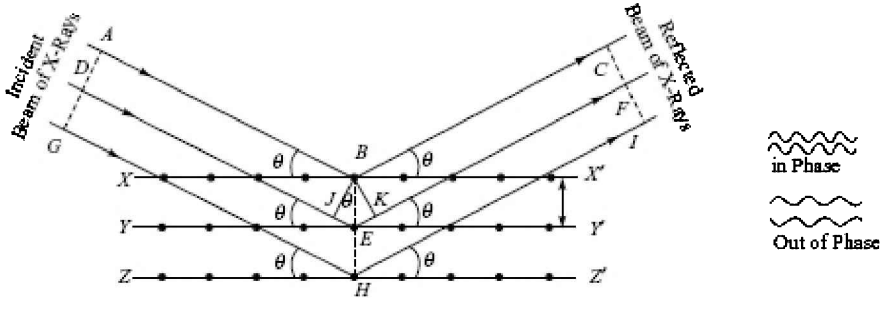


Fig. 5.42 *Reflection of X-rays by equidistant parallel planes*

A crystal may be considered to be made up of a number of parallel equidistant atomic planes, as represented by the lines *XX'*, *YY'*, *ZZ'*, etc. in Fig. 5.42. Suppose a beam of X-rays is incident on the crystal at angle θ. A part of the beam, e.g. the ray *AB*, is reflected at the point *B* along the path *BC*. On the other hand, some rays like *DE*, *GH*, etc., penetrate into the crystal and are reflected by the atoms present in the atomic planes *YY'*, *ZZ'*, etc., as shown.

Obviously, as compared to the ray AB, a ray like *DE* has to travel a longer distance equal to *JEK* in order to emerge out of the crystal where *BJ* and *BK* are perpendiculars drawn on the lines *DE* and *EF* respectively. The reflected beams like *BC*, *EF*, etc., then undergo interference with each other. If these reflected rays are in phase (i.e., in the reflected rays crests fall over the crests and troughs over troughs), they reinforce each other and the intensity of the reflected rays is maximum. On the other hand, if the reflected rays are out of phase (i.e. crests fall over troughs), the intensity of the reflected beam is very low. If a photographic plate is placed to receive the reflected rays, a diffraction pattern is obtained.

We can say, in order that the reflected rays *BC* and *EF* may be in phase, the extra distance *JEK* traversed by the ray *DE* should be an integral multiple of the wavelength λ of the X-rays, i.e.,

$$\text{Distance } JEK = n\lambda \qquad (5.11)$$

where n is an integer, i.e. 1, 2, 3, 4, etc. If d is the distance between the successive atomic planes, it is obvious from Fig. 5.42 that

$$JE = EK = d \sin\theta \left(\because \sin\theta = \frac{JE}{BE} = \frac{JE}{d} \right)$$

So that $$JEK = 2d \sin\theta \tag{5.12}$$

Putting the value in Eq. (5.11), we get

$$2d \sin\theta = n\lambda \tag{5.13}$$

This equation is called ***Bragg's equation.*** When monochromatic X-rays are used, l is constant. Also for a particular crystal when a particular face is facing the X-rays, d is constant. Thus, by gradually increasing the value of θ, a number of positions are observed corresponding to n = 1, 2, 3, 4,…, etc., where the reflected beam will have maximum intensity. Other values of θ lying in between the reflected beam will have intensity less than the maximum. Thus, a diffraction pattern will be obtained in which the various maxima correspond to n = 1, 2, 3, etc. These are respectively called diffraction maxima of the first order, second order, third order, etc.

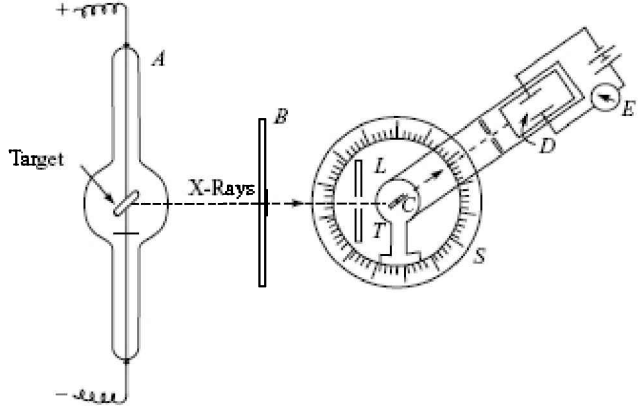


Fig. 5.43 *X-ray spectrometer*

By measuring the angle θ at which the first maxima occurs (i.e. first maximum intensity is observed) so that n = 1, and knowing the wavelength λ of X-rays used, the value of d can be calculated using Eq. (5.13).

1. Apparatus The apparatus used by Bragg for studying the internal structure of crystals is called Bragg's *X*-ray spectrometer and is shown in Fig. 5.43. *X*-rays are generated in the *X*-ray tube *A*. These are made monochromatic, i.e. of single wavelength by passing through the absorbing screen *B*. Then they are passed through the slit *L*, to obtain the rays in the fine beam. This beam is then made to fall on some particular face of the crystal *C* which is mounted on a turntable *T*. The turntable can be moved over a circular scale *S*. The reflected beam is passed into the ionisation chamber *D* which is connected to an electrometer *E*. The ionisation chamber can also be moved on the circular scale *S* independent of the turntable *T*. The chamber contains some easily ionisable gas such as sulphur dioxide. Greater the intensity of the reflected beam, greater is the ionization produced in the gas and larger is the reading on the electrometer. When the crystal face is rotated by rotating the turntable, the direction of the reflected beam changes. To receive the reflected beam into the ionisation chamber every time, the ionisation chamber is rotated through double the angle θ through which crystal face is rotated. From these plots the angles corresponding to the first, second, third maxima, etc., are noted and the value of d calculated using Bragg's equation.

2. Calculation of d For the face (100) of NaCl crystal; when $n = 1$, $\theta = 5.9°$ so that $\sin\theta = 0.103$ Substituting these values in the Bragg equation,

$2d \sin\theta = n\lambda$

we get
$$d = \frac{n\lambda}{2\sin\theta} = \frac{\lambda}{2 \times 0.103} = 4.85\,\lambda \tag{5.14}$$

Knowing the wavelength of the X-rays used, distance d, between the planes parallel to the face on which the X-rays are incident, can be calculated.

5.12.2 Powder Method

When a single undistorted crystal of a solid is not available, we can use the powder method for crystal structure determination. In this technique, the powdered crystalline substance is taken in a capillary tube. It is placed inside a camera containing a film strip (Fig. 5.44).

The sample is rotated with the help of a small motor. X-rays pass through the gap between the ends of the film strip. The powder contains small crystals oriented in all directions. Some of these will reflect X-rays from each lattice plane simultaneously. The reflected X-rays will make an angle 2θ with the original direction. Lines of constant θ are obtained on the film. From the design of the camera, θ can be calculated for different crystal planes.

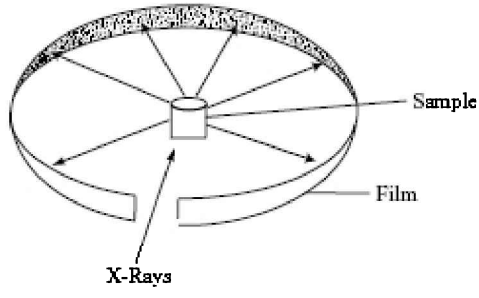


Fig. 5.44 *The powder method*

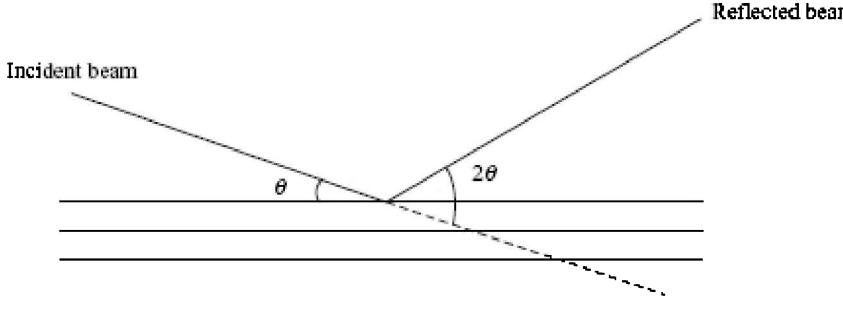


Fig. 5.45 *Reflection of X-rays from crystal planes (powder method)*

To calculate d, the interplanar distance, the Bragg's equation as discussed in the previous section, may be used.

$$n\lambda = 2d \sin\theta \tag{5.15}$$

5.12.3 Laue Photographic Method

In 1912, Max von Laue suggested that because the wavelength of X-rays is comparable in magnitude to the distances between lattice points in a crystal, the lattice should be able to diffract X-rays. An X-ray diffraction pattern is the result of interference in the waves associated with the X-rays

The Laue method of examining the diffraction of X-rays by a crystal differs from other methods in that a homogeneous beam of X-rays is used. The beam falls upon a small crystal and the diffracted beams are recorded on a photographic plate placed at a distance of a few centimetres from the crystal. The rays are reduced to a narrow beam by slit system B, the crystal *C* is set on a holder which permits the adjustment of its orientation and the photographic plate is placed at *S* (Fig. 5.47). A beam with a continuous range of wavelengths is conveniently obtained by using a bulb with a tungsten anticathode and a potential of about 65,000 volts.



Fig. 5.46 *Max von Laue (1879-1960) was a German physicist. He received the Nobel Prize in Physics in 1914 for his discovery of X-ray diffraction.*

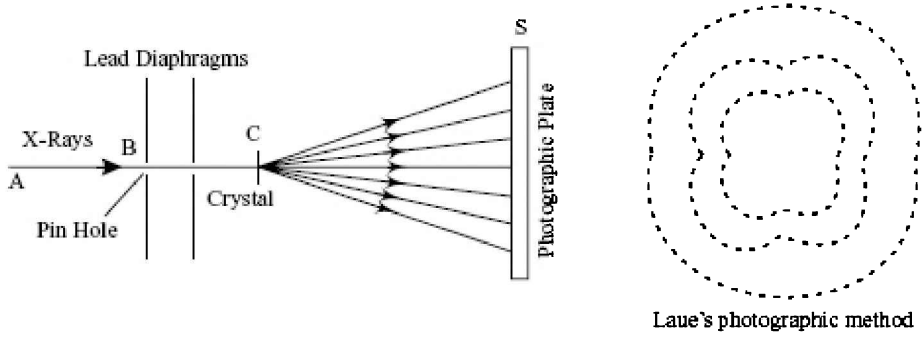


Fig. 5.47 *Laue's photographic method*

A special feature of the Laue photograph is the arrangement of the spots on the ellipses which have one end of their major axis at the central spot. The same feature is shown more or less distinctly by all Laue photographs, the spot occurring where the ellipses intersect. All the spots which lie on any one ellipse are due to reflections by planes parallel to a common zone axis (Fig. 5.48). Incident rays fall upon a crystal at *C*, which has a zone axis parallel to *ZC'*. We

consider rays which are reflected by a plane of the corresponding zone. Suppose a reflecting plane is to be rotated about ZC'; the reflected beam will trace out a curve EE' on the plate. If the incident rays make an angle θ with the zone axis, the reflected rays will always make the same angle with it, so that they lie on a cone of semivertical angle θ around the zone axis. Thus, ellipses in the Laue photograph are the intersections of such cones with the photographic plate. Each spot is at an intersection of ellipses, since a plane parallel to two zone axes is a crystal plane and can affect the X-ray beam.

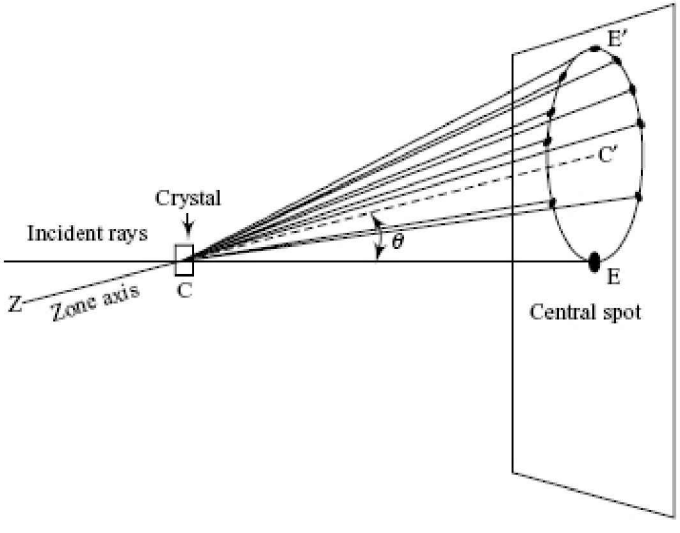


Fig. 5.48 *Reflection of X-rays*

5.12.4 Structure of Sodium Chloride using Bragg's Equation

There are three types of cubic lattices possible, namely, simple, face-centred and body-centred. Possible planes passing through the atoms are (100), (110) and (111), as shown in Fig. 5.49.

If a is the distance between the 100 planes of the simple cubic lattice, the distances between the planes of the three types of cubic lattices can be calculated theoretically and are given below each figure.

Thus, the ratios $d_{100} : d_{110} : d_{111}$ for simple cubic, face-centred cubic and body-centred cubic lattice will be

$$\textbf{\textit{Simple cube:}}\ d_{100} : d_{110} : d_{111}, a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : 0.707 : 0.577$$

$$\textbf{\textit{Face-centred cubic:}}\ d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}}$$

$$= 1 : 0.707 : 1.154$$

$$\textbf{\textit{Body-centred cubic:}}\ d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}} = 1 : 1.414 : 0.577$$

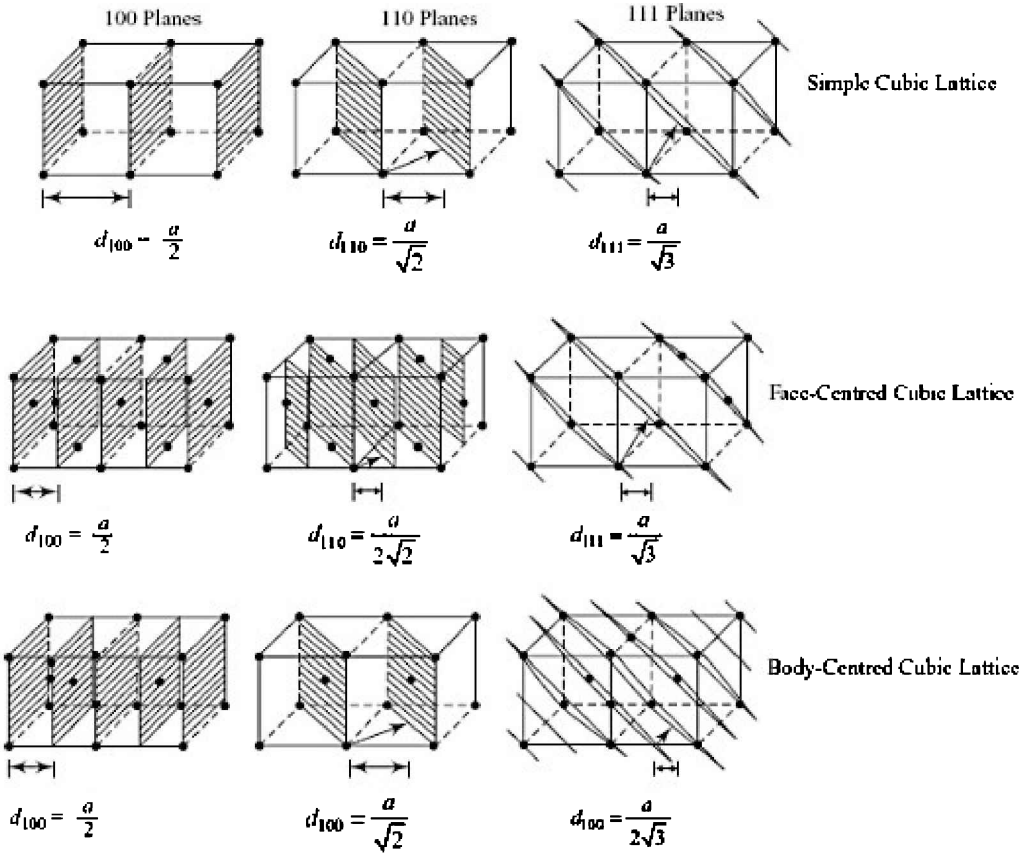


Fig. 5.49 *Distance between the planes of different cubic lattices*

To find out the type of the cubic lattice in the given crystal, the angles at which the first, second, or third-order reflections that take place from different planes are studied. The values of d_{100}, d_{110} and d_{111} are calculated using Bragg's equation, viz. $d = \frac{n\lambda}{2\sin\theta}$ where n is the order of reflection. The ratio $d_{100} : d_{110} : d_{111}$ is then calculated and compared with the ratios given above for different types of lattices.

Carrying out the study as above, it is found that NaCl (as well as KCl) has face-centred cubic lattice as shown in Fig. 5.50. The basis of this structure is Na^+ at (000) and Cl^- at $\left(\frac{1}{2}00\right)$.

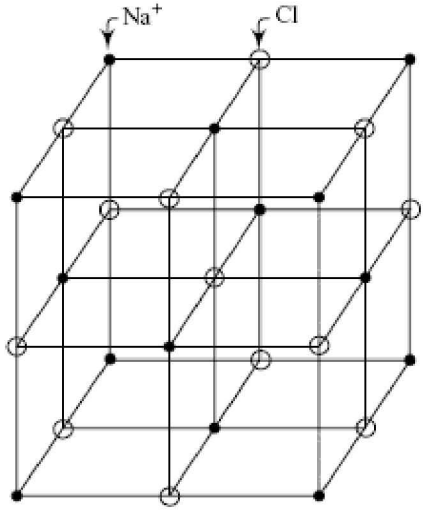


Fig. 5.50 *Structure of NaCl (fcc)*

Example 27 *Answer the following:*

(a) $a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$; identify the crystal system.

(b) The interplanar distance d_{hkl} ratio is 1 : 0.707: 0.577, identify the cubic lattice.

(c) The Weiss indices of a plane are 2, 2, ∞. What are its Miller indices?

Solution:

(a) The crystal system is monoclinic.

(b) It is simple cubic system.

(c) The Miller indices may be obtained as follows:

Take the reciprocal of Weiss indices:

$$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{\infty} \quad \text{or} \quad \frac{1}{2}\ \frac{1}{2}\ 0$$

The Miller indices are 110.

Example 28 *The second-order reflection of X-rays from (100) plans of NaCl occurs at 29.3°. If the wavelength used is 1.54Å, calculate the distance between two successive (100)planes in NaCl.*

Solution: The Bragg's equation relating the angle, wavelength of light and the distance between successive planes is

$2d \sin \theta = n\lambda$, where n is the order of reflection

Substituting the values, we have

$$2d \sin 29.3° = 2 \times 1.54 \quad \text{or} \quad d = \frac{1.54}{\sin 29.3} = 3.17\ \text{Å}$$

Example 29 *The first-order reflections from the 100, 110 and 111 planes of a given cubic crystal (NaCl crystal) were found to occur at angles 5.9°, 8.4° and 5.2° respectively. Determine the type of cubic lattice to which the crystal belongs.*

Solution: For first-order reflections, $n = 1$

So that we have

$$d = \frac{n\lambda}{2\sin\theta} = \frac{\lambda}{2\sin\theta}$$

$$\therefore \quad d_{100} = \frac{\lambda}{2\sin 5.9^\circ} = \frac{\lambda}{2 \times 0.103} = 4.845\ \lambda$$

$$d_{110} = \frac{\lambda}{2\sin 8.4^\circ} = \frac{\lambda}{2 \times 0.146} = 3.425\ \lambda$$

$$d_{111} = \frac{\lambda}{2\sin 5.2^\circ} = \frac{\lambda}{2 \times 0.094} = 5.319\ \lambda$$

$$\therefore \quad d_{100} : d_{110} : d_{111} = 4.845 : 3.425 : 5.319 = 1 : 0.706 : 1.096$$

This ratio is very close to that of the face-centred cubic. Hence, the given crystal is a face-centred cubic.

Example 30 *What type of structure is exhibited by KCl?*

Solution: X-ray diffraction studies reveal that KCl possesses simple cubic structure. In simple cubic structure,

$$d_{100} : d_{110} : d_{111} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}}$$

$$= 1 : 0.707 : 0.577$$

Example 31 *Calculate the angle at which first-order reflection and second-order reflection will occur in an X-ray spectrophotometer using X-ray of 0.154 nm wavelength. Given that the interplanar distance is 0.404 nm.*

Solution: *For first-order reflection, n* = 1. The Bragg's equation is $2d \sin\theta = \lambda$ or $\theta = \sin^{-1}(\lambda/2\,d) = \sin^{-1}(0.154/0.808) = \sin^{-1} 0.191 = 10^\circ\ 59'$

For second-order reflection, n = 2, The Bragg's equation is $2d \sin\theta = 2\lambda$ or $\theta = \sin^{-1}(\lambda/d) = \sin^{-1}(0.154/0.404) = \sin^{-1} 0.381 = 22^\circ\ 24'$

Note We need not convert λ and d into metres or centimetres because eventually the convention factor will cancel in the numerator and denominator.

SUMMARY

1. There are two types of solids, crystalline solids and amorphous solids. Atoms or ions are arranged in definite geometric pattern in crystalline solids while the particles are not arranged in any regular pattern in amorphous solids.

2. Properties like refractive index and electrical conductivity are different in different directions in a crystalline solid. This property is known as *anisotropy*.
3. There are four types of crystals, viz. ionic crystals, molecular crystals, covalent crystals and metallic crystals.
4. Regular arrangement of ions, atoms or molecules constituting the crystal in the three-dimensional space within the crystal is called *space lattice*.
5. The smallest portion of the complete space lattice which when repeated over and again in different directions produces the complete space lattice is called *unit cell*.
6. Different types of unit cells are simple unit cell, face-centred unit cell, end-face-centred unit cell and body-centred unit cell.
7. Number of spheres which are in direct contact with a particular sphere is called *coordination number* of that sphere.
8. In the structure of *sodium chloride*, every sodium ion is surrounded by six chloride ions and every chloride ion is surrounded by six sodium ions. There are four units of sodium ions and chloride ions each in a unit cell.
9. Zinc blende has FCC structure. The coordination number of Zn^{2+} ions as well as S^{2-} ions is 4. In calcium fluoride, each F^- ion is surrounded by four Ca^{2+} ions, while each Ca^{2+} ion is surrounded by eight F^- ions.
10. Two-dimensional packing can be done in two ways, square close packing and hexagonal close packing.
11. A void or empty space in a lattice which is surrounded by four spheres is called a *tetrahedral void*, and a void which is surrounded by six spheres is called an *octahedral void*.
12. Radius ratio is given by the ratio of the radius of the cation to the radius of the anion.
13. The fundamental laws of crystallography are
    (a) the law of constancy of interfacial angles
    (b) the law of rationality of indices
    (c) the law of symmetry
14. Different symmetry elements of a crystal are centre of symmetry, plane of symmetry, rotation axis of symmetry, rotation-reflection axis of symmetry, rotation-inversion axis of symmetry. A cubic crystal always possesses 23 different elements of symmetry.
15. Three suitable axes chosen to describe the relative directions and orientation of the faces and planes are called crystallographic axes. The axial ratio $a : b : c$ may be defined as the ratio of the intercepts made by unit plane on the crystallographic axes.
16. Miller indices may be defined as the reciprocal of the coefficient of the intercepts expressed as integers.
17. Internal structure of a solid can be determined by X-ray diffraction by the following techniques: (a) Bragg's method (b) Powder method (c) Laue method

Key relations

Radius ratio	Coordination no.	Arrangement
1.0–0.732	8	Cubic
0.732–0.414	6	Octahedral
0.414–0.225	4	Tetrahedral
0.255–0.155	3	Triangular

No. of atoms in a unit cell of	Relation atomic radius (r) and edge length (a)
Simple cubic – 1	Simple cubic, $r = \frac{a}{2}$
Face-centred cubic – 4	Body-centred, $r = \frac{\sqrt{3}}{4}a = 0.433\,a$
Body-centred cubic – 2	Face-centred, $r = \frac{a}{2\sqrt{2}} = 0.3535\,a$

Relation between density and edge length:

$$\text{Density} = \frac{Z \times \text{Atomic mass}}{6.023 \times 10^{23} \times a^3 \times 10^{-30}}\ \text{g cm}^{-3}$$

Interplanar distance d_{hkl} between the planes hkl in a cubic lattice is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Bragg's equation: $2d \sin\theta = n\lambda$

EXERCISES

Based on Different University Papers

I. Objective Questions

(A) Fill in the Blanks

1. Ionic solids are _____ in polar solvents but_in nonpolar solvents.
2. The ratio of the radius of the cation to the radius of the anion is called _____.
3. Reciprocal of the coefficients of the intercepts on the axes, expressed as integers are called _____.
4. The expression for Bragg's equation is _____.
5. The equation for separation between the lattice planes is _____.
6. _____ solids melt sharply at their melting point whereas _____ solids melt gradually over a range of temperature.
7. Co-ordination numbers of Na^+ and Cl^- in NaCl are _____.
8. The relation between atomic radius and the edge length in a body centred cubic solid is given by _____.
9. When there are atoms present at the centre of end faces of the unit cell, in addition to atom at the corners, the structure is called _____.
10. The methods for the determination of structure of a solid are _____ and _____.

(B) Multiple-Choice Questions

1. In a body-centred cubic arrangement, A ions occupy the centre whil e B ions occupy corners of the cubic. The formula of the solid is.

(a) AB_2

(b) AB

(c) A_2B

(d) None of these

2. Radius ratio r_{Na^+}/r_{C1^-} in NaCl crystal is

(a) 0.524

(b) 0.414

(c) 0.732

(d) 0.80

3. The number of atoms per unit cell in simple cubic, face-centred cubic and body-centred cubic are:

(a) 1, 4, 2

(b) 4, 1, 2

(c) 2, 4, 1

(d) 4, 8, 2

4. Crystals can be classified into

(a) 7 systems

(b) 9 systems

(c) 10 systems

5. Close packing is maximum in the crystal lattice of

(a) face-centred cubic

(b) BCC

(c) simple cubic

6. Bragg's equation is

(a) $2\,n\,\lambda = d \sin\theta$

(b) $n\lambda = 2\,d \sin\theta$

(c) $\frac{n}{\lambda} = d \sin\theta$

7. In Bragg's equation for diffraction of X-rays, *n* represents

(a) number of moles

(b) quantum number

(c) order of reflection

(d) Avogadro number

8. Axis of symmetry are called "Hexad"

(a) if original appearance is repeated twice

(b) if original appearance is repeated 6 times

(c) if original appearance is repeated after an angle of 90°

9. Total number of planes, axes and centre of symmetries in a crystal is termed as

(a) elements of symmetry (b) symmetries

(c) symmetry operations

10. If in a crystal intercepts are 1, ∞ and ∞, the Millar indices are:

(a) (100)

(b) (101)

(c) (110)

(d) (000)

11. Millar indices in a crystal indicate

(a) designation of plane crystals

(b) intercepts of plane on X-axis

(c) reciprocals of fractional intercepts of that plane on various axes

(c) none

12. Which crystal has the highest melting point?

(a) Ionic crystal

(b) Covalent crystal

(c) Metallic crystal

(d) Molecular crystal

13. Axis of symmetry in crystals is given by the general formula

(a) $\frac{360^\circ}{n}$

(b) $n \times 360^\circ$

(c) $n \times 180^\circ$

(d) $n/90^\circ$

14. Coordination number for an atom in a primitive cubic unit cell is,

(a) 6

(b) 8

(c) 10

(d) 12

15. If a plane is parallel to an axis of crystal its Miller index will be:

(a) zero

(b) infinity

(c) one

(d) none

16. In a unit cell of NaCl lattice there are:

(a) 4 NaCl units

(b) 3 Na^+ ions

(c) 6 Na^+ ions

(d) 6 Cl^- ions

17. Name of equation related to X-ray diffraction by crystals is:

(a) Laue equation

(b) Bragg's equation

(c) Lewis equation

18. The geometrical form consisting only of a regular array of points in space is called:

(a) Unit cell

(b) lattice

(c) Crystal

(d) amorphous solids

19. How many different ways were suggested by Bravais in which similar points can be arranged in a three dimensional space

(a) 14

(b) 10

(c) 7

(d) 9

20. Interplanar distances in crystal can be determined by equation

(a) $n\lambda = 2d \sin \theta$

(b) $n = \lambda d \sin \theta$

(c) $\frac{n}{\lambda} = 2\, d \sin \theta$

Answers

(A) Fill in the Blanks

1. Soluble
2. Radius ratio
3. Miller
4. $2\, d \sin \theta = n\lambda$
5. $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$
6. Crystalline
7. 6 and 6
8. $r = \frac{\sqrt{3}}{4} a$
9. End-centred

10. Powder method, Laue method

(B) Multiple-Choice Questions

1. (b)	2. (a)	3. (a)	4. (a)	5. (a)	6. (b)	7. (c)
8. (b)	9. (a)	10. (a)	11. (c)	12. (c)	13. (a)	14. (a)
15. (a)	16. (a)	17. (b)	18. (b)	19. (a)	20. (a)	

GENERAL QUESTIONS

1. Define clearly the following terms:
(a) Axis of symmetry (c) Inversion centre
(b) Mirror plane (d) Improper rotation
2. What is meant by external feature of crystals?
3. Draw the planes with Miller indices (112), (210)
4. In how many crystallographic groups are the crystallographic elements grouped?
5. Show various axis of symmetry and planes of symmetry in a cubic crystal.
6. What is meant by:
(a) Rotation axis of symmetry
(b) Rotation reflection axis of symmetry
(c) Rotation inversion axis of symmetry
7. Describe the law of rational indices.
8. What is meant by total elements of symmetry? Explain by taking an example of symmetry.
9. What are Bravais lattices?
10. How will you calculate the number of particles per unit cell in the following:
    (a) Simple cubic lattice
    (b) Face-centred cubic lattice
    (c) Body-centred cubic lattice
11. Name different type of crystals. Name the units which occupy the lattice points with suitable examples.
12. The crystallographic axes of a unit cell are a, b and c. Draw a plane of which Miller indices are 221. Can there be more than one plane with the same Miller indices?
13. (a) What is meant by space groups or point groups?
    (b) In how many space lattices are a total of 230 point groups distributed?
14. Explain the following terms with suitable examples.
    (a) Plane of symmetry
    (b) Axis of symmetry
    (c) Centre of symmetry
15. Explain why a five-fold axis of symmetry does not exist in any crystal.
16. What is crystallography?

17. What is meant by crystallographic elements and point groups?
18. Represent diagrammatically the Bravais lattices of
    (a) Simple cubic lattice
    (b) Face-centred cubic lattice
    (c) Body-centred cubic lattice
19. What is plane of symmetry? Show diagrammatically the various planes of symmetry in a cubic crystal.
20. Calculate the number of the points per unit call in
    (a) a face-centred cubic lattice
    (b) a body-centred orthorhombic lattice
    (c) a simple cubic lattice
21. What do you understand by space group? How many space groups are there in crystallography?
22. (a) State and explain the law of constancy of interfacial angles.
    (b) What is meant by mirror plane and inversion centre.
    (c) Define improper rotation.
23. Show that for the given Miller indices in a crystal there is a whole set of equally spaced parallel plane.
24. What are the crystallographic dimensions of the unit cells of the following crystal systems:
    (a) Triclinic
    (b) Tetragonal
25. Represent the following diagrammatically:
    (a) Body-centred cubic lattice
    (b) Face-centred cubic lattice
    (c) Hexagonal lattice
    (d) Simple tetragonal lattice
26. Differentiate between crystalline and amorphous solids. Justify that amorphous solids are liquids at all temperatures.
27. (a) Name the different crystal systems. Give their axial characteristics with one example of each.
    (b) What are the crystallographic dimensions of the unit cells of the following systems?
        (i) Triclinic
        (ii) Tetragonal
28. State and explain the laws of crystallography.
29. Differentiate between isomorphism and polymorphism.
30. What is meant by mirror plane and inversion centre?
31. Briefly explain the terms:
    (a) Unit cell
    (b) Crystal lattice

32. (a) Show that for the given Miller indices in a crystal, there is a whole set of equally spaced parallel planes.

(b) Draw the planes with Miller indices (112), (210).

33. Identify for the crystal system to which each of the following belongs from the given data of their unit cells.

(a) $a = b = c$; $\alpha = \beta = \gamma \neq 90°$

(b) $a = b = c$; $\alpha = \beta = \gamma = 90°$

(c) $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$

(d) $a = b \neq c$; $\alpha = \beta = \gamma = 90°$

(e) $a \neq b \neq c$; $\alpha = \beta = 90°$, $\gamma = 120°$

(f) $a \neq b \neq c$; $\alpha = \beta \neq \gamma = 90°$

(g) $a \neq b \neq c$; $\alpha = \gamma = 90° \neq \beta$

34. (a) Differentiate between isomorphism and polymorphism.

(b) What is meant by separation between lattice planes? Derive the equation

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

in case of a cubic lattice.

35. Describe in detail the structure of sodium chloride. Show that the ratio $\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}}$ $1 : \sqrt{2} : \frac{\sqrt{3}}{2}$ is obtained in sodium chloride crystal.

36. Calculate the number of points per unit cell in

(a) a simple cubic lattice

(b) a face-centred cubic lattice

(c) a body-centred orthorhombic lattice

37. (a) Name different types of space lattices associated with cubic system.

(b) Represent the following diagrammatically:

(i) Hexagonal lattice

(ii) Simple tetragonal lattice

38. Explain the following terms with suitable examples:

(a) Plane of symmetry

(b) Axis of symmetry

(c) Centre of symmetry

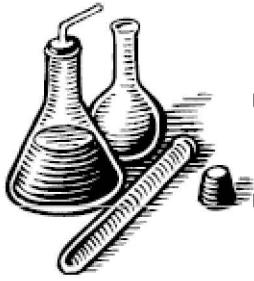
39. An element with 2.7×10^{-2} kg mol^{-1} molar mass forms a cubic unit call with 405 pm edge length. If its density is 2.7×10^{3} kg m^{-3}, what is the nature of the cubic unit cell?

[Ans. It is FCC]

40. Niobium crystallizes in body-centred cubic structure. If the density is 8.55 g cm^{-3}, calculate

the atomic radius of niobium using its atomic mass of 9.3 u

[Ans. 143.1 pm]



Colloidal State

6

LEARNING OBJECTIVES

- Differentiate between true solutions, colloidal solutions and suspensions
- Understand the terms *dispersed phase* and *dispersion medium.*
- Classify colloids on the basis of physical state of dispersed phase and dispersion medium, appearance and solvent affinity
- Understand dispersion colloids, multimolecular colloids and macromolecular colloids
- Follow the cleansing action of soaps on the basis of micelle formation.
- Know the methods of preparation of colloids by dispersion methods, condensation methods and chemical methods.
- Study the mechanical, optical and electrical proportion of colloids
- Understand Hardy-Schulze rule and flocculation value
- Know about protective colloids and gold number
- Study different kinds of emulsions, emulsifiers and demulsification
- Study different classes of gels
- Determine the size of colloidal particles by different methods
- Study applications of colloids.

6.1 INTRODUCTION

Colloidal state was first conceptualised by Thomas Graham in 1861. He observed that solutions of certain substances such as sugar, salt, acids and bases diffused readily through parchment membrane while those of glue, gelatin and silicic acid could not. The substances belonging to the former category were called ***crystalloids*** and those from the second category were given the name ***colloids.*** This is how a new branch, ***colloid chemistry,*** emerged. However, it was realised that distinction between crystalloids and colloids was not rigid because many crystalloids could be converted into colloids by suitable methods. Also, it came to be known that the same substance behaves as a crystalloid in one solvent and a colloid in another solvent. For example, soaps show colloidal behaviour in water while they show crystalloidal behaviour in alcohol in which they dissolve completely.

A solution of a crystalloids in a solvent in which it dissolves completely giving a transparent solution is called ***true solution.***

When water-soluble substances like glucose, copper sulphate, potassium chloride, etc., are put into water they dissolve and a homogeneous mixture is obtained. The particles of the solute are not visible and their size is molecular. Such mixtures are called ***molecular solutions*** or ***true solutions.***

Take muddy river water or an insoluble substance like lead sulphate or calcium sulphate and put it into water. The particles of the solute are visible even with the naked eye because their size

is large. On keeping for some time, the particles settle down. These mixtures are called ***suspensions.*** Between these two extremes, there are particles which are bigger than molecules but are too small to be seen even by a microscope. The colloidal state can thus be regarded as the intermediate stage between molecules and particles of a coarse suspension. A colloidal solution is also referred to as solution. These three states are illustrated in Fig. 6.1.

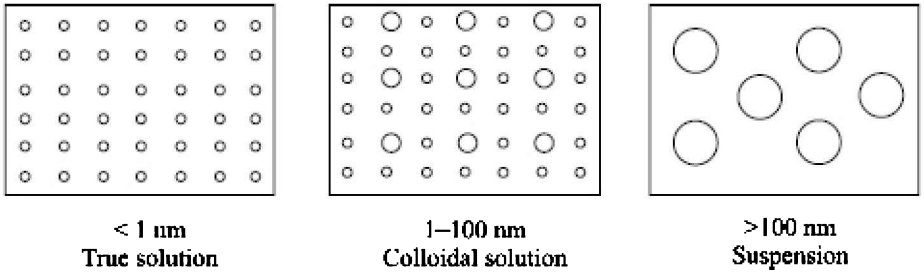


Fig. 6.1 *Representation of true solution, colloidal solution and suspenstion.*

Colloidal particles have an enormous surface area per unit mass. This can be explained in terms of their small size. Consider a cube with one edge equal to 1 cm. It has a total surface area of 6 cm^2. If we divide this cube into 10^{12} smaller cubes, each small cube will have the size of a large colloidal particle. The total surface area of the 10^{12} smaller cubes would be 60,000 cm^2. Such a large surface area of colloidal particle is of great importance as we shall study later. The distinguishing characters of the three types of solutions are given in Table 6.1.

Table 6.1 *Difference between a true solution, colloidal solution and suspension*

	True Solution	Colloidal Solution	Suspension
1.	The solute molecules in a true solution are not visible, even with a powerful microscope.	The molecules of the dispersed phase cannot be seen with naked eyes. However, they can be made visible through a powerful microscope called ultramicroscopie.	The particles are so big that they are visible even with naked eye. They sometimes settle at the bottom of the container, when the mixture is allowed to stand.
2.	The solute molecules can pass through even fine filter papers.	The colloidal particles can also pass through ordinary filter papers but cannot pass through filter papers called ultra filters.	The suspended particles are retained even by ordinary filter papers.
3.	A true solution forms a homogenous mixture.	A colloidal solution is heterogeneous.	Suspension is completely a heterogeneous mixture.
4.	When a strong beam of light is thrown on a true solution, the path of light is not illuminated.	The path of light is visible due to scattering of light, when a strong beam of light is passed through a colloidal solution (Tyndall effect).	No Tyndall effect is observed.

5. No electrical properties such as electro-osmosis, cataphoresis and coagulation are observed.	Colloidal solutions exhibit these electrical properties to a great extent.	No such electrical properties are exhibited.
6. The particle size is below 1 mm in diameter.	The particle size is 1-100 nm in diameter.	The particle size is above 100 nm in diameter.
7. The particles of the solute in true solution can pass through a parchment membrane.	The particles of a colloidal solution can pass through a parchment membrane.	The suspension particles are retained by a parchment membrane.
8. The osmotic pressure exerted by the solution is relatively more.	Colloidal solutions exert a very low osmotic pressure.	No osmotic pressure is observed.
9. The solutions do not possess the property of adsorption (a surface phenomenon).	Colloidal solutions possess remarkable property of adsorption.	The phenomenon of adsorption is much less marked.

Various Phases in a Colloidal Solution

A colloidal solution is a heterogeneous system consisting of two phases, viz. the dispersed phase and the dispersion medium.

1. Dispersed Phase It is comparable to the solute in a solution. It can be said that the component which is present in smaller proportion is the dispersed phase. For example, in a colloidal solution of starch in water, starch is the dispersed phase.

2. Dispersion Medium It is comparable to the solvent in a true solution. It is the component which is present in greater proportion. In the example of colloidal solution of starch in water, water is the dispersion medium.

It may be remembered that particles of the dispersed phase (colloidal particles) are bigger than those of the dispersion medium (molecules or ions).

6.2 CLASSIFICATION OF COLLOIDS

Colloids can be classified on the basis of physical state of dispersed phase and dispersion medium on the basis of appearance and on the basis of solvent affinity. Each of these is discussed as under.

6.2.1 Classification of Colloids on the Basis of Physical State of

Dispersed Phase and Dispersion Medium

Dispersed phase or the dispersion medium can be a solid or liquid or gas; there are eight different combinations possible. Table 6.2 describes the various colloids in which the dispersed phase and dispersion medium may have the same or different physical states. A colloidal solution with both the components in the gaseous state is not possible as according to Graham's law of diffusion, they form a homogeneous mixture.

Table 6.2 *Classification of colloids based on physical state of the phases*

S.No.	Dispersed Phase	Dispersion Medium	Name	Examples
1.	Solid	Solid	Solid sol	Coloured glass, alloys, gems
2.	Solid	Liquid	Sol	Paints, inks, egg white, colloidal Au, Colloidal Pt.
3.	Solid	Gas	Aerosol	Smoke, dust
4.	Liquid	Solid	Gel	Curds, cheese, jelly, pudding
5.	Liquid	Liquid	Emulsion	Milk butter, oil in water
6.	Liquid	Gas	Aerosol	Mist, fog, clouds
7.	Gas	Solid	Solid foam	Cake, bread. pumice stone
8.	Gas	Liquid	Foam	Soap lather, aerated water

6.2.2 Classification of Colloids on the Basis of Appearance

Colloids may be divided into the following two main categories on the basis of appearance:

1. Sols When a colloidal solution appears as a fluid, it is termed sol. Sols are named after the dispersion medium. For example, when the dispersion medium is water, they are called hydrosols. If the dispersion medium is alcohol, they are called alcosols and if it is benzene, they are called benzosols.

2. Gels When a colloid has a solidlike rigid appearance, it is called gel. The ridigity of a gel varies from substance to substance. Some substances may occur both as sols as well as gels. This depends upon the relative concentration of the dispersed phase and dispersion medium.

The colloidal system in which the dispersed phase is a liquid and the dispersion medium is solid is known as gel. A gel is formed by interlocking of the dispersed phase particles. Gelatin dissolves in warm water to form a colloidal solution which sets into a gel.

6.2.3 Classification of Colloidal Solutions on the Basis of Solvent Affinity

When the dispersion medium exerts an attraction on the dispersed phase then we get a lyophilic sol

(solvent loving). When the attraction between the dispersion medium and the dispersed phase is very little then the sol is called lyophobic sol (solvent hating).

1. Examples of Lyophobic Sols (nonreversible) Metals, sulphur, sulphides, silver halides, egg albumen, silicic acid and ferric hydroxide give nonreversible colloidal systems with water.

2. Examples of Lyophilic (Reversible) Sols Protein, starch, glue gelatin and agar-agar give reversible colloidal systems with water. Rubber in benzene is also a reversible colloidal system. The main points of difference between the two are given in Table 6.3.

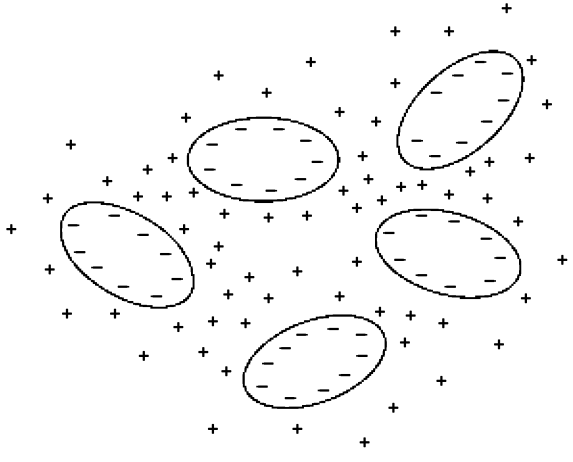


Fig. 6.2 *Colloidal clay particles suspended in solution (Hydrophobic sol)*

Table 6.3 *Difference between lyophilic and lyophobic colloids*

S. No.	Lyophilic (solvent loving) or Hydrophilic Colloids (water as solvent)	Lyophobic (solvent hating) or Hydrophobic Colloids (water as solvent)
1.	Lyophililc colloids pass into the colloidal form readily when brought in contact.	Lyophobic colloids do not form the colloidal solutions easily when treated with solvent.
2.	Substances like starch, proteins, gums, soaps and metasilicic acid are common examples.	Colloids of metals (Au, Pt), sulphur, arsenius sulphide and silver iodide are common examples of this class.
3.	They are called reversible sols because they can be recovered from the colloidal solutions and can be converted into the colloidal form when desired.	They are called irreversible sols because they cannot be recovered from their colloidal forms.
4.	The particles may or may not migrate in an electric field. The migration may be in any direction.	Particles migrate only in one direction in the presence of electric field.

5.	The particles are not easily detected in the ultra microscope.	The particles are easily detected by an ultramicroscope.
6.	Small quantities of electrolytes do not affect precipitation, but only large quantities of electrolytes cause precipitation.	Even small quantities of electrolytes can cause precipitation.

6.2.4 Dispersion Colloids, Multimolecular or Association Colloids, Macromolecular or Molecular Colloids

1. Dispersion Colloids In case of colloidal solutions in which the dispersed phase has little affinity for the dispersion medium (i.e. solid substance is insoluble in the dispersion medium), the size of the solid particles (dispersed phase) lies in the colloidal range. This system is called a dispersion colloid. For example, gold sol, hydrated ferric oxide sol, colloidal sulphur, a colloidal dispersion of As_2O_3 in water, etc. Generally, this type belongs to lyophobic sols.

2. Multimolecular or Association Colloids In this case, an individual colloidal particle consists of an aggregate of a large number of small atoms or molecules. The size of such species lies in the colloidal range. The species thus formed are called associated colloids or multimolecular colloids, for example, soap solution, dyes, surface active agents, etc. Generally in this type, there is occurrence of lyophobic and lyophilic portions in the same molecules. Thus, the aggregates of ions or molecules with lyophilic as well as lyophobic parts are called micelles. Micelles are of colloidal dimension though the individual ions or molecules may not be of the colloidal dimensions.

3. Macromolecular or Molecular Colloids In such systems, each particle of the dispersed phase is of colloidal dimensions. Mostly this type consist of lyophilic sols. This resembles true solutions in some respects. Examples of this type include proteins, cellulose, the solutions of rubber and high polymers in organic solvents, etc.

6.3 MICELLES

There are certain strong electrolytes which give a normal solution at low concentration but show colloidal nature at higher concentration. These are called ***micelles.*** These substance may also be referred to as ***associated colloids.*** Soap is an example of this class. It forms a micelle. These substances commonly act as ***surface active substances.*** They consist of lyophilic as well as lyophobic parts in the same molecule. A long hydrocarbon chain serves as lyophobic and an ionic group like carboxy or sulphuric serves as lyophilic. A micelle may contain as many as 100 molecules.

Cleansing Action of Soaps on the Basis of Micelle Formation

Water is not a good medium for cleaning our body or clothes. This is because of the high surface tension of water. It does not spread evenly over the dirt, particularly grease, in clothes or on the body. The exceptionally high value of surface tension of water could be explained in terms of hydrogen bonding. Without complete wetting of grease by water, we cannot expect efficient cleaning. The function of soap or other synthetic detergents is to decrease the surface tension of water. This is made possible by micelle formation as shown in Fig. 6.3.

Ordinary soap is sodium stearate, $C_{17}H_{35}COONa$. It gives $C_{17}H_{35}COO^-$ in solution. The hydrocarbon chain consisting of 17 carbon atoms is hydrophobic in nature. A number of such hydrocarbon chains are directed towards grease as shown in Fig. 6.3. The negative poles of the

stearate ions then attract the positive ends of water (water is a polar molecule) forming a micelle.

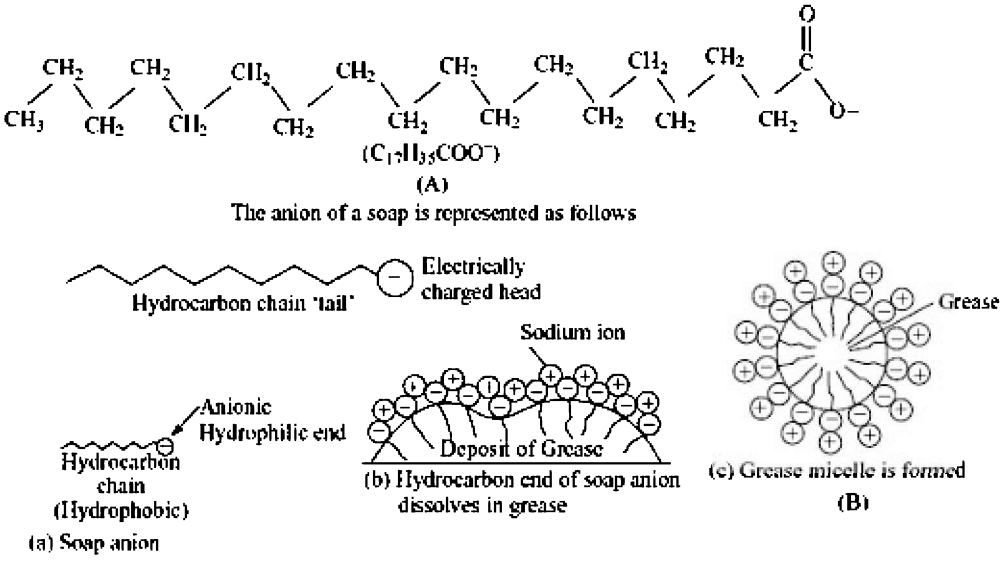


Fig. 6.3 *A. Representation of a soap molecule B. Formation of a micelle.*

The micelles are then washed away with more water. Thus, soap helps in the cleaning of clothes or body. The function of soap is to reduce grease or oil to colloidal particles; therefore, soaps are emulsifying agents. Grease particles are prevented from coming closer because of the covering by soap molecules. Any synthetic detergent like sodium lauryl sulphate $C_{17}H_{25}SO^-_4\ Na^+$ would form a micelle by a similar mechanism.

6.4 PREPARATION OF COLLOIDAL SOLUTIONS

A number of methods are available for the preparation of colloidal solutions. These are described under the following heads:

1. Dispersion (Size Reduction) Methods for the Preparation of Colloidal Solution

persion methods for the preparation of colloidal solutions are described as under:

(a) Mechanical Dispersion or Disintegration It involves the following steps:

(i) First of all, the substance is powdered thoroughly.

(ii) The finely ground substance is brought in the form of coarse suspension, by shaking with the dispersion medium.

(iii) The suspension is then made to pass through a colloid mill (disc mill), which consists of two metallic discs almost touching each other and rotating with a terrific speed in opposite directions (Fig. 6.4).

The suspension is then subjected to a powerful shearing force, resulting in the breaking of suspended particles to form particles of colloidal dimensions.

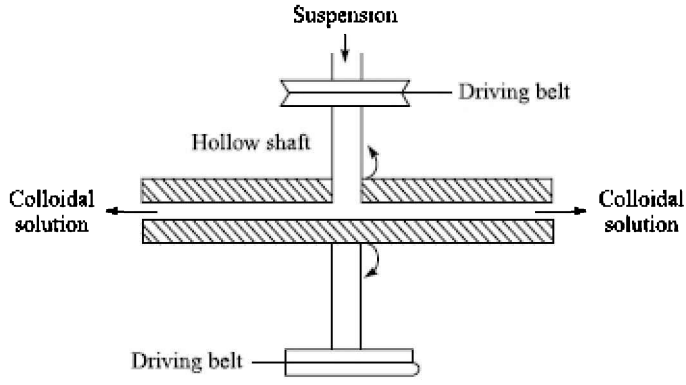


Fig. 6.4 *Colloid mill*

The colloid mills are nowadays used in many industrial processes, such as the manufacture of dyestuffs, printing inks, varnishes, lacquers, paints, ointments, dental creams, oil and water colours, etc.

(b) Peptization (Dispersion of a Precipitate) It is the redispersion of the coagulated sol. Peptization is defined as ***the process by which a colloidal solution can be obtained by dispersing the coagulated mass in which the colloidal particles pre-exist.*** For example, ferric hydroxide is a coagulated sol and is a precipitate. On adding ferric chloride solution (peptizing agent) to it, a reddish brown solution containing ferric hydroxide sol is obtained (Fig. 6.5).

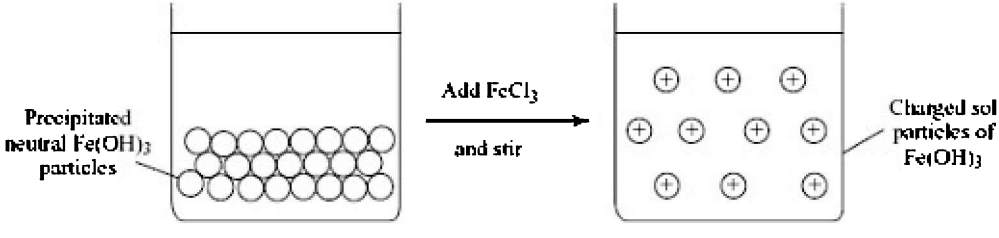


Fig. 6.5 *Preparation of ferric hydroxide sol by peptization*

The excess of ferric chloride if any, can be removed by dialysis. Similarly, a precipitate of silver iodide can be peptised by shaking with dilute solution of either KI or $AgNO_3$. When very dilute HCl acid is added to the freshly precipitated aluminum hydroxide, $Al(OH)_3$, a colloidal solution of aluminum hydroxide is obtained. The acid should be in small quantity.

(c) Electro-dispersion or Bredig's Arc Method This method is employed for getting colloidal solutions of metals like gold, silver, copper, platinum, etc. The metal rods (electrodes) are immersed in the dispersion medium, say water. An arc is struck between the two electrodes (Fig. 6.6). As a result of powerful heat of arc, metal is converted into its vapours which get condensed at once (the vessel being placed in a ice-cold water bath), resulting in the formation of colloidal size particles (to stabilize the solid, a small quantity of NaOH or K_2CO_3 is added).

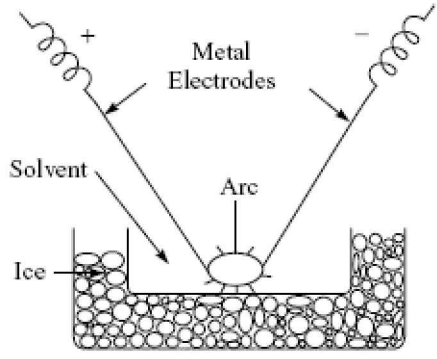


Fig. 6.6 *Bredig's arc method*

2. Condensation or Aggregation Methods for the Preparation of Colloidal Solutions

Condensation methods for the preparation of colloidal solutions are discussed as under:

(a) Exchange of Solvent There are certain substances which are more soluble in one solvent as compared to another. Colloidal solution of such substances can be obtained by pouring the solution of the substances in which it is more soluble to the other solvent, in which it is soluble to a smaller degree. For example,

(i) Sulphur and phosphorus are more soluble in alcohol than water. If their alcoholic solution is added to small quantity of water, hydrosol results.

(ii) Phenolphthalein is soluble in alcohol but not in water. If its alcoholic solution is added to water, a milky solution is obtained which is the sol of phenolphthalein.

(b) Excessive Cooling This method is employed to get colloidal solution of ice in an organic solvent like ether and chloroform. This is done by freezing a solution of water in the given solvent. The molecules of water can no longer be held in solution. They collapse together to yield colloidal-size particles.

3. Chemical Methods for the Preparation of Colloidal Solutions

Chemical methods for preparing colloidal solutions are given below:

(a) Hydrolysis A colloidal solution of *ferric hydroxide* is obtained by adding 2 or 3 ml of 30% solution of ferric chloride to about 500 ml of hot boiling water.

$$\underset{\text{(deep red)}}{FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3} + 3HCl$$

(b) Reduction A colloidal solution of gold (violet coloured) may be obtained by adding stannous chloride solution (reducing agent) to a solution of gold chloride

$$2AuCl_3 + 2Sn\,Cl_2 \rightarrow 3SnCl_4 + \underset{\text{Violet}}{2Au}$$

(c) Double Decomposition A colloidal solution of arsenious sulphide is obtained by adding water saturated with H_2S gas, to a solution of arsenious oxide (one gram in 500 ml of water).

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

(d) Oxidation A colloidal solution of sulphur is obtained by passing H_2S gas through a solution containing some oxidising agent, say oil of HNO_3, or by passing H_2S into a solution of sulphur dioxide in water.

$$H_2S + [O] \rightarrow H_2O + S$$
$$SO_3 + 2H_2S \rightarrow 3S + 2H_2O$$

Purification of Colloidal Solution

A sol contains electrolyte during its preparation. A small amount of electrolyte is essential for stability of the sol, but excess of it can cause coagulation. Therefore, it is essential to remove excess of electrolyte.

The purification of the sol can be achieved by the following processes.

1. Dialysis The process of removing the dissolved electrolytes from the sol by means of a membrane is called dialysis.

A dialyser consists of a bag made of parchment or cellophane and suspended in running water in a trough. The mixture of the colloid and the crystalloid is taken in the bag and apparatus fitted as shown in Fig. 6.7 (a). After some time, whole of the crystalloid in solution passes out while the colloid remains in the bag. It is further observed that the above process of separation can be accelerated if an electric field is applied around the parchment bag. The process is then called ***electrodialysis.*** This is shown in Fig. 6.7 (b).

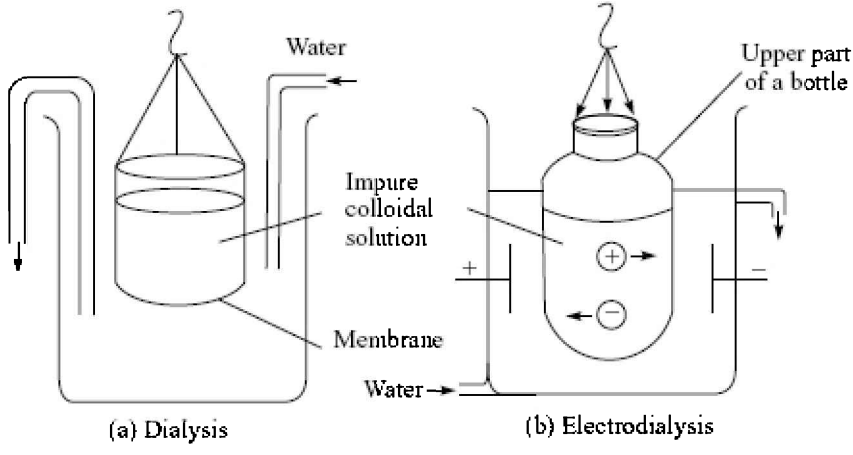


Fig. 6.7 *Dialysis and Electrodialysis*

Explanation Due to bigger size, colloidal particles are unable to pass through the parchment bag while ions of the crystalloid are carried away by the running water in the dialyser. Further, on applying the electric field, the movement of the ions is accelerated

An important application of dialysis is in the purification of blood in the artificial kidney machine.

The dialysis membrane permits small particles to pass through but colloidal haemoglobin does not pass through.

2. Ultra Filtration Colloidal particles pass through an ordinary filter paper. This is because its pores are too big to retain colloidal particles. If the filter paper is impregnated with collodion, the pore size of the filter paper is much reduced. Such a modified filter paper is called ultra filter.

Separation of colloidal particles from a solution by filtration through an ultrafilter is called ultra filtration.

6.5 PROPERTIES OF SOLS (COLLOIDAL SOLUTIONS)

Different properties of colloidal solutions are discussed under the following headings:

1. Mechanical Properties (Brownian Movement) If we examine the colloidal solutions with an ultramicroscope, we find that suspended particles are in a constant rapid zig zag motion (Fig. 6.8). This zig-zag motion is called Brownian movement. Robert Brown first noticed this movement while examining pollen grains suspended in water under a microscope.

The kinetic theory gives a nice explanation of the phenomenon. The motion is due to unequal bombardment by the molecules of dispersion medium. With increase in size of particles, the probability of unequal bombardment diminishes and so Brownian movement decreases with increase of particle size.

This motion counteracts the force of gravity acting on the colloidal particles and is thus responsible to a certain extent for the stability of colloids.

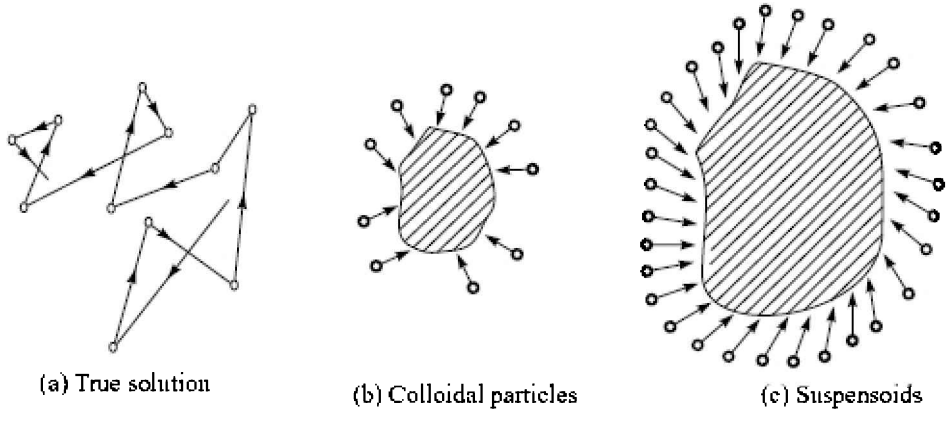


Fig. 6.8 *Brownian movement*

(a) Diffusion Since the rates of diffusion decrease very rapidly with increase in the mass of the particles (Graham's law), colloidal solutions would diffuse much more slowly than ordinary molecular solutions. This property has been made use of in determining molecular weights of colloids. Since the equation to be used for the purpose also has a term for the ***Avogadro's number*** (the number of molecules in a gram molecule), the latter can also be determined from it using solutes of known molecular masses.

(b) Sedimentation of Suspensoids Although colloidal solutions are found to be fairly stable over considerable periods of time, they do very slowly settle down under the influence of gravity even though some may take years to do so. The rates of setting [or sedimentation, as it is called] can be readily determined because the boundary line between the clear medium and the sol can be easily made out.

2. Optical Properties (Tyndall Effect) A beam of light entering a dark room lights up the dust particles floating in air. Similarly, when a strong beam of light is concentrated on a colloidal solution, the path of the beam is illuminated by a bluish light (and becomes visible when observed from the side). This phenomenon is known as Tyndall effect (Fig. 6.9).

The scattering of light by the colloidal particle is responsible for this phenomenon. The intensity of scattered light depends upon the difference between refractive indices of dispersed phase and dispersion medium. Since this difference is quite appreciable in case of lyophobic collides, they show well-defined Tyndall effect. This phenomenon has been employed by Zsigmondy as the basic principle for the construction of ***ultra microscope.*** A normal microscope cannot be used to locate colloidal particles.

It is this effect which is made use of in the 'test box' in testing the purity of SO_2 for the manufacture of sulphuric acid by the Contact Process.

3. Electrical Properties (Cataphoresis or Electrophoresis) Collidal particles carry an electric charge and, therefore, move towards the oppositely charged electrode when the solution is placed under the influence of an electric field (Fig. 6.10). This migration of colloidal particles under the influence of an electric field is called cataphoresis. The type of charge on a sol particle can be determined by noting the direction of their motion.

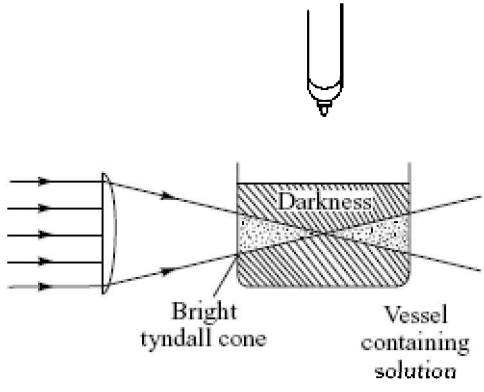


Fig. 6.9 *Tyndall effect*

The important applications of cataphoresis are:

(a) Removal of dirt particles

(b) Electro-deposition of rubber

4. Electro-osmosis A sol is electrically neutral. This reveals that the dispersion medium carries an equal but opposite charge to the dispersed particles. If the dispersed phase is kept stationary by suitable means, it is observed that the dispersion medium itself begins to move under the influence of an electric field. This motion of the dispersion medium under the influence of an electric field is called electro-osmosis.

5. Colour Colour of a sol depends on the wavelength of light scattered by the dispersed phase which, in turn, depends upon the size and nature of the particles. In the case of silver sol, the following data is available.

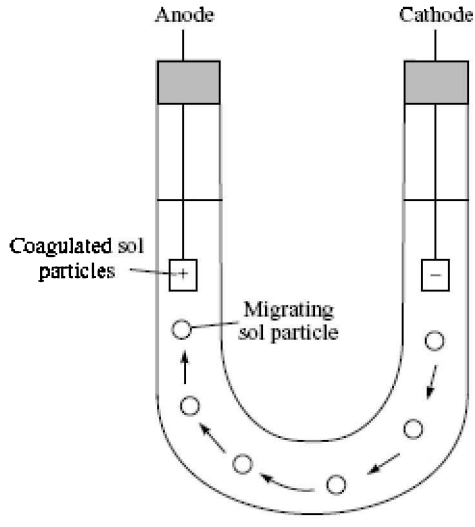


Fig. 6.10 *Cataphoresis*

Table 6.4 *Colour of silver sols*

Colour of Silver Sol	Particle Size (mm)
Orange yellow	6×10^{-5}
Orange red	9×10^{-5}
Purple	13×10^{-5}
Violet	15×10^{-5}

6.5.1 Stability of Colloidal Solutions

Colloidal solutions are stable; this is due to the fact that they are electrically charged. Colloidal particles carry either positive or negative charge. Since all the colloidal particles bear identical charge, they repel each other and do not precipitate easily under the effect of gravity.

The electrical charges carried by colloidal particles of various substances dispersed in water, as determined by electrophoresis experiments, are shown in Table 6.5.

Table 6.5 *Charge on the colloidal particles*

Positively Charged	Negatively Charged
1. Haemoglobin	1. Clay

2. Colloidal particles of $Fe(OH)_3$	2. Metallic particles like those of gold, silver and platinum
3. Basic dye stuffs	3. Sulphides of Cu, Pb, As, Sb and Cd
	4. Silicic acid, stannic acid and vanadium pentoxide
	5. Gum-Arabic and soluble starch
	6. Acid dye stuffs

6.5.2 Origin of Charge on Colloidal Particles

The electric charge is acquired by sol particles by one or more of the following means:

1. Selective Adsorptions The sol particles have a tendency to adsorb anions or cations from the solution. For example, the colloidal particles of As_2S_3 can adsorb either As^{3+} or S^{2-} ions. Since during the precipitation of this sol, only sulphide ions from H_2S are in excess, therefore, on a colloidal particle of As_2S_3, the S^{-2} ions get adsorbed and the particles become negatively changed. Similarly, the sol of $Fe(OH)_3$ obtained by the hydrolysis of $FeCl_3$ is positively charged. In the medium are present $Fe(OH)_3$ particles, Fe^{3+} and Cl^- ions. Fe^{3+} ions get adsorbed on the surface of $Fe(OH)_3$ and particles become positively charged.

*It should be kept in mind that **the ion which is more nearly related chemically to the colloidal particle is preferentially adsorbed** by it.

The AgCl particles can adsorb Cl^- ions from a chloride solution and Ag^+ ions from solution containing Ag^+ ions. The colloidal particle becomes negatively charged in the first case and positively charged in the second case.

*Stannic oxide sol provides an interesting example. If a freshly formed precipitate of stannic oxide is peptized by a small amount of hydrochloric acid, the sol carries a positive charge but if peptized by a small amount of sodium hydroxide, the sol carries a negative charge. In the former case, a small amount of stannic chloride $SnCl_4$ is formed and the sol is positively charged due to preferential adsorption of Sn^{4+} ion. In the latter case, a small amount of sodium stannate, Na_2SnO_3, is formed and the sol is negatively charged due to preferential adsorption of SnO_3^{2-}. The chloride and sodium ions, known as counter ions, are directed towards the liquid phase.

2. Dissociation of Surface Molecules Soap molecules dissociate to give ions. The cations pass into solution whereas the anions ($C_nH_{2n+1}\ COO^-$) aggregate together to form negatively charged big particles called micelles.

3. Friction The charge on the sol particles appears as a result of rubbing of the particles of dispersed phase against those of the dispersion medium.

4. Presence of Acidic or Basic Group Protein molecules yield colloidal solutions. Since a protein molecule contains an acidic group – COOH and also a basic group $–NH_2$, it will give a positive colloidal particle in acidic medium and a negative particle in alkaline medium.

In Acid:

$$H_2N - X - COOH + HCl \rightarrow H_3^+N - X - COOH + Cl^-$$

In Alkani:

$$H_2N - X - COOH + NaOH \rightarrow H_2N - X\ COO^- + Na^+ + H_2O$$

6.5.3 Theory of Electrical Double Layer

The electrical properties of colloids can be explained satisfactorily by postulating the existence of an electrical double layer of opposite charges at the surface of separation between a solid and a liquid, i.e. at a ***solid-liquid interface,*** According to modern views, when a solid is in contact with a liquid, a double layer of ions appears at the surface of separation, as shown in Fig. 6.11. One part of the double layer is fixed on the surface of the solid. This is known as the ***fixed part*** of the double layer, It consists of either positive ions or negative ions. The second part consists of a **diffused** or a ***mobile layer*** of ions which extends into the liquid phase. This layer consists of ions of both the signs but its net charge is equal and opposite to that on the fixed part of the double layer. Such an arrangement of charges is shown in (Fig. 6.11a). In case one, the fixed part of the double layer carries positive charge while in the second case (Fig. 6.11b), the fixed part carries negative charge. It will be seen that in each case, the net charge on the diffuse layer is equal and opposite to that on the fixed layer. For example, in Fig. 6.11a, there are 9 positive charges on the fixed layer and net 9 negative charges (9 positive and 18 negative) on the diffused layer. This theory applies to colloidal systems also. The ions which are preferentially adsorbed by the colloidal particles, are held in the fixed part of the double layer. These ions give the characteristic charge to the colloidal particles. The ions carrying the opposite charge, i.e., the counter ions, are present more in the diffused portion of the double layer giving a net opposite charge to this layer.

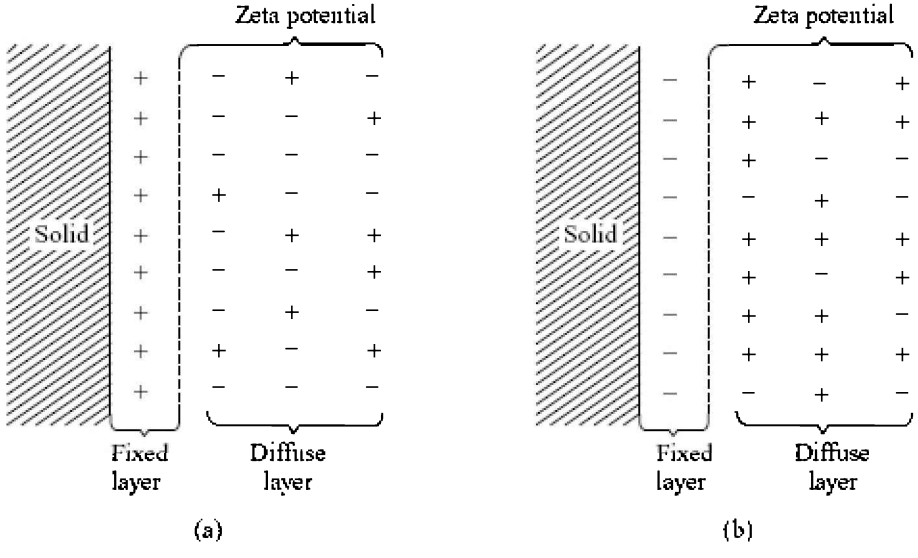


Fig. 6.11 *The electrical double layer.*

The existence of charges of opposite signs on the fixed and diffuse parts of the double layer leads to the appearance of a difference of potential between the two layers, as shown in Fig. 6.11. This difference of potential between the two layers is known as zeta potential or electrokinetic potential. Thus, this theory explains the charge and hence the stability of the collodial particles.

The zeta potential ζ is given by the relation

$$\zeta = 4\pi\eta\ u\ /\varepsilon_r$$

where η and ε_r are the viscosity and dielectric constant respectively of the dispersion medium and u is the mobility of the colloidal particles

Coagulation It is a process in which the charge over colloidal particles is neutralised resulting in the precipitation of the colloidal particles. The process is brought about spontaneously by the addition of an electrolyte. For example, when barium chloride solution is added to arsenious sulphide sol, it becomes turbid and after some time, a precipitate of arsenious sulphide separates out. The charge on the colloidal particles gets neutralised. We know that arsenious sulphide is a negative sol. The colloidal particles carry negative charge. The sol is stable because of the mutual repulsion between the various colloidal particles having similar charge. But when barium chloride solution is added, the negative charge on the colloidal particles is neutralised by the + ve charge on the barium ions. Thus, the colloidal particles accumulate to form particles of larger size and coagulation results (Fig. 6.12). If the coagulated substance floats then it is called flocculation.

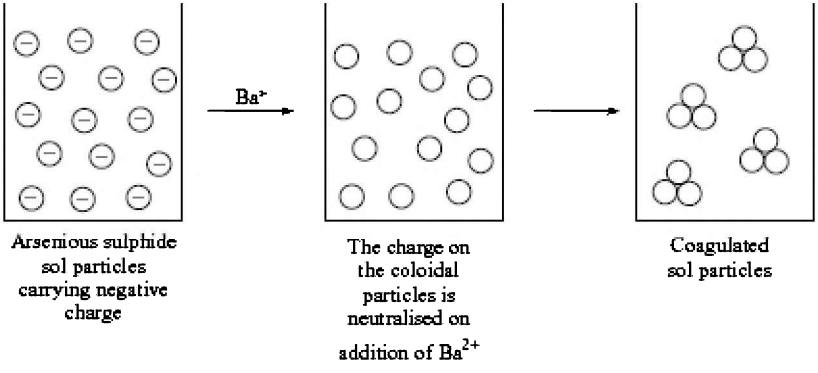


Fig. 6.12 *Coagulation of arrenious sulphide particles by addition of barium ions.*



A cloudburst is an extreme amount of precipitation and is associated with the phenomenon of coagulation. Rapid precipitation from clouds is possible due so called Langmuir precipitation process in which large droplets can grow rapidly by coagulating with smaller droplets which fall down slowly. It is not essential that cloudbursts occur only when a cloud clashes with a mountain or whatever. They can occur even when hot water vapour mingles into the cold cloud. Sudden condensation of water vapours takes place when it happens

In June 2013, a cloudburst occurred in Kedarnath and Rambara region of uttarakhand in India which killed thousands of people. It left nearly 84000 persons stranded for several days. The resulting flash-floods caused massive loss of life and property.

6.5.4 Hardy-Schulze Rule

Oppositely charge ions from the electrolyte are used up to effect coagulation. ***The power of an ion to effect coagulation depends upon its valency.*** According to Hardy-Schulze rule, higher the valency of an active ion, greater will be its power to coagulate colloidal solution, e.g. for the coagulation of negatively charged arsenious sulphide sol, trivalent cations (Al^{3+}) are much more effective than bivalent (Ba^{2+}) or monovalent (Na^{+}) cations.

Similarly, for the coagulation of positively charged ferric hydroxide sols, trivalent anions (PO_4^{-3}) are more effective than divalent (SO^{-2}_4) or monovalent (Cl^{-}) anions. Order of the negatively charged ions will be as under:

Trivalent anion > Divalent anion > Monovalent anion

6.5.5 Flocculation Value

The minimum concentration of an electrolyte in millimoles that must be added to one litre of a colloidal solution so as to bring about complete coagulation or flocculation is called the ***flocculation value.***

Coagulation can also be brought about by mixing two oppositely charged colloidal solutions. For example, by mixing ferric hydroxide sol with arsenious sulphide sol, a mutual coagulation takes place.

Example 1 *Arrange the following in increasing order offlocculation value for a negative sol.*

Solution: For a negative sol, greater the charge on the cation, greater is the flocculation value. The charges on the cation in the given electrolytes are as follows:

Electrolytes	Cation	Charge
$Mg\ Cl_2$	Mg^{2+}	+2
$Al2\ (SO4)_3$	Al^{3+}	+3
$Na_3\ PO_4$	Na^{+}	+1

Hence, the flocculation value of the electrolytes will be in the order

$$Al_2(SO_4)_3 > MgCl_2 > Na_3PO_4$$

6.6 PROTECTIVE COLLOIDS AND GOLD NUMBER

1. Protective Colloids Lyophobic colloids are sensitive and they tend to coagulate in the presence of electrolytes. But they can be stabilised if a small amount of a lyophilic sol like soap, gum, gelatine, etc. is added to them; this is called protective action. Such colloids which prevent the coagulation of other colloids are called protective colloids. It is believed that increase in the stability of the lyophobic colloids is due to the coating of lyophilic colloids on the lyophobic colloids

2. Gold Number The protective action of the colloids is measured in terms of gold number. Gold number is defined as the number of milligrams of the protective colloid which just prevents the coagulation of 10 ml of gold solution when 1 ml of a 10% solution of sodium chloride is added to it. Gold number of a few protective colloids are given below:

Table 6.6. Gold numbers of some protective colloids

Protective Colloid	Gold Number
Gelatin	0.005
Albumin	0.08
Starch	25

Example 2 *Define gold number. The gold numbers of A, B, C, and D are 0.005, 0.05, 0.5 and 5 respectively. Which of these has the greatest protective action? Explain your answer.*

Solution: A has the greatest protective action as we require the minimum quantity of *A* to prevent the coagulation of the gold solution when sodium chloride solution is added to it.

Example 3 *The coagulation of 100 ml of a colloidal solution of gold is completely prevented by addition of 0.25 g of starch to it after adding 1 ml of 10% NaCl solution. Find out the gold number of starch.*

Solution: As per the definition of gold number, it is the number of milligrams of protective colloid (starch in this case), which prevents the coagulation of 10 ml of gold solution when 1 ml of 10% NaCl solution is added to it.

In the present case,

100 ml of colloidal solution required to prevent coagulation = 0.25 g starch

10 ml of colloidal solution required to prevent coagulation = 25 mg starch

Hence, gold number of starch = 25

6.7 EMULSIONS

Colloidal solutions in which the dispersed phase as well as dispersion medium are liquids are called emulsions. Emulsions are of two types:

1. Water in Oil Emulsions are those in which water is the dispersed phase and oil is the dispersion medium e.g., butter, cod liver oil (See Fig. 6.13).

2. Oil-in-water Emulsions are those in which oil is the dispersed phase and water is the dispersion medium, e.g. milk is an emulsion of liquid fat in water.

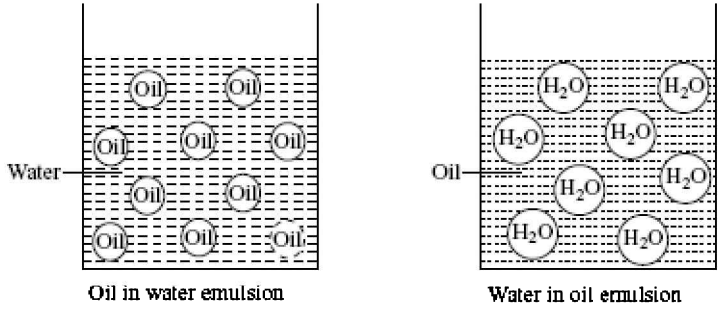


Fig. 6.13 *Two types of emulsions.*

Distinction Between Oil-in-water and water-in-oil emulsions

The two types of emulsions can be distinguished from each other by the following tests:

(a) Conductance Method A small amount of an electrolyte is added to the emulsion. If the conductance increases, the emulsion is oil-in-water type. If there is no appreciable change, it is water-in-oil type.

(b) Dye Test If on heating the emulsion with an oil-soluble dye, the emulsion gains the colour of the dye, it is a water-in-oil emulsion. If the emulsion does not catch the colour of the dye, it must be oil-in-water emulsion.

6.7.1 Emulsifiers or Emulsifying Agents

Generally, emulsions do not form stable colloidal systems. On standing, dispersed phase particles assemble together and form a separate layer. To stabilise emulsions, certain substances known as emulsifying agents or emulsifiers are added.

It is believed that the emulsifier surrounds the oil droplets, thus preventing them to come closer. It prevents them from coagulating. The function of the emulsifiers is to act as a protective layer around the oil droplets of the emulsion, thus increasing its stability as shown in Fig. 6.14.

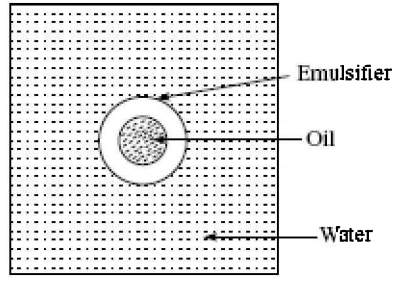


Fig. 6.14 *Action of an emulsifier*

Emulsions tend to coagulate because of the interfacial tension between the components of the emulsions. This effect is pronounced when there is a big difference between the surface tensions of the two components. In a bid to minimise the interfacial tension, they minimise the area of contact between the two components and thus the globules of the oil (e.g. in oil-in-water emulsions) come

together, thus destabilising the emulsion. An emulsifier prevents such a situation to occur.

Commonly used emulsifying agents are soaps and detergents. Other stabilising agents are proteins and gums. Digestion of fats in the intestines is aided by emulsification. A little of the fat forms a sodium soap with the alkaline solution of the intestines and it emulsifies the rest of the digestive enzymes to do their work. Many of the lotions, creams and ointments are emulsions of oil-in-water or water-in-oil type. Emulsions find application in the concentration of ores also.

6.7.2 Demulsification

Emulsion can be broken to recover the constituents by means of heating, centrifuging or by adding a large amount of electrolytes to precipitate out the dispersed phase. This can also be achieved by chemical destruction of the emulsifying agent.

The process of breaking emulsion to yield the constituent liquids is called demulsification. Separation of cream from milk is an example of demulsification by means of centrifugation.

6.8 GELS

A gel is a colloidal system in which the liquid is the dispersed phase and solid is the dispersion medium. A gel is jellylike. The process of formation of a gel is called ***gelation.***

Gels are formed as a result of partial coagulation of a sol. The coagulating particles combine together to form threadlike chains. Interlocking of these chains gives rise to a solid framework. The liquid part of the sol gets trapped in the solid framework, and we obtain a semi-solid porous mass called gel as shown in Fig. 6.15.

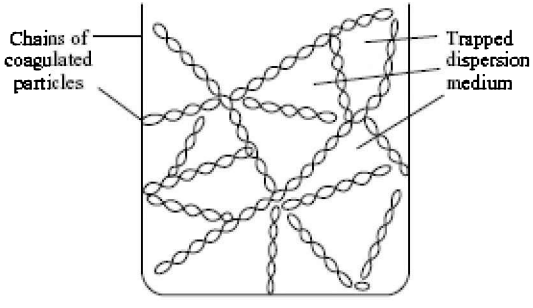


Fig. 6.15 *Structure of a get*

Classification of Gels

Gels may be classified into two types:

1. Elastic Gels Gels which are elastic in nature are called elastic gels. As expected, their shape changes when a force is applied on them. On releasing the force, the elastic gels regain their original shape. Gelatin, starch and soaps are examples of substances that can form elastic gels.

Such gels are formed by cooling concentrated solutions of lyophilic sols. There are no rigid forces of attraction between the particles of elastic gels.

2. Non-elastic Gels Gels which are rigid and do not show elasticity are called non-elastic gels. Silica gel is an example of non-elastic gel. Such gels are obtained by a specific chemical reaction.

Silica gel, for example, is obtaned by the addition of conc. hydrochloric acid to sodium silicate solution of a particular concentration. Silicic acid is formed which polymerises to form silica gel, particles of such a gel are linked by covalent bonds which give the gel a rigid structure.

Elastic gels can imbibe water when placed in it and undergo swelling. However, non-elastic gels are not capable of doing so. This phenomenon is known as ***imbibition*** or ***swelling.***

A property possessed by both elastic and non-elastic gels is to display shrinkage in volume with time. This phenomenon is called ***syneresis.*** Application of external pressure to a gel enhances syneresis.

Some of the gels like gelatin and silica liquefy on shaking and change into the corresponding sol. The sol on standing reverts back to the gel. This phenomenon of sol-gel interconversion is called ***thixotropy.***

6.9 VARIOUS METHODS TO DETERMINE THE SIZE OF COLLOIDAL PARTICLES

1. From Scattering of Light, the Use of Ultramicroscope Zsigmondy and others used the ultra-microscope for determining the size of the particles of colloidal dimensions. Each spot of light viewed in an ultramicroscope corresponds to a particle. The number of particles in a given volume of a solution, therefore, can be counted. The observation is repeated several times and an average is taken. The length and breadth of the field of vision are measured with the help of an eyepiece micrometer. The depth is determined by rotating the slit through 90°. From these dimensions, the exact volume of the solution containing the observed number of particles can be obtained. From this, the number of particles contained per unit volume of the solutions can be determined. Let this number be n.

The next step is to evaporate a known volume of the colloidal solution to dryness. From the weight of the residue, the mass of colloidal particles per unit volume can easily be obtained. Let this be m grams. The particles are supposed to be spherical and the density ρ of the colloidal particles is supposed to be the same as that in the bulk state. Thus, the volume of colloidal phase is m/ρ

$$\therefore \quad m/\rho = \frac{4}{3}\pi r^3 \times n$$

$$\text{or} \quad r = \left(\frac{3m}{4\pi\rho n}\right)^{1/3}$$

2. By Using Ultrafilters As approximate idea about the size of particles in a colloidal system can be obtained by the use of ultrafilters. These are prepared by impregnating filter papers with collodion or gelatin which are subsequently hardened by immersing in formaldehyde. The pores can be made small enough to retain particles of colloidal dimensions. The size of the pores depends on the particular filter paper employed and the concentration of the collodion or gelatin solution used for impregnating it. It is thus possible to obtain a series of graded ultrafilters, by means of which a colloidal solution may be separated into fractions containing particles of different sizes. An approximate estimate of the size of particles can be obtained from a knowledge of the dimensions of the pores of ultrafilters. The latter parameter is determined from the pressure required to force air or water through the pores.

3. From Brownian Movement Colloidal particles suspended in a liquid medium are subjected to Brownian movement. They also tend to settle down due to gravitation. Under the influence of both these effects, the particles distribute themselves in a vertical column in accordance with the equation

$$\frac{RT}{N_o} \ln \frac{n_1}{n_2} = \frac{4}{3} \pi r^3 (h_2 - h_1)(\rho - \rho')$$

Since N_o, the Avogadro's number, is known and since the number of particles n_1 and n_2 at two depths h_1 and h_2 of the vertical column can be counted with the help of an ultramicroscope and densities of the particles of the liquid medium, ρ and ρ', can be determined by the usual methods, the radius of the particles r can be easily calculated.

6.10 APPLICATIONS OF COLLOIDS

Colloidal solution and the charge on colloids find extensive applications in our daily life and various other processes. A few important applications of colloids are summarised below:

1. Pollution Control Chimneys of various industries bring out lot of smoke which acts as health hazard. Smoke is a colloidal solution of carbon particles in air. This smoke is brought in contact with a conductor of opposite charge near the chimney exit. Smoke, thus, gets coagulated. Carbon particles settle down and carbonless fumes or air comes out of chimneys. The design is known as Cottrell smoke precipitator (Fig. 6.16).

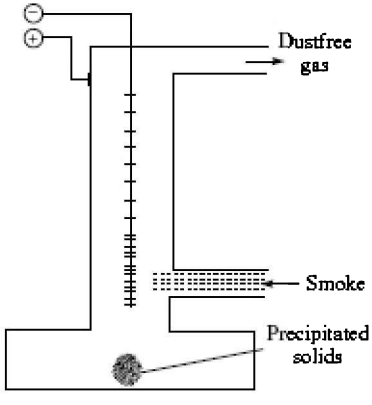


Fig. 6.16 *Cottrell smoke precipitator*

2. Sewage Disposal The sewage disposal carries dirt particles suspended in water. Separation of these particles from water is normally a difficult process. This difficulty is overcome by making the disposal water come in contact with an electrode of opposite charge in a big tank. Dirt particles are precipitated and separated. They serve as manure.

3. Formation of Deltas A delta is formed at a place where the river enters the sea. Sea water is rich in minerals whereas river water contains colloidal particles of clay. At the point of junction of the two waters, clay is deposited. This clay is fertile and is known as delta (Fig. 6.17).

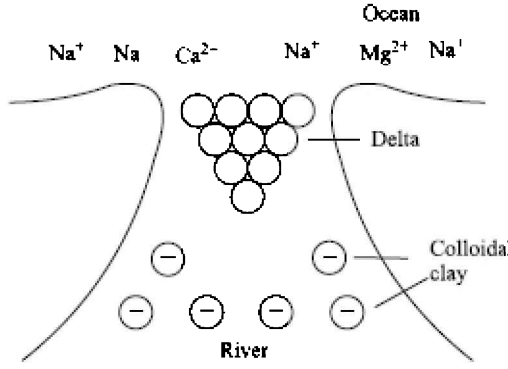


Fig. 6.17 *Formation of delta.*

4. Chemical Warfare Smoke and mist screens are formed by the explosion of bombs. They are harmful to humans, gas masks which contain colloidal charcoal come to the rescue. They adsorb the toxic smoke.

5. Purification of Drinking Water Ordinary water contains suspended impurities of colloidal size which do not settle down due to their charged nature. On adding a little of potash alum, the positive charge on aluminium ions neutralises the charge on colloidal particles, they settle down and water is cleaned for drinking.

6. Blue Colour of Sky Colour of a substance is the colour of the light transmitted by it. Colloidal particles of dust, etc., scatter only the blue light and absorb the rest of the light. Hence blue light reaches us and the sky appears to be blue (Fig. 6.18).

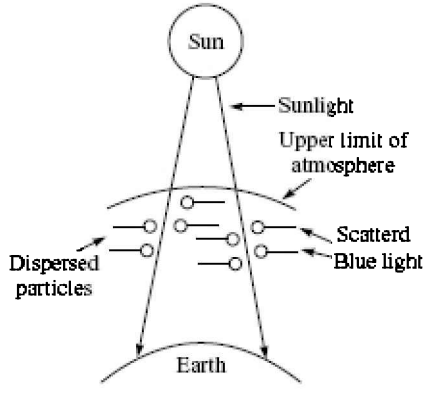


Fig. 6.18 *Blue colour of sky (Illustration)*

7. Photography The photographic film contains a colloidal solution of silver bromide in gelatin. A photographic film can also be obtained on a glass plate by depositing a mixture of silver bromide and gelatin.

8. Artificial Kidney Machines (Dialysers) Those machines which work on the principle of separation of colloidal particles from those of electrolytes have saved the lives of thousands of

people who suffer from kidney failure. The function of kidney is to separate blood (Colloidal solution) from urea and uric acid (true solution). When the normal kidney stops working, it leads to accumulation of poisonous matter into the blood which causes death. In an artificial kidney machine (dialyser), blood is made to pass through a series of cellophane tubes surrounded by a washing solution in water. The toxic chemicals diffuse into the washing solution. Purified blood is returned to the patient (Fig. 6.19).

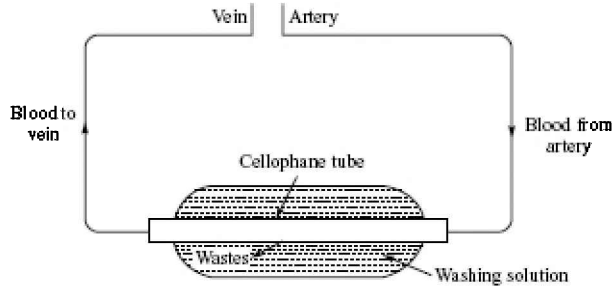


Fig. 6.19 *Artificial kidney machine (dialyser)*

9. Medicines A large number of medicines are being produced in the form of sols these days. Such medicines are more effective as they have greater assimilation and adsorption qualities. It is found that ferric chloride solution checks excessive bleeding from a cut. It coagulates the blood due to its charged nature.

Applying Chemisry to Life

Chrome-tanning of leather is brought about by the penetration of positively charged hydrated chromic oxide into the leather. The rate of penetration can be increased by electrophoresis.

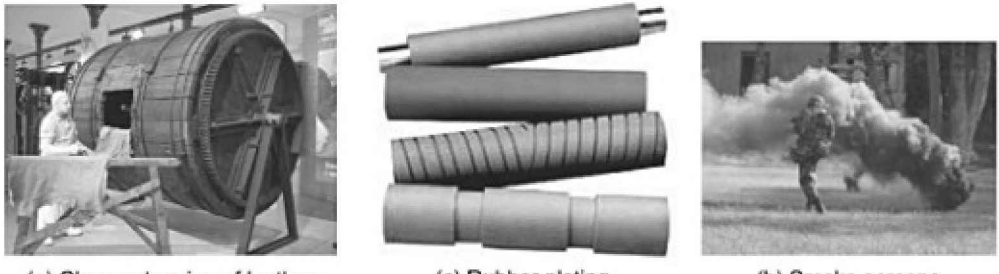


Fig. 6.20 *Applications of colloids*

Smoke screens are usually employed to conceal the movement of infantry in areas of exposure to enemy fire. A typical white screen uses titanium dioxide which shows maximum scattering of light and is, therefore, best for obscuring troops and naval vessels. Some colouring agents may be added for producing colour screens.

The negatively charged particles of rubber (latex) are made to deposit onto various objects for insulation or decoration by electrophoresis. The article to be rubber plated is made the anode. The rubber particles migrate in an electric field towards the anode and deposited on it.

SOLVED PROBLEMS

Example 4 *Comment on the statement "colloid is not a substance but a state of the substance"*

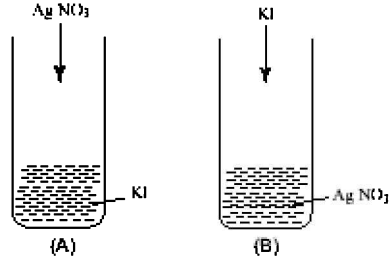
Solution: The same substance may exist as a colloid under certain conditions and as a crystalloid under certain other conditions. For example, NaCl in water behaves as a crystalloid while in benzene, it behaves as a colloid. Similarly, dilute soap solution behaves as a crystalloid while concentrated solution behaves as a colloid. It is the size of the particles which decides whether it is a colloid or a crystalloid.

Example 5 *Why is ferric chloride preferred over potassium chloride in the case of a cut leading to bleeding?*

Solution: Blood is a positively charged colloid. One molecule of ferric chloride produces three negative chloride ions while one molecule of potassium chloride producers one negative chloride ion. The greater the negative charge, the faster is the coagulation of blood.

Example 6 *How does soap help in washing clothes?*

Solution: Soap forms micelles around grease and dust particles. The lyopholic hydrocarbon ends (R) of soap are oriented towards grease droplets while the lyophilic COO^- parts of $RCOO^-$ are oriented towards water. Water washes away the micelles along with the grease and dirt.



Example 7 *A colloidal solution of Ag I is prepared by two different methods as shown below:*

(i) What is the charge of AgI colloidal particles in the two test tubes (A) and (B)?

(ii) Give the reason for the origin of charge.

Solution:

(i) When $AgNO_3$ is added to KI solution, the precipitate 5 of AgI will adsorb I^- from the dispersion medium, i.e. KI solution. AgI and KI have I^- as the common ion, thus, the colloidal particle of AgI will acquire negative charge. When KI is added to Ag NO_3 solution, the precipitate of AgI will adsorb the common ion Ag^+ from the $AgNO_3$ solution; therefore, AgI will acquire a positive charge

(ii) Origin of charge can be explained in terms of adsorption of ions form the dispersion medium and with the help of Helmholtz electrical double layer.

Example 8 *How will you distinguish between dispersed phase and dispersion medium in an emulsion?*

Solution: Emulsion can be diluted to any extent on adding the dispersion medium. The dispersed

phase forms a separate layer if added in excess.

Example 9 *How does it become possible to cause artificial rain by spraying silver iodide on the clouds?*

Solution: Clouds are colloidal in nature and carry a charge. On spraying silver iodide which is an electrolyte, the charge on the colloidal particles is neutralised. Clouds coagulate to form rain.

Example 10 *A colloid is formed by adding $FeCl_3$ in excess of hot water. What will happen if excess sodium chloride is added to this colloid?*

Solution: A positively charged colloidal solution of hydrated ferric oxide is formed. On adding sodium chloride, negatively charged chloride ions neutralise the positive charge of the colloidal solution. Coagulation of the sol takes place.

Example 11 *How does leather gets hardened after tanning?*

Solution: Animal skin is colloidal in nature and carries positive charge. Tannin is a negatively charged colloidal solution. When leather is soaked in tannin, coagulation of leather takes place and it gets hardened.

Example 12 *A sol may be prepared by a precipitation reaction. Give one such example. How can we find the nature of electric charge on the sol particles ?*

Solution: As_2S_3 sol may be prepared by precipitation reaction as per the following reaction:

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

We can find the nature of charge on the colloidal particles by electrophoresis. The colloidal particles move towards the oppositely charged electrode in an electric field. For example, the colloidal particles of As_2O_3 are negatively charged and move towards the positively charged electrode.

Example 13 *What happens in the following activities and why?*

(i) An electrolyte is added to a hydrated ferric oxide sol in water.

(ii) A beam of light is passed through a colloidal solution.

(iii) An electric current is passed through a colloidal solution.

Solution:

(i) On adding an electrolyte to hydrated ferric oxide sol, precipitation of ferric oxide takes place. This is because the charge on the colloidal particles is neutralised by the addition of the electrolyte.

(ii) Scattering of light by the colloidal particles takes place and the path of light becomes visible. This is known as Tyndall effect.

(iii) On passing electric current through a colloidal solution, the colloidal particles move towards the oppositely charged electrodes and are accumulated there. This phenomenon is called electrophoresis.

Example 14 *Explain the following observations:*

(i) A lyophilic colloid is more stable than lyophobic colloid.

(ii) Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.

(iii) The sky appears blue in colour

Solution:

(i) The stability of the lyophobic colloid is only on account of the charge while the stability of the lyophilic colloid is on account of charge as well as solvation of colloidal particles.

(ii) $Fe(OH)_3$ is positively charged which is coagulated by negatively charged Cl^- present in sodium chloride solution.

(iii) Sky appears blue in colour due to scattering of light by colloidal particles like dust, mist, etc.

Example 15 *What is the dispersed phase and dispersion medium of the following colloidal systems:*

(i) Smoke *(ii) Milk*

Solution:	Colloidal system	Dispersed phase	Dispersion medium
(i)	Smoke	Solid (carbon)	Gas (air)
(ii)	Milk	Liquid (fat)	Liquid water

SUMMARY

1. Solutions in which the particle of the solute are not visible are called *true* solutions. Solutions in which the particles of the solute are visible even with the naked eye are called suspensions. Colloidal solutions lie between these two solutions.
2. A colloidal solution is a heterogeneous system consisting of two phases, viz. the dispersed phase and the dispersion medium.
3. Colloids may be classified into different types on the basis of physical state of the dispersed phase and dispersion medium, on the basis of appearance (sols, gels), on the basis of solvent affinity (hydrophilic, hydrophobic) or as dispersion colloid, multimolecular colloid or macromolecular colloid.
4. *Micelles* are strong electrolytes which give a normal solution at low concentration but show colloidal nature at higher concentration. Cleansing action of soaps can be explained on the basis of micelle formation.
5. Colloids can be prepared by dispersion (mechanical, Bredig's arc, peptisation) methods condensation (excessive cooling, exchange of solvent methods) and chemical methods.
6. Purification of colloidal solutions is achieved by *dialysis.*
7. Colloidal solutions show colour, display Tyndall effect, Brownian movement, diffusion and sedimentation. Colloidal solutions also show electrophoresis.
8. Charge on the colloidal particles can be explained on the basis of one or more of the following: friction, selective adsoption, electron capture, dissociation of surface molecules and presence of acidic or basic groups.
9. *Electrical double layer:* The electrical properties of colloids can be explained satisfactorily by postulating the existence of an electrical double layer of opposite charges at the surface of separation between a solid and a liquid, i.e. at the solid-liquid interface.
10. The process in which the charge over colloidal particles is neutralised in the precipitation of the colloidal particles is called *coagulation.*

11. According to *Hardy-Schulze rule*, higher the valency of an active ion, greater will be its power to coagulate colloidal solution.
12. The minimum concentration of an electrolyte in millimoles that must be added to one litre of a colloidal solution so as to bring about complete coagulation or flocculation is called the *flocculation value*.
13. Gold number is defined as the number of milligram of the protective colloid which just prevents the coagulation of 10 ml of gold solution when 1 ml of a 10% solution of sodium chloride is added to it.
14. Colloidal solutions is which the dispersed phase as well as the dispersion medium are liquids are called *emulsions*.
15. A *gel* is a colloidal system in which the liquid is the dispersed phase and solid is the dispersion medium. Gels are of two types: elastic gels and non-elastic gels.
16. Size of the colloidal particles can be determined by using ultrafilters, from Brownian movement and from scattering of light.
17. Colloids find applications in purification of drinking water, pollution control, medicines, sewage disposal, photography, formation of deltas, explaining the blue colour of sky, chemical warfare and dialysers.

KEY EQUATIONS

• *Size of particles by Brownian movement*

$$\frac{RT}{N_o} \ln \frac{n_1}{n_2} = \frac{4}{3}\pi r^3 = (h_2 - h_1)(\rho - \rho')$$

n_1 and n_2 are the number of particles at two depths h_1 and h_2. ρ and ρ' are the densities of the particle and liquid medium. r is the radius of the particle.

• *Size of particles by light scattering method*

$$m/\rho = \frac{4}{3}\pi r^3 \times n(h_2 - h_1)(\rho - \rho') \text{ or } r = \left(\frac{3m}{4\pi\rho n}\right)^{1/3}$$

n is the number of particles per unit volume. m/ρ is the volume of the colloidal phase (volume = mass/density)

EXERCISES

Based on Different University Papers

Objective Questions

(A) Fill in the Blanks

1. Coloured glass is an example of colloidal solution of _____ in _____.
2. A small quantity of an electrolyte can cause precipitation of _____ colloid.
3. _____ action of soaps can be explained on the basis of micelle formation.

4. The process of removing the dissolved electrolytes from the sol by means of a membrane is called _____.

5. Oil-in-water emulsions have oil in the phase and water in _____ medium.

6. Particle size in a colloidal solution is _____.

7. What is a colloial system called if the dispersion medium is benzene?

8. Electrolytes which give a normal solution at low concentration but show colloidal nature at higher concentration are called _____.

9. Bredig's arc method is used for the preparation of colloided solution of _____.

10. The electrical properties of colloids can be explained satisfactorily by postulating the existence of electrical _____.

(B) Multiple Choice Questions

1. The sky looks blue due to

(a) dispersion effect

(b) reflection

(c) transmission

(d) scattering

2. Which method is used to destroy a sol?

(a) Condensation

(b) Dialysis

(c) Diffusion

(d) Addition of electrolyte

3. Which substance gives positive sol?

(a) Gold

(b) Starch

(c) Ferric hydroxide

(d) $As_2 S_3$

4. Which of the following is least effective in causing flocculating of ferric hydroxide sol?

(a) $K_3 Fe (CN)_6$

(b) $K_2 CrO_4$

(c) KBr

(d) K_2SO_4

5. Bleeding is stopped by applying $FeCl_3$ because:

(a) blood starts flowing in opposite direction

(b) $FeCl_3$ seals the blood vessels

(c) blood gets coagulated

(d) blood vessel is sealed

6. Who gave the rule ''Greater the valency, higher is the coagulating power"?

(a) Hardy-Schulze

(b) Grahm

(c) Faraday

(d) Lewis

7. Tyndall phenomenon is shown by

(a) dilute solutions

(b) colloidal solutions

(c) suspension

(d) true solution.

8. Migration of colloidal particles under the influence of electric field is called:

(a) Browian movement

(b) cataphoresis

(c) dialysis

9. The potential difference between fixed charged layer and diffused layer with opposite charge is called

(a) colloidal potential

(b) electrode potential

(c) zeta potential

(d) none

10. An emulsifier is a substance which

(a) helps dispersion of liquid in liquid

(b) stabilises the emulsion

(c) purifies the emulsion

(d) coagulates the emulsion

11. Kinectic activity of colloidal particles in dispersion medium is called

(a) electro-osmosis

(b) Brownian movement

(c) cataphoresis

12. Gold number is measure of

(a) amount of gold present in colloidal solution

(b) amount of gold required to break the colloid

(c) amount of gold required to protect the colloidal

(d) none

13. Which of the following is emulsifier?

(a) Soaps

(b) Detergents

(c) Both

(d) None

14. AgI is used for producing artificial rain because AgI

(a) has crystal structure similar to ice

(b) is easy to spray at high altitudes

(c) is easy to synthesise

(d) is soluble in water

15. Bredig's method is used for preparing

(a) metal sol

(b) organic compound

(c) eutectic mixture

(d) none

16. Which one of the following is +ve sol?

(a) Blood

(b) Clay soil

(c) Smoke

(d) Gelatin in acidic solution

17. The emulsifying agent in milk is

(a) lactic acid

(b) fat

(c) lactose

(d) casein

18. The gold number of sols *A*, *B*, *C* and *D* are 0.04, 0.002, 10 and 25 respectively. The protective powers are in the order:

(a) $A > B > C > D$

(b) $B > A > C > D$

(c) $D > C > B > A$

(d) $C > A > B > D$

19. The minimum concentration of an electrolyte required to cause coagulation of a sol is called:

(a) flocculation

(b) gold number

(c) Coagulation number

(d) none

20. Stability of lyophilic sol is due to

(a) Brownian motion of only

(b) electric charge only

(c) both Brownian motion and charge

(d) particle size

Answers

(A) Fill in the Blanks

1. Solid, solid

2. lyophilic
3. cleansing
4. dialysis
5. dispersed, dispersion
6. 1–100 nm
7. benzosol
8. gels
9. metals
10. double layer

(B) Multiple-Choice Question

1. (d)
2. (d)
3. (c)
4. (c)
5. (c)
6. (a)
7. (b)
8. (b)
9. (c)
10. (b)
11. (b)
12. (d)
13. (c)
14. (a)
15. (a)
16. (c)
17. (d)
18. (b)
19. (a)
20. (c)

GENERAL QUESTIONS

1. (a) What is meant by peptization? Give a suitable example.
   (b) Describe a method for purifying colloidal solutions.
   (c) Discuss the function of a protective colloid.
2. What are emulsions and gels? What distinguishes elastic from non-elastic gels?
3. (a) What are lyophillic colloids? Why are they called reversible colloids?

(b) Why is $MgCl_2$ a better coagulant than KCl for As_2S_3 sol?

4. What are colloids? How are they classified? How would you prepare the colloidal solution of

   (a) gold

   (b) arsenious sulphide and

   (c) sulphur?

5. Discuss the origin of charge on colloidal particles. What is meant by electrical double layers? What is meant by zeta potential?

6. What is electrophoresis? How does this phenomenon provide information about the sign of charge on particles.

7. State different methods of preparation of colloidal dispersions. Describe Bredig's arc method in detail.

8. (a) What is a colloid? Discuss the essential difference between lyophillic and lyophobic colloids.

   (b) Write short notes on

      (i) Tyndall effect and Brownian movement

      (ii) Electrophoresis and its applications

9. Give three points of difference between lyophobic and lyophillic colloids.

10. (a) What is the size range of colloidal particles? Distinguish between a molecular solution and a colloidal dispersion.

    (b) Describe one method for the preparation of colloidal solutions.

11. What are emulsions? How are they classified? How are they prepared?

12. Explain why:

    (a) Alum is used in town water supply

    (b) Alum is used in shaving

    (c) Tyndall concentrated is formed when a beam of light is concentrated on a colloidal solution

13. (a) What are emulsions and what is emulsifying agent?

    (b) What are micelles? Give examples.

14. Write a short note on origin of charge on colloidal particles.

15. Define gold number. The gold numbers of A, B, *C* and *D* are 0.005, 0.05, 0.5 and 5 respectively. Which of these has the greatest protective action? Explain your answer.

16. (a) Explain the stability of colloids.

    (b) Write the difference between gels and emulsions.

    (c) Explain the Hardy-Schulze rule for coagulation.

17. (a) What is a protective colloid? How does a hydrophilic colloid stablise a hydrophobic one? Give an account of gold number in this context.

    (b) What do you understand by the coagulation value of an electrolyte?

    (c) What are gels? Give examples.



Chemical Kinetics 7

LEARNING OBJECTIVES

- Express the rate of a reaction
- Learn the factors that affect the rate of a reaction
- Differentiate between order and molecularity of a reaction
- Learn the terms *rate law* and *rate constant*
- Derive the rate equation for zero-order reaction and calculate half-life period
- Derive the rate equation for first-order reaction, study their characteristics and study some first-order reactions in detail.
- Derive the rate equations for second and third-order reactions, study their characteristics and learn some second and third-order reactions
- Derive a relationship between half-life period and order of a reaction.
- Formulate the mechanism of a reaction based on kinetics studies
- Use different methods for the determination of order of a reaction
- Learn reversible, consecutive, side and parallel reactions
- Correlate the rate of reaction with temperature
- Understand collision theory and transition state theory of reaction rates
- Understand different experimental methods of chemical kinetics studies.

7.1 INTRODUCTION

We can predict the feasibility of a reaction from our knowledge of thermodynamics (if $\Delta G < 0$, the reaction is feasible). We can know the extent to which a reaction will proceed from chemical equilibrium. Along with feasibility and extent, it is equally important to know the rate and factors controlling the rate of a reaction for its complete understanding. For example, thermodynamics tells us that a reaction between H_2 and O_2 to give H_2O is feasible at room temperature. We know from observation that the reaction takes place so slowly that it might take years for the formation of water to be visible. In fact, rate of a reaction depends upon structural and energy factors which are not taken into consideration by thermodynamic quantities like free energy change. We can say that chemical kinetics is supplementary to thermodynamics for the study of reactions and processes.

To safely handle and use chemicals, users must understand the hazards associated with these materials. While thermodynamics allows a view of whether a specific reaction can or cannot occur under given conditions of temperature and pressure, the rate at which the reaction will occur has to be determined by following the kinetics of the reaction. This way it will be possible to predict whether a specific chemical combination will cause runaway chemical reaction.



Fig. 7.1 *Hazards associated with materials*

The branch of chemistry that deals with the rates of reactions is called ***chemical kinetics.*** The following aspects are covered in chemical kinetics.

1. Rate of a reaction and rate laws
2. Effect of concentration, temperature, pressure and catalyst on the rate of reaction
3. Mechanism of the reaction. The knowledge of reaction kinetics is of great importance and utility in deciding optimum conditions for all industrial processes.

7.1.1 Rate of a Reaction

Rate of reaction may be defined as the change in the concentration of any one of the reactants or products per unit time. For example, consider the dissociation of PCl_5 to give PCl_3 and Cl_2.

$$\text{Rate of reaction} = \frac{dx}{dt}$$

Since the concentration is usually expressed in moles/litre and time is taken in seconds or minutes, the units of the rate of reaction are moles litre^1 s^{-1} or moles litre^1 min^{-1}.

Rate of a reaction does not remain constant throughout. Hence, we can consider rate of a reaction at a particular instant which is defined as follows.

The rate of a reaction at any time is defined as the change in the concentration of any one of the reactants or products per unit time at that particular instant of time.

7.1.2 Expression of the Rate of a Reaction

Rate of a reaction is changing continuously throughout the course of the reaction; therefore, to state the rate of reaction at any particular instant of time, a small interval of time *dt* may be taken during which the rate of a reaction may be assumed to be almost constant. Suppose *dx* is the small change in concentration of any one of the reactants or products during the small interval of time *dt* (Fig. 7.2). Then the rate of a reaction may be expressed as

$$\text{Rate of reaction} = \frac{dx}{dt}$$

Further, if the rate is expressed in terms of one of the reactants, a negative sign is attached to show that the concentration is decreasing.

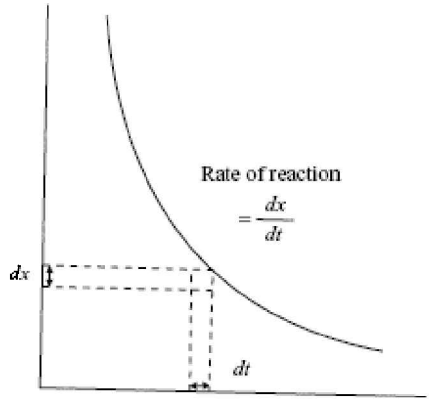


Fig. 7.2 *Expressing Rate of a reaction*

For example, consider the reaction

$$A + B \rightarrow P + Q$$

The rate of this reaction may be expressed in any one of the following ways:

Rate of reaction

$$\left(\frac{dx}{dt}\right) = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = +\frac{dC_P}{dt} = +\frac{dC_Q}{dt}$$

where dC_A and dC_B represent small decrease in the concentrations of A and B respectively and dC_P and dC_Q represent small increase in concentrations of P and Q respectively in the small interval of time dt.

For a more general reaction of the type

$$aA + bB \rightarrow pP + qQ$$

a unique value of the rate of reaction can be obtained by expressing the rate of the reaction as follows:

$$\text{Rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{P}\frac{d[P]}{dt} = +\frac{1}{q}\frac{d[Q]}{dt}$$

Example 1 *For the reaction* $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$, *how is the rate of the reaction expressions* $-\frac{d[H_2]}{dt}$ *and* $\frac{d[NH_3]}{dt}$ *interrelated?*

Solution: $$-\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

7.1.3 Measurement of Rate of a Reaction

In order to measure the rate of a reaction, the concentration of one of the reactants or products is observed at different intervals of time. A common procedure is to withdraw a small amount of the reaction mixture (2 ml or 5 ml) at different intervals of time, cool it down immediately to nearly 0°C to arrest the reaction and then find out the concentration of the reactant or the product by a suitable method, usually by titration against a suitable reagent. When some observable property like volume, pressure, optical rotation, etc., changes with time and can be observed directly at different intervals of time without stopping the reaction, it is preferably utilised. It is important to mention that factors like

temperature which affect the rate of a reaction are kept constant during the kinetic study of the reaction.

If concentration of one of the reactants is studied at different intervals of time and these values are plotted against the corresponding times, a graph of the type shown in Fig. 7.3 is obtained. The rate of a reaction at any time may be obtained. The rate of a reaction at any time may be obtained by the following procedure.

A tangent is drawn on the curve at the point corresponding to the time at which the rate is required (Fig. 7.3). The slope of the tangent will then obviously give the rate of a reaction at that time.

$$\text{Rate} = \tan\theta = \frac{OB}{OA} = \frac{\Delta x}{\Delta t} = -\frac{dx}{dt}$$

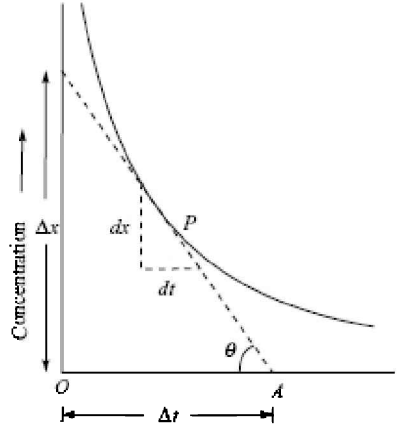


Fig. 7.3 *Graphical method for measurement of the rate of a reaction*

7.2 FACTORS AFFECTING RATE OF A REACTION

The following factors affect the rate of a reaction:

1. Nature of the reactants 2. Concentration and pressure of reactants 3. Temperature 4. Catalyst. These are discussed separately as under:

1. Nature of Reactants Consider the oxidation of ferrous ions and oxalate ions by acidified $KMnO_4$ solution. Both reactions are similar as represented below:

$$MnO_4^- + 8H^+ + 5Fe^{+2} \xrightarrow{\text{Fast}} Mn^{+2} + 5Fe^{+3} + 4H_2O$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{-2} \xrightarrow{\text{Slow}} 2Mn_2^+ + 10CO_2 + 8H_2O$$

At room temperature, the first reaction is very fast whereas the second reaction is quite slow as indicated by the rate of disappearance of pink colour of $KMnO_4$. In fact, in the titrations, the second reaction is so slow that heating is required. Thus, in the above case, even if the same concentrations of similar reactants are taken into the two reactions and the temperature is also kept the same, the rates of these two reactions are still different. This is obviously only due to the difference in the nature of the reducing agents, i.e. Fe^{+2} ions and $C_2O^{-2}_4$ ions.

The difference in the rate may be ascribed to the fact that a reaction involves breaking of the bonds of the reacting molecules and the formation of new bonds in the product molecules. Energy is required for the breaking of bonds and energy is released when a bond is formed. The net energies involved are different for different reactions and hence the rates are different.

2. Concentration of Reactants As a reaction proceeds, the reactants are consumed. Therefore, the concentration of the reactants decreases with the passage of time. It is observed experimentally that the rate of a reaction also decreases as time passes. This shows that the rate of a reaction is directly proportional to the concentration of the reactants. The variation of the concentration of a reactant and hence that of the rate of a reaction with time may be represented graphically as shown in Fig. 7.4.

The effect of concentration is explained on the basis of collision theory of reaction rates. The rate of a reaction depends upon the number of collisions between the molecules. Higher the concentration, greater is the number of collisions.

In the case of gaseous reactions, the rate of a reaction is proportional to the pressure of reacting molecules.

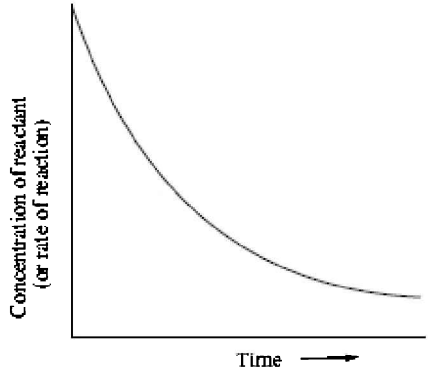


Fig. 7.4 *Variation of concentration of a reactant (or the rate of reaction with time)*

3. Effect of Temperature on the Rate of a Reaction Temperature has a very significant effect on the rate of a reaction. A rise of temperature not only increases the speed of a reaction, in many cases, it actually initiates the reaction. In the study of the effect of temperature on the reaction rates, two types of cases are observed.

(a) For Most Reactions, the Rate of a Reaction Increases with Rise of Temperature As a rough rule, rate of a reaction becomes nearly double or sometimes even treble for every 10°C rise of temperature. This is generally expressed in the form of temperature coefficient as

$$\text{Temperature coefficient} = \frac{k_{(t+10)}}{k_t} \simeq 2 \text{ to } 3$$

where k_t and $k_{(t+10)}$ are the specific reaction rates at $t°C$ where $(t + 10)°C$ respectively. It is really a wonderful observation because the number of collisions increase only by about 2% for 10° rise at ordinary temperatures whereas the reaction velocity may increase by 100% or 200% or even more.

(b) A Large Number of Reactions are Known Which do not Take Place at Room Temperature but Occur Readily at Higher Temperature e.g., reaction between hydrogen and oxygen to form water takes place only when an electric spark is passed. Similarly, it is well known that coal can be kept in oxygen for years without burning but once the ignition is initiated, it goes on till the whole of the coal burns away.

The above observations are explained on the basis of ***collision theory.*** According to this theory, substances react because their molecules collide with each other. All collisions are, however, not effective collisions. An ***effective collision*** is that collision which results into a chemical reaction. In order that a collision may prove effective, the colliding molecules must possess a certain minimum amount of energy called threshold energy. Thus, ***threshold energy may be defined as the minimum***

amount of energy which the colliding molecules must possess in order that the collision between them may be an effective collision.

The two types of cases may be explained as under.

Explanation of the Increase in Reaction Rate with Rise of Temperature The different molecules of the reactants do not possess the same energy. If the energies of the reacting molecules are plotted against the corresponding fractions, at a particular temperature T, a curve of the type shown in Fig. 7.5(a) is obtained (called Maxwell's distribution of energies). In the figure, E_t represents threshold energy. The shaded area represents the fraction of molecules with energies equal to or greater than the threshold energy E_t. As the temperature is increased from t to $(t + 10)°C$, the curve shifts upwards as shown in Fig. 7.5(b). The shaded area beyond E_t now becomes almost double. This shows that the fraction of molecules possessing energy equal to or greater than the threshold energy becomes almost double. Hence, the rate of the reaction also becomes almost double. Hence, the rate of the reaction also becomes almost double.

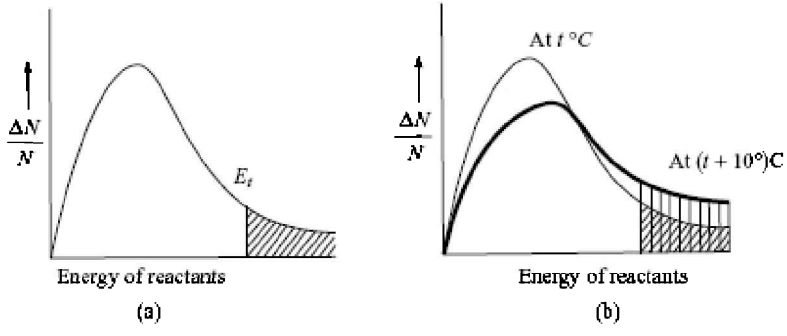


Fig. 7.5 *Distribution energies of reactants*

Explanation of the Non-occurrence of Reactions at Room Temperature and Occurrence at Higher Temperature At room temperature, there are no molecules possessing energy greater than the threshold energy and so there is no reaction. When temperature is increased, the molecules of the reactants absorb heat energy and thus a number of molecules start attaining energy equal to or greater than the threshold energy and hence, the reaction starts.

The extra amount of energy which the molecules of the reactants have to absorb so that their energy becomes equal to the threshold energy is called the activation energy. In other words,

Activation energy = Threshold energy – Energy actually possessed by the reacting molecules

Thus, in order that the reactants may change over to products, they have to absorb some energy and thus cross a barrier called ***activation energy barrier.*** The situation may be represented graphically in Fig. 7.6.

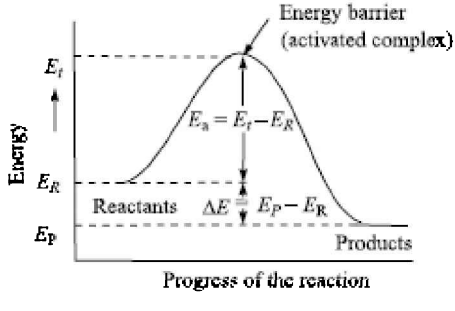


Fig. 7.6 *Illustration of the concept of activation energy*

4. Effect of Catalyst A catalyst is a substance which increases the speed of a reaction without itself undergoing any chemical change. For example, the decomposition of $KClO_3$ is greatly accelerated by the addition of a small quantity of MnO_2 which itself does not undergo any chemical change during the reaction.

The presence of a catalyst provides an alternate path with lower energy barrier as shown in Fig. 7.7

Thus, the energy of activation is lowered and hence a greater number of molecules can cross the barrier and change over to products, thereby increasing rate of the reaction. In activation for the uncatalysed and catalysed reactions respectively, E_t and E_t *(ap)* represent total energy of the activated complex in the two paths.

The following observations are made from Fig. 7.7.

(a) ΔE (= $E_p - E_r$) for the catalysed reaction is the same as ΔE for the uncatalysed reaction

(b) For reversible reactions, the energy of activation for the reverse reaction is lowered to the same extent as for the direct reaction. Hence, the presence of the catalyst in such reactions increases the speed of the forward reaction and that of the backward reaction to the same extent. Consequently, the equilibrium is not disturbed.

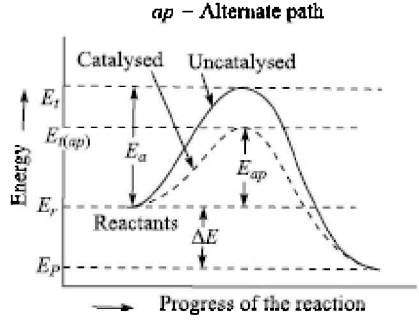


Fig. 7.7 *Effect of addition of a catalyst*

7.3 MOLECULARITY OF A REACTION_

The number of reacting species (atoms, molecules or ions) which collide simultaneously to bring about a chemical reaction is defined as ***molecularity*** of a reaction. Molecularity of a reaction is always a whole number.

When the reaction involves decomposition of a single species, it will be unimolecular reaction. Decomposition of H_2O_2 is a unimolecular reaction.

$$H_2O_2(l) \rightarrow H_2O(l) + 1/2\ O_2(g)$$

Similarly, when the reaction involves collision between *two* species, it will be a ***bimolecular*** reaction and if ***three*** species take part in the collision, it is called trimolecular or termolecular reaction.

Dissociation of HI into H_2 and I_2 is a ***bimolecular reaction***

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

Reaction between NO and O_2 is a ***trimolecular reaction.***

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Reactions involving three or more molecules are uncommon. This is because occurrence of such reactions require simultaneous collisions of three are more molecules. The chances of occurrence of such collisions are very small. Reactions involving three or more molecules are bound to be slow.

The reactions in many cases do not occur in single step but in a sequence of many steps. Each step of the reaction is, however, a simple reaction, i.e. an elementary reaction.

Each step involves the simultaneous collision of two or at the most three molecules. Such type of reaction takes place through a sequence of two or more consecutive steps and are called complex reactions. Each elementary step has a molecularity of its own and none of the steps has a molecularity of more than three.

7.4 RATE LAW AND RATE CONSTANT

Consider the following general reaction:

$$aA + bB \rightarrow \text{Products}$$

Experimentally, it is observed that the rate of this reaction may not depend upon all the a concentration terms of A and all the b concentration terms of B. Suppose, experimentally the rate of the reaction is found to depend upon α concentration terms of A and β concentration terms of B. Then we may write

$$\text{Rate} \propto [A]^{\alpha} \cdot [B]^{\beta}$$
$$\text{Rate} = k[A]^{\alpha} \cdot [B]^{\beta} \quad \ldots(7.1)$$

Equation (7.1) is called ***rate law.***

Here, $[A]$ and $[B]$ are the molar concentrations of A and B respectively and k is a constant called ***velocity constant*** or ***rate constant.*** If all concentrations are taken as unity,

i.e. $[A] = [B] = 1$ mol/litre

then Rate $= k$

Hence, ***the rate constant may be defined as the rate of the reaction when the concentration of each reactant is taken as unity. That is why the rate constant is also called specific reaction rate.***

Order of a Reaction Consider again the reaction:

$$\alpha A + \beta B \rightarrow \text{Products}$$

According to rate law,

$$\text{Rate} = [A]^{\alpha}[B]^{\beta}$$

The sum of concentration terms on which the rate of a reaction actually depends is called the order of the reaction. Thus, in the above case, order of a reaction $= \alpha + \beta$

Hence, the order of a reaction may be defined as the sum of the exponents to which the concentration terms in the rate law are raised to express the observed rate of a reaction.

Depending upon whether $\alpha + \beta$ is equal to 0, 1, 2 or 3, the reactions are said to be of zero order, first order, second order and third order respectively. α and β are called the orders of the reaction with respect to A and B respectively.

Further, it may be mentioned here that the order of a reaction may not be always a whole number.

For example, at 450°C, acetaldehyde decomposes as

$$CH_3CHO \xrightarrow{450°C} CH_4 + CO$$

Experimentally, it is found that

Rate of reaction $\alpha [CH_3CHO]^{1.5}$

$\therefore$ Order of reaction = 1.5

The order of a reaction is generally a small integer but under certain conditions, it can be a fraction or zero. Some reactions of different orders are given below.

Table 7.1 *Orders of reactions*

	Reactions	Conc. Variable	Order
(i)	Decomposition of NH_3 on W, Mo	– –	Zero
(ii)	Decomposition of HI on gold	– –	Zero
(iii)	$N_2O_5(g) \rightarrow N_2O_4(g) + \frac{1}{2} O_2(g)$	$C_{N_2O_5}$	One
(iv)	$2HI(g) \rightarrow H_2(g) + I_2(g)$	C^2_{HI}	Two
(v)	$3KClO \rightarrow KClO_3 + 2KCl$	C^2_{KClO}	Two
(vi)	$2NO + Cl_2 \rightarrow 2NOCl$	$C^2_{NO} \times C_{Cl_2}$	Three
(vii)	$CH_3CHO \xrightarrow{723\ K} CH_4 + CO$	$C^{1.5}_{CH_3CHO}$	1.5

Difference Between Molecularity and Order of a Reaction

Order of reaction is the sum of the powers to which the concentration terms are raised in the rate law. In other words, order of a reaction is a number of reacting species whose concentration determines the rate of the reaction. On the other hand, ***molecularity*** is the total number of reacting species which colloide simultaneously to form the products in an elementary reaction.

The reaction can be unimolecular, for example, the decomposition of ammonium nitrite.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

An example of a bimolecular reaction involving collision between two molecules of the same substance is the decomposition of hydrogen iodide.

$$2HI \rightarrow H_2 + I_2$$

Reactions in which simultaneous collision between three molecules takes place are called trimolecular or termolecular reactions.

For example,

$$2NO + O_2 \rightarrow 2NO_2$$

The probability that more than three species shall collide simultaneously is very small. Hence, molecularity of more than three is not observed.

Therefore, complex reactions in which more than three species appear to be participating in the stoichiometric equation, actually take place in more than one step. Consider the following reaction:

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

This reaction takes place in a number of steps. The molecularity of each step will be different. For complex reactions, molecularity has no meaning.

Consider the decomposition of hydrogen peroxide catalysed by I^- ions in alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline}]{I^-} 2H_2O + O_2$$

The rate equation for this reaction is found to be

$$\text{Rate} = -\frac{d[H_2O_2]}{dt} = k[H_2O_2]\,[I^-]$$

Then, the reaction is of first order with respect to both H_2O_2 and I^-.

The decomposition of H_2O_2 is not an elementary reaction because it does not take place in a single step. Had it been so the reaction would be of second order w.r.t. H_2O (collision between the molecules of H_2O_2). Also, I^- ions appear in the first step of the reaction and do not appear in the overall reaction.

The following mechanism is proposed for the reaction.

(i) $H_2O_2 + I^- \rightarrow H_2O + IO^-$

(ii) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

The first step of the reaction is the rate-determining step. IO^- is an intermediate because it is produced in the first step and consumed in the second step. Decomposition of H_2O_2 is thus a first-order reaction. This reaction can also be studied by titrating H_2O_2 solution with $KMnO_4$ solution.

The order of a single-step reaction or an elementary step of a multistep reaction is the same as its molecularity.

In some cases, one of the reactants is taken in such a large amount that its concentration does not change appreciably in the reaction and has no contribution to the order of a reaction. For example, hydrolysis of ethyl acetate in the presence of dilute mineral acid.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{\text{Acid}} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

The molecularity of the above reaction appears to be ***two*** as it involves a reaction between two reacting species. However, the concentration of only ethyl acetate changes during the reaction while that of water remains unchanged. Thus, rate of the reaction only depends upon the concentration of ethyl acetate.

The order of reaction, therefore, is one. The reaction appears to be of the second order but it follows first-order kinetics. Such types of reactions are called ***pseudo unimolecular reactions.***

Table 7.2 *Difference between molecularity and orders of reactions*

	Molecularity	Order of Reaction
1.	Molecularity is the number of reacting species which undergo simultaneous collisions in the elementary or simple reactions.	It is the sum of powers of the concentration terms in the rate law equation.
2.	It is always a whole number.	It can be a whole number as well as fraction.
3.	It is a theoretical concept.	It can be determined experimentally.
4.	It can never be zero.	It can be zero.
5.	It has no significance for a complex reaction and can be expressed for each elementary step in case of a complex reaction.	It is always the same for the overall reaction whether the reaction is complex or simple.

Example 2 *A reaction is second order in A and first order in B.*

(a) Write the differential rate equation.

(b) How is the rate affected on increase in the concentration of A three times?

(c) How is the rate affected when the concentrations of both A and B are doubled?

Solution: (a) It is given that the reaction is second order in *A* and first order in *B*. Therefore, the differential rate equation is

$$\frac{dx}{dt} = k[A]^2\,[B]$$

(b) When the concentration of A is increased three times, A becomes $3A$. The rate will be given by

$$\text{Rate} = k\,[3A]^2\,[B] = 9k\,[A]^2\,[B]$$

i.e., the rate will increase 9 times.

(c) On doubling the concentration of both A and B, A becomes $2A$ and B becomes $2B$. The rate equation will be given by

$$\text{Rate} = k\,[2A]^2\,[2B] = 8k\,[A]^2\,[B]$$

i.e., the rate will increase 8 times.

PROBLEM FOR PRACTICE

1. In a reaction if the concentration of the reactant A is tripled, the rate of the reaction becomes twenty-seven times. What is the order of the reaction.

[Ans. 3]

Example 3 *For the thermal decomposition of acetaldehyde at 800 K,*

$$CH_3CHO \rightarrow CH_4 + CO$$

the following data is obtained:

Experiment	C_{CH_3CHO}	*Rate of decomposition*
(i)	$0.1\ mol\ L^{-1}$	$9.0 - 10^{-7}\ mol\ L^{-1}\ sec^{-1}$
(ii)	$0.2\ mol\ L^{-1}$	$36 \times 10^{-7}\ mol\ L^{-1}\ sec^{-1}$
(iii)	$0.4\ mol\ L^{-1}$	$144 \times 10^{-7}\ mol\ L^{-1}\ sec^{-1}$

(a) What is the order of reaction?

(b) Write rate of equation for the reaction.

(c) Calculate the rate constant at 800 K.

Solution: Let the rate law for the decomposition of acetaldehyde be

$$r = k\,C^{a}_{CH_3CHO}$$

(a) The following equation can be generated from experiments (i) and (ii):

$$9.0 \times 10^{-7} = k(0.1)^a \quad \ldots(i)$$

and

$$36 \times 10^{-7} = k(0.2)^a \quad \ldots(ii)$$

Dividing (ii) by (i), $\dfrac{36 \times 10^{-7}}{9.0 \times 10^{-7}} = \left(\dfrac{0.2}{0.1}\right)^a$

$$4 = 2^a \quad \text{or} \quad 2^2 = 2^a \therefore a = 2$$

(b) The rate equation for the reaction is

$$\text{Rate} = \frac{dx}{dt} = k\,C^{2}_{CH_3CHO}$$

(c) Rate constant k is given by $k = \dfrac{r}{C^2_{CH_3CHO}}$

Substituting the data of the experiment (i), we get

$$\therefore \quad k = \frac{9.0 \times 10^{-7}}{(0.1)^2} = 9.0 \times 10^{-5} \quad \text{or} \quad k = 9.0 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$$

PROBLEM FOR PRACTICE

1. A reaction is of second order with respect to a reactant. How is the rate affected if the concentration of the reaction is (a) doubled? (b) reduced to half?

[Ans. (a) The rate increases four times. (b) The rate is reduced to one-fourth.]

7.5 ZERO-ORDER REACTION

A reaction is said to be of zero order if the rate of the reaction is independent of the concentration of all the reactants.

For such reactions, the rate of the reaction remains constant throughout.

The following reactions are found to be of zero order:

1. Photochemical Reactions Such reactions have been found to be of zero order. For example, the combination between hydrogen and chloride presence of light may be studied by enclosing these gases in a tube and inverting the tube in a trough of water (Fig. 7.8). When the reaction takes place between H_2 and Cl_2, HCl is formed which dissolves into water and the level of water in the tube rises. Thus, though the quantities of H_2 and Cl_2 decrease, their amounts per unit volume remain the same or the concentrations of H_2 and Cl_2 remain constant.

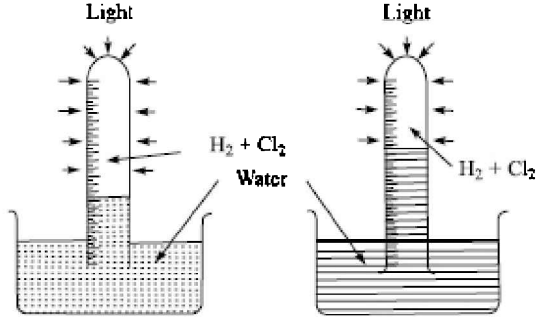


Fig. 7.8 *Study of kinetics of a photochemical reaction*

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

2. Heterogeneous Reactions Two well- known examples of this type are (a) the decomposition of hydrogen iodide on the surface of gold, and (b) the decomposition of ammonia on the surface of tungsten, molybdenum or platinum at high temperatures. The gaseous molecules of the reacting substance get absorbed on the surface of the catalyst. The surface is thus fully occupied with the molecules of the reactant. Some of these molecules react to form the products but immediately new molecules take up their position and thus the concentration of the reacting molecules remains constant on the surface and hence the rate of reaction remains constant irrespective of the total amount of the gaseous reactants taken initially.

7.5.1 Rate Equation for Zero-Order Reaction

If a is the initial concentration and $(a - x)$ is the concentration after the time t, the expression for the rate of a reaction of zero order may be written as follows:

$$\frac{dx}{dt} \propto (a-x)^0 \text{ or } \frac{dx}{dt} = k(a-x)^0$$

or

$$\frac{dx}{dt} = k \qquad \text{(anything raised to the power zero is equal to zero)}$$

or rate of reaction remains constant (equal to k) throughout where k is the rate constant for the zero-order reaction.

The above expression may be written as

$$dx = kdt$$

Integrating this equation, we get

$$x = kt + I$$

where I is the constant of integration.

When $t = 0$, $x = 0$; therefore, $I = 0$

Hence, $$x = kt$$

i.e., the amount of substance reacted $\propto$ time.

The expression for the half-life period (i.e. the time taken for half the reaction to complete) may be obtained as follows.

When

$$x = \frac{a}{2}, \quad t = t_{1/2}$$

Substituting these values in the equation above, we get

$$\frac{a}{2} = kt_{1/2} \quad \text{or} \quad t_{1/2} = \frac{a}{2k}$$

i.e., the half-life period $\propto$ initial concentration.

Example 4 *Determine the order of reaction and the rate constant of the decomposition of NH_3 on a tungsten wire at 857°C from the following data.*

Total Pressure (P) torr	*228*	*250*	*273*	*318*
Time (t) seconds	*200*	*400*	*600*	*1000*

Solution: The rate of the reaction will be the rate of change of pressure, i.e.,

$$\text{Rate} = \frac{\Delta P}{\Delta t}$$

From the above data

ΔP	22	45	90
Δt	200	400	800

$\Delta P/\Delta t$	0.1100	0.1125	0.1125

It is obvious that

$$\text{Rate} = \frac{\Delta P}{\Delta t} = \text{constant } (k) = 0.1117$$

It indicates that the rate of reaction does not depend on the partial pressure of the reactant.
∴ the reaction is of zero order.

The specific reaction rate

$$k = 0.1117 \text{ torr } s^{-1}$$

Example 5 *The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?*

Solution: For a zero order reaction,

$$kt = x \qquad \ldots \text{(i)}$$

where x is the amount that undergoes the change.

Substituting the values in the rate equation,

$$0.003 \times t = 0.10 - 0.075 = 0.025$$

or
$$t = \frac{0.025}{0.003} = 8.33 \ s$$

Example 6 *Derive an expression to calculate the time required for completion of a zero-order reaction.*

Solution: For a zero-order reaction,

$$kt = x \quad \text{or} \quad kt = a - (a - x)$$

For the completion of the reaction $(a - x) = 0$

$$\therefore \qquad kt = a \qquad \text{or} \qquad t = \frac{a}{k}$$

PROBLEM FOR PRACTICE

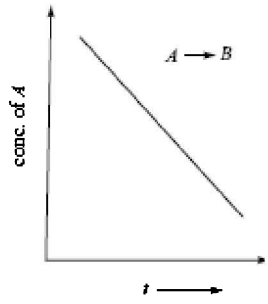
1. For a general reaction $A \rightarrow B$, plot of concentration of A vs. time is given in the figure below. Answer the following questions on the basis of the graph

   (a) What is the order of the reaction?

   (b) What is the slope of the curve?

   (c) What are the units of rate constant?

[Ans. (a) Zero (b) Slope = $-k$ (c) mol L^{-1} s^{-1}]



7.6 FIRST-ORDER REACTION

A reaction is said to be of the first order if the rate of the reaction depends upon one concentration term only.

Let us consider a hypothetical case.

$$A \rightarrow \text{Product}$$

Suppose we start with a moles per litre of the reactant A. After time t, suppose x moles per litre of it have decomposed. Therefore, the concentration of A after time $t = (a - x)$ moles per litre. Then according to the law of mass action,

Rate of reaction $\propto (a - x)$

i.e. $$\frac{dx}{dt} \propto (a - x)$$

or $$\frac{dx}{dt} = k(a - x) \qquad (7.2)$$

where k is called the ***rate constant*** or the ***specific reaction rate*** for the reaction of first order.

The expression for the rate constant k may be derived as follows:

Equation (7.2) may be rewritten in the form

$$\frac{dx}{a - x} = k\,dt \qquad \ldots(7.3)$$

Integrating Eq. (7.3) we get

$$\int \frac{dx}{a - x} = \int k\,dt$$

i.e $$-\ln(a - x) = kt + I \qquad \ldots(7.4)$$

where I is a constant of integration.

In the beginning when $t = 0$, $x = 0$ (as no substance has decomposed at the start of the reaction),

$$-\ln(a - 0) = k \times 0 + I$$

or $$-\ln a = I \qquad \ldots(7.5)$$

Substituting this value of I in Eq. (7.4), we get

$$-\ln(a-x) = -kt + (-\ln a)$$

or
$$kt = \ln a - \ln(a-x)$$
$$= \ln \frac{a}{(a-x)}$$

or
$$k = \frac{1}{t} \ln \frac{a}{a-x} \quad \ldots (7.6a)$$

or
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad \ldots (7.6b)$$

Equation (7.6b) is sometimes written in another form which is obtained as follows:

If the initial concentration is C_o and the concentration after time t is C_t then putting $a = C_o$ and $(a - x) = C_t$, Eq. (7.6b) becomes

$$k = \frac{2.303}{t} \log \frac{C_o}{C_t} \quad (7.6c)$$

When the initial concentration is not known, the value of k can be calculated as follows:

From Eq. (7.6b),

i.e.
$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

or
$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

or
$$t = \frac{2.303}{k} \log a - \frac{2.303}{k} \log (a-x)$$

Let $(a - x_1)$ be the concentration of the reactant at time t_1 and $(a - x_2)$ be the concentration of the reactant time t_2.

$$t_2 = \frac{2.303}{k} \log a - \frac{2.303}{k} \log (a-x_2) \quad \ldots (7.7)$$

$$t_1 = \frac{2.303}{k} \log a - \frac{2.303}{k} \log (a-x_1) \quad \ldots (7.8)$$

Subtracting (7.8) from (7.7), we get,

$$(t_2 - t_1) = \frac{2.303}{k} \log (a-x_1) - \frac{2.303}{k} \log (a-x_2)$$

$$(t_2 - t_1) = \frac{2.303}{k} \log \frac{(a-x_1)}{(a-x_2)}$$

$$k = \frac{2.303}{(t_2 - t_1)} \log \frac{(a-x_1)}{(a-x_2)}$$

7.6.1 Units of First-Order Rate Constant (k)

As the value of k, i.e. the rate constant for the first-order reaction depends upon the ratio $\frac{C_o}{C}$ or $\frac{a}{a-x}$, i.e. the ratio of the two concentration terms, the value k will be independent of the units in which the concentration of the reactants is expressed. It has the dimension of reciprocal time, i.e., t^{-1}. If time is measured in seconds, k will be expressed in the unit s^{-1}.

7.6.2 Some Characteristics of First-Order Reactions

1. Any reaction of the first order must obey equations (7.6) or (7.6a). This may be tested by the following method.

Substitution Method Starting with a known concentration a, the concentration of the reactant ($a - x$) at different intervals of time may be noted. For every value of t, the corresponding value of ($a - x$), may be substituted in Eq. (7.6). It the values of k thus obtained are nearly constant (within experimental error), the reaction is of the first order.

2. The time taken for any fraction of the reaction to be completed is independent of the initial concentration. For example, let us test this statement for half the reaction to be completed. Writing the first-order equation,

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

When half the reaction is completed, $x = a/2$. Representing the time taken for half the reaction to be completed by $t_{1/2}$, the above equation becomes

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - a/2} = \frac{2.303}{k} \log 2 = \frac{0.693}{k} \qquad \ldots(7.9)$$

Thus, a does not appear in this equation so that $t_{1/2}$ is independent of a. Similarly, it can be seen that $t_{1/3}$, $t_{2/3}$, etc., will also be independent of the initial concentration.

The time taken for half of its original value is called ***half-life-period*** of ***the reaction.***

3. ***The units of*** **k** ***are independent of the units in which the concentrations are expressed.*** This is obvious from Eq. (7.6) because in this equation k depends upon the ratio of two concentrations, viz. $\frac{a}{a - x}$ and the time t. Thus, so long as both a and ($a - x$) are expressed in the same concentration units, the value of k is not affected. The unit of k, however, depends only upon the units, of time t.

7.6.3 Examples of First-Order Reactions

1. Decomposition of nitrogen peroxide
2. Decomposition of hydrogen peroxide
3. Decomposition of diazonium chloride ($C_6H_5N = NCl$) in water
4. Conversion of *N*-chloroacetanilide into *p*-chloroacetanilide
5. Inversion of cane sugar
6. Hydrolysis of ethyl acetate in acidic medium
7. Thermal decomposition of Azo isopropane

The kinetics of the above reactions are discussed separately as under:

1. Decomposition of Nitrogen Pentoxide Nitrogen pentoxide is a volatile solid which decomposes in the gaseous state as well as in the form of its solution in an inert solvent like carbon tetrachloride or chloroform according to the equation

$$N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2} O_2$$
$$\Updownarrow$$
$$2NO_2$$

When the reaction is carried out in solution, N_2O_4 and NO_2 remain in the solution and the volume of

oxygen gas collected is noted at different intervals of time (Fig. 7.9). It can be observed that

$$\left.\begin{array}{l}\text{Volume of oxygen gas collected}\\ \text{at any time}(V_t)\end{array}\right\} \propto \text{Amount of } N_2O_5 \text{ decomposed}(x)$$

i.e., $$x \propto V_t$$

$$\left.\begin{array}{l}\text{Volume of oxygen gas}\\ \text{collected at infinite time}(V_\infty)\end{array}\right\} \propto \text{Amount of } N_2O_5 \text{ initially taken (a)}$$

i.e., $$a \propto V_\infty$$

Substituting these values in the first-order equation, viz.

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

we get

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

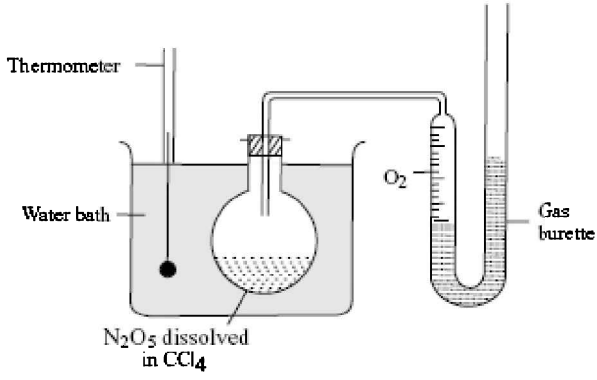


Fig. 7.9 *Apparatus for monitoring the volume of O_2 evolved in the decomposition of N_2O_5 dissolved in carbon tetrachloride*

Example 7 *From the following data for the decomposition of N_2O_5 in carbon tetrachloride solution at 48°C, show that the reaction is of the first order and calculate the rate constant.*

Time (in minutes):	*10*	*15*	*20*	*25*	*∞*
Vol. of O_2 evolved (in ml):	*6.30*	*8.95*	*11.40*	*13.50*	*34.75*

Solution: If the reaction is of the first order, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$= \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

In the present case, V_∞ = 34.75 ml

The value of k at each time can be calculated as follows:

Time (min)	V_t	$V_\infty - V_t$	$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$ (min^{-1})
10	6.30	34.75 – 6.30 = 28.45	$k = \frac{2.303}{10}\log\frac{34.75}{28.45} = 0.01997$
15	8.95	34.75 – 8.05 = 25.80	$k = \frac{2.303}{15}\log\frac{34.75}{25.80} = 0.01985$
20	11.40	34.75 – 11.40 = 23.35	$k = \frac{2.303}{20}\log\frac{34.75}{23.35} = 0.01987$

Since the value of k comes out to be nearly constant, the given reaction is of the first order. The average value of the rate constant = 0.01989 min^{-1}

Example 8 *The decomposition of an aqueous solution of ammonium nitrite was studied by placing the apparatus in a thermostat maintained at a particular temperature. The volume of nitrogen gas collected at different intervals of time was as follows:*

Time (minutes)	*10*	*15*	*20*	*25*	*∞*
Vol. of N_2 (ml)	*6.25*	*9.00*	*11.40*	*13.65*	*35.05*

From the above data, prove that the reaction is of the first order.

Solution: Ammonium nitrite decomposes as follows:

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Volume of nitrogen produced is observed after different intervals of time.

Vol. of N_2 at any time $\propto x$

Vol. of N_2 after infinite time $\propto a$

Substitute the values in the equation below:

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

In the present case, V_∞ = 35.05 ml

The value of k after each time can be calculated as follows:

Time (min)	V_t	$V_\infty - V_t$	$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$ (min^{-1})
10	6.25	35.05 – 6.25 = 28.80	$k = \frac{2.303}{10}\log\frac{35.05}{28.80} = 0.0196$
15	9.00	35.05 – 9.00 = 26.05	$k = \frac{2.303}{15}\log\frac{35.05}{26.05} = 0.0198$
20	11.40	35.05 – 11.40 = 23.65	$k = \frac{2.303}{15}\log\frac{35.05}{26.05} = 0.0196$

Since the value of k comes out to be nearly constant, the given reaction is of first order.

2. Decomposition of Hydrogen Peroxide The decomposition of hydrogen peroxide in aqueous solution takes place according to the equation

$$H_2O_2 \xrightarrow{Pt} H_2O + 1/2\ O_2$$

The kinetics of this reaction may be studied by making use of the fact that H_2O_2 solution can be titrated against $KMnO_4$ solution. Thus, by withdrawing equal amounts of the solution (usually 5 ml) at regular intervals of time and titrating against the $KMnO_4$ solution, the amount of H_2O_2 present can be found everytime. It is obvious that **for the same volume of the reaction solution withdrawn,**

Volume of $KMnO_4$ solution used before the commencement of the reaction, i.e., at zero time (V_o) $\propto$ Initial concentration of H_2O_2 (a)

i.e. $V_o \propto a$

Volume of $KMnO_4$ solution used $\propto$ Amount of H_2O_2 present at any instant of time t (V_t) at that instant, i.e. $(a - x)$

i.e., $V_t \propto (a - x)$

Substituting these values in the first-order equation, we get

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

or

$$k = \frac{2.303}{t} \log \frac{V_o}{V_t}$$

The decomposition of hydrogen peroxide as tested by applying this equation is found to be of the first order.

Example 9 *From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order.*

t (min)	*0*	*10*	*20*
V (ml)	*46.5*	*29.8*	*19.3*

Here, t is the time in minutes and V is the volume of standard $KMnO_4$ solution required for titrating the same volume of the reaction mixture.

Solution: Volume of $KMnO_4$ solution used $\propto$ Amount of H_2O_2 present. Hence, if the given reaction is of the first order, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{V_o}{V_t}$$

In the present case, $V_o = 46.1$

The value of k at each instant can be calculated as follows:

t (min)	V_t	$k = \frac{2.303}{t} \log \frac{V_o}{V_t}$
10	29.8	$k = \frac{2.303}{10} \log \frac{46.1}{29.8} = 0.0436\ \text{min}^{-1}$
20	19.3	$k = \frac{2.303}{10} \log \frac{46.1}{19.3} = 0.0435\ \text{min}^{-1}$

Thus, the value of k comes out to be nearly constant. Hence, it is a reaction of the first order.

3. Decomposition of Benzene Diazonium Chloride (C_6H_5N = NCl) in Water Benzene dia-zonium chloride decomposes in water according to the following reaction:

$$\underset{\text{Benzene diazonium chloride}}{C_6H_5N = NCl} + H_2O \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

The progress of the reaction is studied by measuring the volume of N_2 produced by the decomposition of benzene diazonium at different intervals of time.

The volume of N_2 librated is proportional to the decrease in concentration of benzene diazonium chloride.

Let V_∞ be the volume of N_2 measured at the end of the reaction and V_t be the volume at any time t. Then,

$$a \propto V_\infty$$
$$(a - x) \propto (V_\infty - V_t)$$

Substituting the values of a and $(a - x)$ in Eq.(7.6), we get

$$k = \frac{2.303}{t} \log \frac{V_\infty}{(V_\infty - V_t)}$$

Example 10 *Benzene diazonium chloride in aqueous solution decomposes according to the equation*

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

Starting with an initial concentration of 10 g/litre, the volume of N_2 gas obtained at 50°C at different intervals of time was found to be as under:

t (min):	*6*	*12*	*18*	*24*	*30*	*∞*
Vol. of N_2 (ml):	*19.3*	*32.6*	*41.3*	*46.5*	*50.4*	*58.3*

Show that the above reaction follows the first-order kinetics. What is the value of the rate constant?

Solution: lf the given reaction follows first-order kinetics, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

In this case,

Volume of N_2 obtained at infinite time $V_\infty \propto a$

Volume of N_2 obtained at any time (t) $V_t \propto x$

$$\therefore \quad \frac{a}{a - x} \propto \frac{V_\infty}{V_\infty - V_t} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

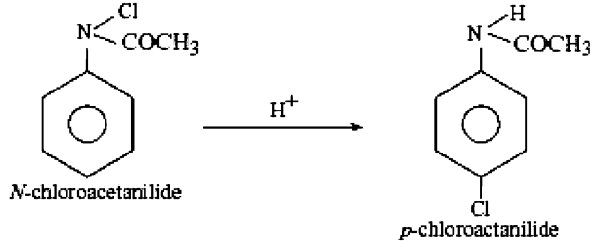
In the present case, V_∞ = 58.3 ml

The value of k after each time can be calculated as follows:

Time (min)	V_t	$V_\infty - V_t$	$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$
6	19.3	58.3 – 19.3 = 39.0	$k = \frac{2.303}{6} \log \frac{58.3}{39.0} = 0.0670\ \text{min}^{-1}$
12	32.6	58.3 – 32.6 = 25.7	$k = \frac{2.303}{12} \log \frac{58.3}{25.7} = 0.0683\ \text{min}^{-1}$
18	41.3	58.3 – 41.3 = 17.0	$k = \frac{2.303}{12} \log \frac{58.3}{17.0} = 0.0685\ \text{min}^{-1}$
24	46.5	58.3 – 46.5 = 11.8	$k = \frac{2.303}{12} \log \frac{58.3}{11.8} = 0.0666\ \text{min}^{-1}$

Since the value of k comes out to be nearly constant, the reaction is of the first order. The mean value of k = 0.0676 min^{-1}

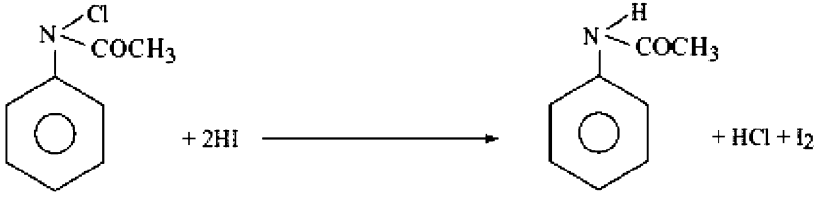
4. Conversion of N-chloroacetanilide into p-chloroacetanilide This conversion reaction may be represented as under:



N-chloroacetanilide reacts with KI in the presence of the acid to give iodine whereas *p*-chloroacetanilide does not.

The reactions take place as follows:

$$2KI + H_2SO_4 \rightarrow K_2SO_4 + 2HI$$



The iodine thus liberated can be found by titration against a standard hypo solution using starch as indicator. For the same volume of the reaction solution withdrawn at different times,

$$\left.\begin{matrix}\text{Volume of hypo}\\ \text{solution used in}\\ \text{the beginning, i.e.}\\ \text{at time } t-0 (V_o)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of } I_2\\ \text{liberated at}\\ \text{that stage}\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of N-chloro}\\ \text{acetanilide present}\\ \text{initially } (a)\end{matrix}\right\}$$

or
$$V_o \propto a$$

$$\left.\begin{matrix}\text{Volume of hypo}\\ \text{solution used at}\\ \text{any instant of}\\ \text{time } t\ (V_t)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of } I_2\\ \text{liberated at}\\ \text{that stage}\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of N-chloro}\\ \text{acetanilide present}\\ \text{at that instant of time } (a-x)\end{matrix}\right\}$$

$$V_t \propto (a-x)$$

Hence, for the above reaction,

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{V_o}{V_t}$$

Example 11 *In acidic solution, N-chloroacetanilide changes into p-chloroacetanilide. The former can be estimated volumetrically by withdrawing a definite volume of the reaction mixture adding KI and titrating the iodine liberated against hypo solution. The following results were obtained in a particular experiment:*

Time (hours):	*0*	*1*	*2*	*3*	*4*	*∞*
Hypo sol. used (ml):	*49.3*	*35.6*	*25.8*	*18.5*	*13.8*	*0.0*

Show that the above data conforms to the first-order reaction.

Solution:

Volume of hypo solution used ∝ amount of *N*-chloroacetanilide present.

Hence, if the reaction is of the first order, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

As $V_o \propto a$ and $V_t \propto (a - \text{x})$, we have

$$k = \frac{2.303}{t} \log \frac{V_o}{V_t}$$

In the present case,

V_o = 49.3 ml

The value of *k* at different instants may be calculated as follows:

t (hours)	V_t	$k = \frac{2.303}{t} \log \frac{V_o}{V_t}$
1	35.6	$k = \frac{2.303}{1} \log \frac{49.3}{35.6} = 0.3256\ hr^{-1}$
2	25.8	$k = \frac{2.303}{2} \log \frac{49.3}{25.8} = 0.3238\ hr^{-1}$
3	18.5	$k = \frac{2.303}{3} \log \frac{49.3}{18.5} = 0.3267\ hr^{-1}$
4	13.8	$k = \frac{2.303}{4} \log \frac{49.3}{13.8} = 0.3183\ hr^{-1}$

Since the value of k comes out to be nearly constant, the reaction is of the first order.

5. Inversion of Cane Sugar The hydrolysis of sucrose in presence of a mineral acid takes place according to the equation

$$\underset{\text{Sucrose (dextro-rotatory)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose (dextro-rotatory)}}{C_6H_{12}O_6} + \underset{\text{Fructose (laevo-rotatory)}}{C_6H_{12}O_6}$$

A noteworthy point is that sucrose is dextro-rotatory whereas the products, glucose and fructose, are dextro-rotatory and laevo-rotatory respectively. Further, the laevo-rotation of fructose is more (-92°) than the dextro-rotation of glucose (+52.5°) so that the mixture as a whole is laevo rotatory. Thus, on hydrolysis, the dextro-rotatory sucrose gradually changes into the laevo-rotatory mixture.

It is for this reason that the reaction is called ***inversion of sucrose.***

The kinetics of the above reaction is studied by noting the angle of rotation at different intervals of time with the help of a polarimeter.

Suppose

Reading of the polarimeter at zero time = r_o

Reading of the polarimeter at any time $t = r_t$

Reading of the polarimeter at infinite time = r_∞

(i.e., after 24 hours or more)

It is evident that the reading at zero time will be positive and it would decrease with the passage of time, pass through zero and ultimately become negative.

$$\left.\begin{matrix}\text{Angle of rotation at any} \\ \text{instant of time } (r_o - r_t)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{The amount of sucrose} \\ \text{hydrolysed } (x)\end{matrix}\right.$$

i.e., $$x \propto (r_o - r_t) \qquad \ldots(7.10)$$

$$\left.\begin{matrix}\text{Angle of rotation} \\ \text{at infinte } (r_o - r_\infty)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{The initial concentration} \\ \text{of scurose } (a)\end{matrix}\right.$$

i.e., $$a \propto (r_o - r_\infty) \qquad \ldots(7.11)$$

From results (7.10) and (7.11), we have

$$(a - x) \propto (r_o - r_\infty) - (r_o - r_t)$$

i.e. $$(a - x) \propto (r_t - r_\infty)$$

Substituting the values of a and $(a - x)$ from equations (ii) and (iii) in the first order equation,

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

We have

$$k = \frac{2.303}{t} \log \frac{r_o - r_\infty}{r_t - r_\infty}$$

Example 12 *The inversion of cane sugar was studied in 0.9 N HCl at 25°C. The following Polarimetrie readings were obtained at different intervals of time:*

Time (minutes):	*0.0*	*7.18*	*18.00*	*27.05*	*∞*
Reading (degrees):	*+24.09*	*+21.41*	*+17.74*	*+15.00*	*10.74*

Solution: If the reaction is of the first order, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{r_o - r_\infty}{r_t - r_\infty}$$

In the present case,

$$r_o = 24.09 \qquad r_\infty = 10.74$$

$$\therefore \qquad r_o - r_\infty = +24.09 - (-10.74) = 34.83$$

The values of k at different instants may be calculated as under:

t(min)	r_t	$r_t - r_\infty$	$k = \frac{2.303}{t} \log \frac{r_o - r_\infty}{r_t - r_\infty}$
7.18	+21.41	21.41 – (–10.74) = 32.15	$k = \frac{2.303}{7.18} \log \frac{34.83}{32.15} = 0.01116$
18.00	+17.74	17.74 – (–10.74) = 28.48	$k = \frac{2.303}{18.00} \log \frac{34.83}{28.48} = 0.01118$
27.05	+15.00	15.00 – (–10.74) = 25.74	$k = \frac{2.303}{27.05} \log \frac{34.83}{25.74} = 0.01119$

The constant value of k proves that the reaction is of the first order.

6. Hydrolysis of Ethyl Acetate in Acidic Medium Hydrolysis of ethyl acetate in acidic medium may be represented as under:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

In this reaction, acetic acid is one of the products, the amount of which can be found by titration against standard NaOH solution. But being an acid-catalysed reaction, the acid present originally as a catalyst also reacts with NaOH solution. Hence, for the same volume of reaction mixture withdrawn at different times,

$$\left.\begin{array}{l}\text{Volume of NaOH solution} \\ \text{used in the beginning, i.e.,} \\ \text{at zero time } (V_o)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Amount of acid present} \\ \text{only as catalyst as} \\ \text{no } CH_3COOH \text{ is produced at } t = 0\end{array}\right. \qquad \ldots(7.12)$$

$$\left.\begin{matrix}\text{Volume of NaOH}\\ \text{solution used at any}\\ \text{instant of time } t\ (V_t)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of acid present}\\ \text{as catalyst + Amount of}\\ CH_3COOH \text{ produced}\end{matrix}\right. \quad \ldots(7.13)$$

Combining results (7.12) and (7.13), we find that

$$\left.\begin{matrix}\text{Amount of } CH_3COOH\\ \text{produced at any}\\ \text{instant of time}\end{matrix}\right\} \propto (V_t - V_o) \quad \ldots(7.14)$$

$$\left.\begin{matrix}\text{But amount of } CH_3COOH\\ \text{produced at any}\\ \text{instant of time}\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of } CH_3COOC_2H_5\\ \text{that has reacted } (x)\end{matrix}\right.$$

Hence

$$(V_t - V_o) \propto x \quad \ldots(7.15)$$

Further,

$$\left.\begin{matrix}\text{Volume of NaOH solution}\\ \text{used after the reaction}\\ \text{has taken place for a}\\ \text{long time, called}\\ \text{infinite time } (V_\infty)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of acid present}\\ \text{as catalyst + Max.}\\ \text{amount of } CH_3COOH\\ \text{produced}\end{matrix}\right. \quad \ldots(7.16)$$

Combining results (7.12) and (7.16), we find that max. amount of CH_3COOH produced $\propto (V_\infty - V_o)$

$$\left.\begin{matrix}\text{But max. amount of}\\ CH_3COOH \text{ produced}\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Initial concentration of}\\ CH_3COOC_2H_5\ (a)\end{matrix}\right.$$

Hence

$$(V_\infty - V_o) \propto a \quad \ldots(7.17)$$

From equations (7.15) and (7.17), we have

$$(a - x) \propto (V_\infty - V_o) - (V_t - V_o)$$

or

$$(a - x) \propto (V_\infty - V_t) \quad \ldots(7.18)$$

Substituting the values of a and $(a - x)$ from equations (7.17) and (7.18) in the first-order equation,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

we have

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t}$$

Example 13 *1.0 ml of ethyl acetate was added to 25 ml of N/2 HCl. 2 ml of the mixture were withdrawn from time to time during the progress of the hydrolysis of the ester and titrated against standard NaOH.*

The amount of NaOH required for titration at various intervals is given below:

Time (min):	*0*	*20*	*75*	*119*	*183*	*∞*
NaOH used (ml):	*20.24*	*21.73*	*25.20*	*27.60*	*30.22*	*43.95*

The value at infinite time was obtained by completing the hydrolysis on boiling. Show that it is a reaction of the first order and find the average value of the velocity constant.

Solution: Amount of NaOH used at $t = 0$

i.e. $(V_o) \propto$ HCl Present.

Amount of NaOH used at any time t

i.e. $(V_t) \propto$ HCl present + CH_3COOH formed.

CH_3COOH formed at any time $\propto$ ethyl acetate reacted

$$(V_t - V_o) \propto x$$

Amount of NaOH used at time $t = \infty$

i.e. $(V_\infty) \propto$ HCl present + Max CH_3COOH formed

Max. CH_3COOH formed $\propto$ Initial conc. of ethyl acetate, i.e. $(V_\infty - V_,) \propto a$

Hence, it the given reaction is of the first order, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t}$$

In the present case $V_o = 20.24$ ml

$$V_\infty = 43.95 \text{ ml}$$

$$\therefore \quad V_\infty - V_o = 43.95 - 20.24 = 23.71 \text{ ml}$$

The value of k at different instants can be calculated as follows:

t (min)	V_t	$V_\infty - V_t$	$k = \frac{2.303}{t} \log \frac{V_\infty - V_o}{V_\infty - V_t}$
20	21.73	43.95 – 21.73 = 22.22	$k = \frac{2.303}{20} \log \frac{23.71}{22.22} = 0.00324$
75	25.20	43.95 – 25.20 = 18.75	$k = \frac{2.303}{75} \log \frac{23.71}{18.75} = 0.00313$
119	27.60	43.95 – 27.60 = 16.35	$k = \frac{2.303}{119} \log \frac{23.71}{16.35} = 0.00312$
183	30.22	43.95 – 30.32 = 13.73	$k = \frac{2.303}{183} \log \frac{23.71}{13.73} = 0.00299$

Since the value of k comes out to be nearly constant, it is a reaction of the first order. The average value of $k = 0.00312 \text{ min}^{-1}$.

7. Thermal Decomposition of Azo-isopropane Azo-isopropane decomposes on heating to form hexane and N_2 according to the equation

$$\underset{\text{Azo-ispropane}}{(CH_3)_2 CHN = NCH (CH_3)_2} \xrightarrow{(250-290^\circ C)} \underset{\text{Hexane}}{C_6H_{14}} + N_2$$

The reaction is of first order. It is a homogeneous reaction because all the reactants and the

products are present in the gaseous state. The progress of the reaction can be studied by measuring the pressure of the reaction mixture at different intervals of time. From the values of the pressure at different intervals of time, we can calculate the rate (k) constant for the reaction.

Let the initial pressure of azo-isopropane be P_o, and P be the total pressure of the reaction system.

Let p be the decrease in pressure of azo-isopropane at time t and P_A be the pressure of azo-isopropane.

For every molecule of azo-isopropane that decomposes, 1 molecule of N_2 and 1 molecule of hexane (C_6H_{14}) are produced. As a result, the pressure increases with the passage of time. At each stage of the reaction, pressure of azo-isopropane, i.e. $P_A = (P_o - p)$. p is the decrease in pressure of azo-isopropane, the pressure of each of N_2 and C_6H_{14} increases and will be p. The total pressure of the system is given by the sum of partial pressures of azo-isopropane ***(P_A)***, nitrogen ***(P_{N_2})*** and hexane ($P_{C_6H_{14}}$),

i.e.
$$P = P_A + P_{N_2} + P_{C_6H_{14}}$$
$$= (P_o - p) + p + p \qquad \ldots(7.19)$$
$$P = P_o + p \qquad \ldots(7.20)$$
$$[\because P_{N_2} = P_{C_6H_{14}} = p \text{ and } P_A = (P_o - p)]$$

Now from (7.20), $p = (P - P_o)$

But $P_A = P_o - p \qquad \ldots(7.21)$

Substituting from (7.21) the value of p, we get

$$P_A = P_o - (P - P_o) = 2P_o - P \qquad \ldots(7.22)$$

$\therefore$ $P_A = 2P_o - P$

The initial concentration of azo-isopropane, i.e. P_o, will be proportional to a and P_A, i.e. concentration of azo-isopropane left after the time t will be proportional to $(a - x)$,

i.e.
$$a \propto P_o$$
$$(a - x) \propto P_A \quad \text{or} \quad (a - x) \propto (2P_o - P)$$

Substituting the values of a and $(a - x)$ in first order equation, we get

$$k = \frac{2.303}{t} \log \frac{P_o}{P_A}$$

$$\boxed{k = \frac{2.303}{t} \log \frac{P_o}{2(P_o - P)}}$$

Example 14 *Decomposition of azo-isopropane is represented as*

$$\underset{\text{Azo-isopropane}}{(CH_3)_2CHN = NCH(CH_3)_2} \xrightarrow{270°C} \underset{\text{Hexane}}{N_2 + C_6H_{14}}$$

as studied at 270°C. The following results were obtained:

Time (t) in seconds	*0*	*200*	*400*	*1050*
Pressure P_A in mm of Hg	*36.00*	*47.42*	*55.21*	*67.14*

Show by using the above data that the thermal decomposition of azo-isopropane is a reaction of the first order.

Solution: For the thermal decomposition of azo-isoprane, the rate constant k is given by

$$k = \frac{2.303}{t} \log \frac{P_o}{2P_o - P}$$

Here, P_o = 36.00 so that $2P_o$ = 72.00

The value of rate constant k at different intervals of time can be determined as follows.

Time t (seconds)	$P_{(mm)}$	$2P_o - P$	$k = \frac{2.303}{t} \log \frac{P_o}{2P_o - P}$
200	47.42	24.50	$k = 1.908 \times 10^{-3}$
500	55.21	16.79	$k = 1.907 \times 10^{-3}$
1050	67.14	4.86	$k = 1.907 \times 10^{-3}$

The constancy in the value of k indicates that the thermal decomposition of azo-isopropane is a reaction of the first order.

Example 15 *A first-order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?*

Solution:

(a) For the first-order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

when $x = \frac{40}{100} a = 0.4\,a$

and $t = 50$ minutes

Then $$k = \frac{2.303}{50} \log \frac{a}{a - 0.4\,a} = \frac{2.303}{50} \log \frac{1}{0.6}$$ $\mathbf{k = 0.010216\ min^{-1}}$

(b) $t = ?$

when $x = 0.8\,a$

$k = 0.010216\ min^{-1}$ (Calculated above)

$$\therefore \quad t = \frac{2.303}{k} \log \frac{a}{a - x} = \frac{2.303}{0.010216} \log \frac{a}{a - 0.8\,a} = \frac{2.303}{0.010216} \log \frac{1}{0.2} = \mathbf{157.58\ min}$$

Example 16 *At 100°C, the half-life period for the thermal decomposition of N_2O_5 is 4.6 seconds and is independent of the initial pressure of N_2O_5. Calculate the specific rate constant at this temperature.*

Solution: Since the half-life period is independent of the initial pressure, this shows that the reaction is of the ***first order.***

Hence, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

For half life period, $t = t_{1/2}$, $x = a/2$

$$\therefore \quad k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - a/2} = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303}{4.6} (0.3010) = 0.1507\ s^{-1}$$

Example 17 *Show that in case of a first-order reaction, the time required for 99.9% of the reaction to take place is about ten times that required for half the reaction.*

Solution: Time for half changes is worked out as under:

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - a/2} = \frac{2.303}{k} \log 2 \frac{2.303}{k} (0.3010)$$

Time for 99.9% change is worked out as under

$$t_{99.9\%} = \frac{2.303}{k} \log \frac{a}{a - 0.999\,a} = \frac{2.303}{k} \log 10^3 = \frac{2.303}{k} \times 3$$

$$\frac{t_{99.9\%}}{t_{1/2}} = \frac{2.303}{k} \times 3 \times \frac{k}{2.303 \times 0.3010} = \frac{3}{0.3010} \approx 10$$

Example 18 *A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$ for this reaction.*

Solution: Use the equation for first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \qquad \ldots(i)$$

30% decomposition means $(a - x) = 0.7 \times a$

Substituting the values in eq. (i), we have

$$k = \frac{2.303}{40} \log \frac{10}{7} \text{ min}^{-1}$$

$$= \frac{2.303}{40} \times 0.1548 \text{ min}^{-1} = 8.913 \times 10^{-3} \text{ min}^{-1}$$

To calculate $t_{1/2}$, use the relation

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.913 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$$

Example 19 *A first order gas reaction $A_2B_2(g) \rightarrow 2A(g)$ at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4}\ s^{-1}$. What percentage of A_2B_2 is decomposed on heating for 900 seconds?*

Solution: For the first order reaction, use the relation:

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

Given that $k = 2.0 \times 10^{-4}\ s^{-1}$ and $t = 900$ s

Substituting the values in the first order equation, we have

$$2.0 \times 10^{-4} = \frac{2.303}{900} \log \frac{a}{a - x}$$

or $$\log \frac{a}{a-x} = \frac{2.0 \times 10^{-4} \times 900}{2.303}$$

or $$\log \frac{a}{a-x} = 0.0781$$

Taking antilogs, we have

$$\frac{a}{a-x} = 1.197 \quad \text{or} \quad \frac{a-x}{a} = 0.08354$$

or $$1 - \frac{x}{a} = 0.8354 \quad \text{or} \quad \frac{x}{a} = 0.1646$$

Percentage of A_2B_2 decomposed = 0.1646 × 100 = 16.46

Example 20 *The reaction*

$$SO_2Cl_2 \xrightarrow{k_1} SO_2 + Cl_2$$

is a first-order reaction with $k_1 = 2.2 \times 10^{-5}\ s^{-1}$ at 302°C. What percentage of SO_2Cl_2 will get decomposed in 90 minutes when the reaction is carried out at 302°C?

Solution: Since the reaction is of the first order (given),

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Here, we are given that

$$k = 2.3 \times 10^{-5}\ s^{-1}$$

$$t = 90 \text{ minutes} = 90 \times 60 = 5400 \text{ seconds}$$

$\therefore$ $$2.2 \times 10^{-5} = \frac{2.303}{5400} \log \frac{a}{a-x} \quad \text{or} \quad \log \frac{a}{a-x} = 0.0516$$

or $$\frac{a}{a-x} = \text{antilog } (0.0516) = 1.127 \quad \text{or} \quad a = 1.127\,a - 1.127\,x$$

or $$0.127\,a = 1.127\,x$$

$\therefore$ $$\frac{x}{a} = \frac{0.127}{1.127} = 0.113 = 11.3\%$$

PROBLEMS FOR PRACTICE

1. Rate constant for a first-order reaction has been found to be $2.54 \times 10^{-3}\ s^{-1}$. Calculate the three-fourth life.

[Ans. 5.46×10^2 s]

2. The thermal decomposion of HCO_2H is a first-order reaction with a rate constant of $2.4 \times 10^{-3}\ s^{-1}$ at a certain temperature. Calculate how long will it take for three-fourth of the initial quantity of HCO_2H to decompose [log 0.25 = –0.6021]

[Ans. 578 seconds]

3. In a first-order reaction, the concentration of the reactant is reduced from 0.6 mol L^{-1} to 0.2 mol L^{-1} in S minutes. Calculate the rate constant of the reaction.

[Ans. $k = 0.2198$]

4. Sucrose decomposes in acid solution into glucose and fructose according to first-order rate law with $t_{1/2} = 3$ hours. Calculate the fraction of sucrose which remains after 8 hours.

[Ans. 0.1576]

5. The reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is a first order reaction with half life 3.15×10^4 s at 320°C. What percentage of SO_2Cl_2 would be decomposed on heating at 320°C for 90 minutes?

[Ans. 11.2%]

7.7 RADIOACTIVE DECAY AS A FIRST-ORDER PHENOMENON

Radioactive substances emit α, β and γ particles. The mass of the substance decreases continuously as a result of decay. It has been found that radioactive decay follows first-order kinetics. The rate constant in the case of nuclear decay in called *decay constant.*

Example 21 *The radioactive decay of atomic nucleus is a first-order reaction. The half-life period of radium, i.e.* $_{88}Ra^{226}$ *is 1590 years. What is decay constant?*

Solution: We know that for the first-order reaction, half-life period is given by

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1590} = 0.000435849 \text{ yr}^{-1}$$

7.8 SECOND-ORDER REACTION

A reaction is said to be of the second order if the rate of reaction depends upon two concentration terms.

Case 1: When only one reactant is involved

The general equation for a reaction involving one reactant is

$$2A \rightarrow \text{Products}$$

Suppose the initial concentration of $A = a$ moles/litre

Decrease in the concentration of A at any instant of time = x moles/litre

$\therefore$ concentration of A at the instant of time

$$t = (a - x) \text{ mole/litre}$$

Applying the law of mass action, the rate of reaction may be written as

$$\frac{dx}{dt} \propto [A]^2$$

$$\propto (a - x)^2$$

or

$$\frac{dx}{dt} = k(a - x)^2 \qquad \ldots(7.23)$$

where k is the rate constant for the second-order reaction.

Equation (7.23) may be rewritten as

$$\frac{dx}{(a-x)^2} = k\,dt$$

Integrating this equation, we get

$$\int \frac{dx}{(a-x)^2} = \int k\,dt$$

i.e., $$\frac{(a-x)^{-1}}{-1} \times (-1) = kt + I$$

or $$\frac{1}{(a-x)} = kt + I \qquad \ldots(7.24)$$

where I is the constant of integration. In the beginning, i.e. at time $t = 0$, $x = 0$ (as no substance has reacted at zero time). Putting these values in Eq. (7.24), we get

$$\frac{1}{a} = I$$

Substituting this value of I in Eq. (7.24), we get

$$\frac{1}{(a-x)} = kt + \frac{1}{a}$$

$$kt = \frac{1}{(a-x)} - \frac{1}{a} \qquad \ldots(7.25)$$

$$= \frac{a-(a-x)}{a(a-x)} = \frac{x}{a(a-x)}$$

$$k = \frac{1}{t}\frac{x}{a(a-x)} \qquad \ldots(7.26a)$$

If the initial concentration is written as C_o and concentration at any instant of time t as C_t then $a = C_o$, and $(a - x) = C_t$, Substituting these values in Eq. (7.25), we get

$$k = \frac{1}{t}\left[\frac{1}{C_t} - \frac{1}{C_o}\right] \qquad \ldots(7.26b)$$

This is another form of the expression for the rate constant of a second-order reaction.

Case II: When two different reactants with different initial concentrations are involved

The general equation for such reaction is

$$A + B \rightarrow \text{Products}$$

Suppose the initial concentration of $A = a$ moles/litre, the initial concentration of $B = b$ moles/litre, amount of A that reacts in time $t = x$ moles/litre then the amount of B that would react in the same time would also be x moles/litre.

$\therefore$ at any instant of time t,

$$\text{concentration of } A = (a-x) \text{ moles/litre}$$
$$\text{and concentration of } B = (b-x) \text{ moles/litre}$$

Applying the law of mass action, we get

$$\text{Rate of reaction}, \frac{dx}{dt} \propto [A][B]$$

$$\propto (a-x)(b-x)$$

or
$$\frac{dx}{dt} = k(a-x)(b-x) \quad \ldots (7.27)$$

where k is the rate constant.
Equation (7.27) may be rewritten as

$$\frac{dx}{(a-x)(b-x)} = k dt \quad \ldots (7.28)$$

Resolving the left-hand side into partial fractions, Eq. (7.28) may be rewritten as

$$\frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right] dx = k dt$$

Integrating this equation, we get

$$\frac{1}{(a-b)}\left(\int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)}\right) = \int k\, dt$$

or
$$\frac{1}{(a-b)}\left[-\ln(b-x) - \{-\ln(a-x)\}\right] = kt + I$$

or
$$\frac{1}{(a-b)}\left[\ln(a-x) - \ln(b-x)\right] = kt + I$$

or
$$\frac{1}{(a-b)}\left(\ln\frac{a-x}{b-x}\right) = kt + I \quad \ldots (7.29)$$

where I is the constant of integration.
But at $t = 0$, $x = 0$. Putting these values in Eq. (7.29), we get

$$\frac{1}{(a-b)}\left(\ln\frac{a}{b}\right) = I \quad \ldots (7.30)$$

Putting this value in Eq. (7.29), we get

$$\frac{1}{(a-b)}\ln\frac{a-x}{b-x} = kt + \frac{1}{(a-b)}\ln\frac{a}{b}$$

or
$$kt = \frac{1}{(a-b)}\ln\frac{a-x}{b-x} - \frac{1}{(a-b)}\ln\frac{a}{b}$$

$$= \frac{1}{(a-b)}\left[\ln\frac{a-x}{b-x} - \ln\frac{a}{b}\right]$$

$$= \frac{1}{(a-b)}\ln\left(\frac{a-x}{b-x} \times \left(\frac{b}{a}\right)\right)$$

or
$$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)} \quad \ldots (7.31)$$

Example 22 *What would be the units of rate constant in the following rate law:*

$$Rate = k[A][B]$$

if the concentration is expressed in moles per litre and time in seconds?

Solution: For a second-order reaction,

$$k = \frac{1}{t}\frac{x}{a(a-x)} = \frac{1}{\text{time}} \times \frac{\text{concentration}}{\text{concentration} \times \text{concentration}}$$

or

$$k = \frac{1}{\text{time} \times \text{concentration}}$$

Substituting for the units of time and concentration,

$$k = \frac{1}{s \times \text{mol litre}^{-1}} = \text{litre mol}^{-1}\ \text{s}^{-1}$$

7.8.1 Some Characteristics of Second-Order Reactions

A second order reaction has the following characteristics:

1. Any Reaction of the Second Order Must Obey the Equation

$$k = \frac{1}{t}\frac{x}{a(a-x)}$$

If on substituting the values of t, x, a and $(a - x)$, constant values of k are obtained, it means the reaction is of second order.

Graphical method can also be used.

We may use the second-order equation in the form

$$kt = \frac{1}{C_t} - \frac{1}{C_o}$$

or

$$\frac{1}{C_t} = kt + \frac{1}{C_o}$$

This equation is like $y = mx + c$, i.e. the equation of a straight line. Hence, a plot of $\frac{1}{C_t}$ vs. t should be a straight line if the reaction is of the second order (Fig. 7.10). The slope of the line will directly give the value of k.

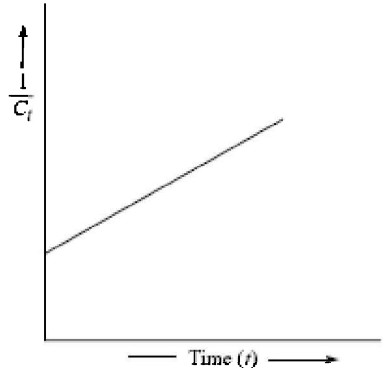


Fig. 7.10 *Plot of* $\frac{1}{C_t}$ *vs t*

2. Time Taken for Any Fraction of the Reaction to be Completed is Inversely Proportional to the Initial Concentration As an example, let us calculate the time taken for half of the reaction to be completed (i.e. half-life period). Time taken for half the reaction to be completed is represented by $t_{1/2}$. Thus, when $x = a/2$, $t = t_{1/2}$. Putting these values in the equation for second-order reaction, we get

$$t_{1/2} = \frac{1}{k}\frac{a/2}{a(a-a/2)} = \frac{1}{k}\cdot\frac{1}{a}$$

i.e., $$t_{1/2} \propto \frac{1}{a}$$

Similarly, it can be seen that for any fraction of the reaction to be completed, the time taken $\propto \frac{1}{a}$,

3. Units of the Rate Constant k Depend not only Upon the Units of Time but Also upon the Units in Which the Concentrations are Expressed This is obvious because there is one extra concentration term in the denominator in the equation for a second-order reaction.

$$k = \frac{1}{t}\frac{x}{a(a-x)} = \frac{1}{\text{time}}\cdot\frac{\text{concentration}}{\text{concentration}\times\text{concentration}}$$

$$= \frac{1}{\text{concentration}\times\text{time}}$$

Thus, the units of k for second-order reaction are $\text{conc}^{-1}\ \text{time}^{-1}$.

7.8.2 Examples of Second-Order Reactions

1. Gaseous Reactions There are many reactions which occur in the gaseous state and are kinetically of the second order, e.g.

(a) Conversion of O_3 into O_2 at 100°C

$$2O_3(g) \xrightarrow{100°C} 3O_2(g)$$

(b) Thermal decomposition of N_2O

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

(c) Thermal decomposition of Cl_2O to Cl_2 and O_2 at 200°C

$$2Cl_2O(g) \xrightarrow{200°C} 2Cl_2(g) + O_2(g)$$

(d) Thermal decomposition of acetaldehyde at 518°C

2. Reactions Taking Place in Solutions

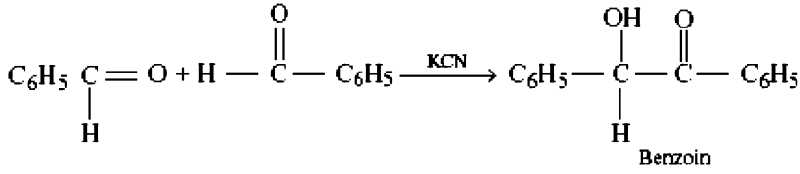
(a) Conversion of ammonium cyanate to form urea

$$\underset{\text{Amm. Cyanate}}{NH_4CNO} \longrightarrow \underset{\text{urea}}{H_2N-\overset{\overset{O}{\|}}{C}-NH_2}$$

(b) Saponification of esters

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

(c) Benzoin condensation



7.8.3 Kinetics of Thermal Decomposition of Acetaldehyde

The thermal decomposition of acetaldehyde vapour takes place according to the equation

$$CH_3CHO \xrightarrow{791\,K} CH_4 + CO$$

From this equation, the reaction appears to be of the first order but experimentally it has been found to be of second order and hence, it is preferably written as

$$2CH_3CHO \rightarrow 2CH_4 + 2CO$$

As the reactants and products are all gaseous, the progress of the reaction is studied by simply noting the pressure of the reaction mixture at different intervals of time. Further, as one molecule of acetaldehyde on decomposition produces two molecules (one of CH_4 and the other of CO), the pressure increases as reaction progresses. It is obvious that

$$\left.\begin{matrix}\text{Pressure in the beginning} \\ \text{i.e. at zero time, } (P_o)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Initial concentration} \\ \text{of acetaldehyde } (a)\end{matrix}\right.$$

i.e. $$a \propto P_o \qquad \ldots(7.32)$$

At any other instant of time t, the total pressure of the reaction mixture (P_t) will be given by

$$P_t = P_{CH_3CHO} + P_{CH_4} + P_{CO} \qquad \ldots(7.33)$$

If at this instant of time, p is the decrease in pressure of CH_3CHO then p will increase in the pressure of each of CH_4 and CO that we have :

$$\begin{aligned} P_{CH_3CHO} &= P_o - p \qquad \ldots(7.34) \\ P_{CH_4} &= p \\ P_{CO} &= p \end{aligned}$$

Substituting these values in Eq. (7.33), we get

$$\begin{aligned} P_t &= (P_o - p) + p + p \\ &= P_o + p \\ p &= P_t - P_o \qquad \ldots(7.35) \end{aligned}$$

or $$\left.\begin{matrix}\text{But decrease in the} \\ \text{pressure of acetaldehyde } (P)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Acetaldehyde} \\ \text{decomposed } (x)\end{matrix}\right.$$

i.e $$x \propto p \qquad \ldots(7.36)$$

Combing this result with Eq. (7.35), we get

$$x \propto P_t - P_o \qquad \ldots(7.37)$$

From Eq. (7.32),

$$a \propto P_o$$

$\therefore$ $$a - x \propto P_o - (P_t - P_o)$$

or $$(a - x) \propto 2P_o - P_t$$

Substituting these values in the second-order equation,

$$k = \frac{1}{t}\frac{x}{a(a-x)} = \frac{1}{t}\frac{P_t - P_o}{P_o(2P_o - P_t)}$$

Example 23 *The thermal decomposition of acetaldehyde was studied by Hinshelwood and Hutchison at 518°C. Starting with an initial pressure at 363 mm of Hg, the following results were obtained at different intervals of time.*

t (seconds):	*42*	*73*	*105*	*190*
Increase in pressure, ΔP (mm):	*34*	*54*	*74*	*114*

Show that the reaction is of the second order.

Solution: If the reaction is of second order, it must obey the equation

$$k = \frac{1}{t}\frac{P_t - P_o}{P_o(2P_o - P_t)}$$

Here, we are given that

P_o = 363 mm of Hg

ΔP means $P_t - P_o$

The value of k at different intervals may be calculated:

t (seconds)	$P_t - P_o$	$2P_o - P_t = P_o - (P_t - P_o)$	$k = \frac{1}{t}\frac{P_t - P_o}{P_o(2P_o - P_t)}$
42	34	363–34 = 329	$k = \frac{1}{42} \times \frac{34}{363 \times 329} = 6.79 \times 10^{-6}$
73	54	363–54 = 309	$k = \frac{1}{73} \times \frac{54}{363 \times 309} = 6.59 \times 10^{-6}$
105	74	363–74 = 289	$k = \frac{1}{105} \times \frac{74}{363 \times 289} = 6.71 \times 10^{-6}$
190	114	363–114 = 249	$k = \frac{1}{190} \times \frac{114}{363 \times 249} = 6.64 \times 10^{-6}$

The constancy in the value of k shows the reaction to be of second order.

7.8.4 Saponification (Alkaline Hydrolysis) of Esters

The reaction of esters with sodium hydroxide solution is called saponification of esters. For example, the reaction of ethyl acetate with sodium hydroxide solution takes place as follows:

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \rightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

This is a reaction of second order. The reaction involves NaOH as one of the reactants, the concentration of which decreases as the reaction progresses. Starting with known concentration of ethyl acetate and sodium hydroxide (preferably equal concentrations), the concentration of NaOH at any instant of time can be found by withdrawing a definite amount of the reaction mixture and titrating against a standard acid. It is obvious that for the same volume of the reaction mixture withdrawn at different intervals of time,

$$\left.\begin{array}{l}\text{Volume of the standard}\\ \text{acid used at the beginning}\\ \text{of the experiment, i.e. at}\\ \text{zero time } (V_o)\end{array}\right\} \propto \left\{\begin{array}{l}\text{Initial concentration}\\ \text{of NaOH } (a)\end{array}\right.$$

i.e., $$a \propto V_o \qquad \ldots(7.38)$$

$$\left.\begin{array}{l}\text{Volume of the standard}\\ \text{acid solution used at any}\\ \text{instant of time } t, (V_t)\end{array}\right\} \propto \left\{\begin{array}{l}\text{concentration of}\\ \text{NaOH at that instant, i.e. } (a-x)\end{array}\right.$$

i.e., $$(a-x) \propto V_t \qquad \ldots(7.39)$$

From equations (7.38) and (7.39) we get

$$x \propto V_o - V_t \qquad \ldots(7.40)$$

Substituting the values of a, x and $(a - x)$ from equations (7.38), (7.39) and (7.40) in the second-order equation,

$$k = \frac{1}{t}\frac{x}{a(a-x)}$$

we have

$$k = \frac{1}{t}\frac{(V_o - V_t)}{V_o V_t}$$

Example 24 *Starting with equal concentration of ethyl acetate and sodium hydroxide, the saponification of ethyl acetate was carried out. The same volume of the reaction mixture was withdrawn at different intervals of time and titrated with the same acid. The following data were obtained:*

Time (min)	*0*	*5*	*15*	*25*
Acid used (ml)	*16*	*10.24*	*6.13*	*4.32*

Show that the reaction is of the second order.

Solution: If the reaction is of the second order, it must obey the equation

$$k = \frac{1}{t}\frac{x}{a(a-x)} = \frac{1}{t}\frac{(V_o - V_t)}{V_o V_t}$$

In the present case, V_o = 16 ml

The value of k at different instants of time can be calculated as follows:

t (min)	V_t	$(V_o - V_t)$	$k = \frac{1}{t}\frac{(V_o - V_t)}{V_o V_t}$
5	10.24	5.76	$k = \frac{1}{5} \times \frac{5.76}{16 \times 10.24} = 0.00703$
15	6.13	9.87	$k = \frac{1}{15} \times \frac{9.87}{16 \times 6.13} = 0.00671$
25	4.32	11.68	$k = \frac{1}{25} \times \frac{11.68}{16 \times 4.32} = 0.00676$

Thus, the value of k is fairly constant. The reaction is of the second order.

Example 25 *Decomposition of a gas is of second order. It takes 40 minutes for 40% of a gas to be decomposed when its initial concentration is 4×10^{-2} mole/litre. Calculate the specific reaction rate.*

Solution: For a second-order reaction,

$$k = \frac{1}{t}\frac{x}{a(a-x)} \text{ Given that } a = 4 \times 10^{-2} \text{ mole/litre, } t = 40 \text{ minutes}$$

$$x = \frac{40}{100} \times a = 0.4 \text{ a}$$

Substituting the values in the above formula, we get

$$k = \frac{1}{40} \times \frac{0.4a}{a(a-0.4a)} = \frac{1}{40} \times \frac{0.4}{0.6a} = \frac{1}{40} \times \frac{0.4}{0.6 \times 4 \times 10^{-2}}$$

$$= \mathbf{0.4167 \text{ litre mol}^{-1} \text{ min}^{-1}}$$

Example 26 *A second-order reaction in which the initial concentrations of both the reactions are same is 25% complete in 600 seconds. How long will it take for the reaction to go to 75% completion?*

Solution: For a second-order reaction,

$$k = \frac{1}{t}\frac{x}{a(a-x)}$$

For the first case, $x = \frac{25}{100}a = 0.25a$ and $t = 600$ s

$$\therefore \quad k = \frac{1}{600} \times \frac{0.25a}{a(a-0.25a)} = \frac{1}{600} \times \frac{0.25}{0.75a} = \frac{1}{1800a}$$

For the second case, $x = \frac{75}{100}a = 0.75\,a$, t = To be calculated

$$\therefore \quad k = \frac{1}{t} \times \frac{0.75a}{a(a-0.75a)} = \frac{1}{t} \times \frac{0.75a}{0.25a} = \frac{3}{ta}$$

But $k = \frac{1}{1800a}$ (from the first case)

$$\therefore \quad \frac{1}{1800a} = \frac{3}{ta} \quad \text{or} \quad t = 3 \times 1800 = 5400 \text{ sec}$$

7.9 THIRD-ORDER REACTION

A reaction is said to be of the third order if the rate of reaction depends upon three concentration terms.

The simplest case of this type can be represented as

$$3A \rightarrow \text{Products}$$

The expression for the rate constant of such a reaction may be derived as follows:

Suppose a is the initial concentrations of A and x is the decrease in the concentration of A in time t.

Then the concentration of A after time $t = (a - x)$. Now, according to the law of mass action, the rate of the above reaction at the instant of time t will be given by

$$\frac{dx}{dt} \propto [A]^3$$

i.e., $$\frac{dx}{dt} \propto (a-x)^3$$

or $$\frac{dx}{dt} = k(a-x)^3 \qquad \ldots(7.41)$$

where k is the rate constant for the third-order reaction.

Equation (7.41) may be rewritten as

$$\frac{dx}{(a-x)^3} = k\,dt$$

Integrating this equation, we get

$$\int \frac{dx}{(a-x)^3} = \int k\,dt$$

i.e. $$\frac{(a-x)^{-2}}{-2} \times (-1) = kt + I$$

where I is the constant of integration.

Now at $t = 0$, $x = 0$

Putting these values in Eq. (7.41), we get

$$\frac{1}{2a^2} = I \qquad \ldots(7.42)$$

Substituting this value in Eq. (7.42), we get

$$\frac{1}{2(a-x)^2} = kt + \frac{1}{2a^2}$$

or

$$kt - \frac{1}{2(a-x)2} - \frac{1}{2a^2} = \frac{1}{2}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

$$= \frac{1}{2}\left[\frac{a^2-(a-x)^2}{a^2(a-x)^2}\right] = \frac{1}{2}\left[\frac{a^2-(a^2+x^2-2ax)}{a^2(a-x)^2}\right]$$

$$= \frac{1}{2}\left[\frac{2ax-x^2}{a^2(a-x)^2}\right] = \frac{1}{2}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$$

or

$$k = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] \qquad \ldots(7.43)$$

Replacing a by C_o (i.e. initial concentration of A and x by $C_o - C_t$ (i.e. decrease in the concentration of A), Eq. (7.43) may be rewritten as

$$k = \frac{1}{2t}\left[\frac{(C_o-C_t)(2C_o-C_o+C_t)}{C_o^2(C_o-C_o+C_t)^2}\right]$$

$$k = \frac{1}{2t}\frac{(C_o-C_t)(C_o+C_t)}{C_o^2C_t^2} = \frac{1}{2t}\frac{C_o^2-C_t^2}{C_o^2C_t^2}$$

$$k = \frac{1}{2t}\left[\frac{1}{C_t^2} - \frac{1}{C_o^2}\right]$$

7.9.1 Characteristics of Third-Order Reactions

Characteristics of third order reactions are discussed as under:

1. A reaction is of the Third Order if it Obeys the Equation

$$k = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] \qquad \ldots(7.44)$$

Thus, on substituting the values of t, x and a, constant values of k must be obtained.

2. Time Taken for any Fraction of the Reaction to be Completed is Inversely Proportional to the Square of the Initial Concentration For example, the time taken for half of the reaction to be completed (i.e. half period) may be calculated as follows:

when

$$x = \frac{a}{2}, \quad t = t_{1/2}$$

Putting these values in Eq. (7.44), we get

$$t_{1/2} = \frac{1}{2k}\left\{\frac{\frac{a}{2}\left(2a - \frac{a}{2}\right)}{a^2\left(a - \frac{a}{2}\right)^2}\right\} \text{ or } t_{1/2} = \frac{1}{2k}\left\{\frac{\frac{a}{2}, \frac{3a}{2}}{a^2 - \frac{a^2}{4}}\right\}$$

or

$$t_{1/2} = \frac{1}{2k}\frac{3}{a^2} \text{ or } t_{1/2} \propto \frac{1}{a^2}$$

3. Units of the Rate Constant k Depend Upon the Units of the Concentration This may be seen by calculating the dimensions of with the help of equation for third order:

$$k = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] = \frac{1}{\text{time}}\left[\frac{\text{concentration} \times \text{concentration}}{(\text{concentration})^2 \times (\text{concentration})^2}\right]$$

$$= \frac{1}{\text{Time}}\frac{1}{(\text{concentration})^2}$$

Thus, any change in the unit of concentration will change the value of *k*.

4. Some Examples of Third-Order Reactions Five reactions in gaseous phase, each involving nitric oxide as one of the reactions are known to be third-order reactions:

(a) $2NO + Cl_2 \longrightarrow 2NOCl$

(b) $2NO + Br_2 \longrightarrow 2NOBr$

(c) $2NO + O_2 \longrightarrow 2NO_2$

(d) $2NO + H_2 \longrightarrow N_2O + H_2O$

(e) $2NO + D_2 \longrightarrow N_2O + D_2O$

Reduction of ferric chloride by stannous chloride is an example of third-order reaction in solution

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

Why are the Reactions of Higher Order Rare? This may be explained on the basis of ***collision theory.*** According to this theory, in order that a reaction may take place between certain molecules, these molecules must come together simultaneously to collide with each other. As the probability for three molecules to come together simultaneously and collide are less than those for two molecules, the reactions of third order are fewer than those of second order. Similarly, the chances for four or more molecules to come together simultaneously and collide are still less (Fig. 7.11); hence the reactions of fourth or higher order are very rare.

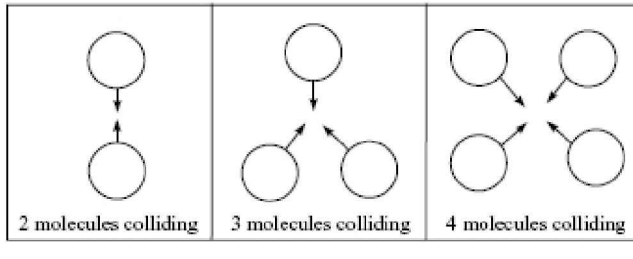


Fig. 7.11 *Chances of collision between reactingmolecules decrease as the molecularity increases.*

7.10 RELATIONS BETWEEN HALF-LIFE PERIOD AND ORDER OF A REACTION

The relations between half-life period and order of a reaction are described as under:

1. For Reactions of Zero Order

$$kt = x \quad \text{when} \quad t = t_{1/2},\ x = \frac{a}{2}$$

$$\therefore \qquad t_{1/2} = \frac{a}{2k} \text{ or } t_{1/2} \propto a$$

i.e. half-life period is directly proportional to the initial concentration.

2. For Reactions of the First Order

$$t_{1/2} = \frac{2.303}{k} \log 2$$

$$= \frac{2.303}{k}(0.3010) = \frac{0.693}{k}$$

i.e. half-life period is independent of the initial concentration.
For reactions of the second order,

$$t_{1/2} \propto \frac{1}{a}$$

i.e. half-life period is inversely proportional to the initial concentration.

3. For Reactions of Third Order

$$t_{1/2} \propto \frac{1}{a^2}$$

i.e. half-life period is inversely proportional to the square of the initial concentration.
In general, for a reaction of the *n* th order

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

7.11 FORMULATION OF MECHANISM OF A REACTION

A series of step reactions, proposed to account for the overall reaction is called the mechanism of the reaction.

The writing of step reactions is usually based upon experimental evidence. The slowest step (called the rate-determining step) must involve the molecules on which the rate of reaction actually depends as observed experimentally. The following examples will illustrate the point more clearly.

1. Bromination of Propanone (Acetone) The bromination of propane in dilute aqueous solution is represented by the equation

$$CH_3COOCH_3 + Br_2 \rightarrow CH_3COCH_2Br + HBr$$

Experimentally, it is found that

Rate of reaction $\propto [CH_3COCH_3]$ only (and is independent of the concentration of bromine)

Hence, the rate-determining step (slow step) would involve a molecule of acetone only. The suggested steps are as follows:

(a) $CH_3COCH_3 \xrightarrow{\text{Slow}} CH_3 - \underset{\underset{OH}{|}}{C} = CH_2$

Ketonic form — Enolic form

(b) $CH_2 - \underset{\underset{OH}{|}}{C} = CH_2 + Br_2 \xrightarrow{\text{Fast}} CH_3COCH_2Br + HBr$

2. Thermal Decomposition of Dinitrogen Peroxide The balanced equation may be written as

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

However, according to the rate law, it is found that

$$\text{Rate or reaction} = k\,[N_2O_5]$$

Hence, the above reaction must be split into steps in such a way that the slowest step should involve only one molecule of N_2O_5.

Thus, the probable mechanism is as follows:

$$N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3$$

$$N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$$

Hence, the above reaction is a ***reaction of the first order.***

3. Combination of NO_2 and F_2 to form NO_2F.

The Reaction may be Represented as

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

Experimentally, it is found that

$$\text{Rate of reaction} = k[NO_2]\,[F_2]$$

i.e. the rate law equation involves only one molecule of NO_2 and one molecule of F_2. Hence, the probable mechanism is as follows:

$$NO_2 + F_2 \xrightarrow{\text{Slow}} NO_2F + F$$

$$NO_2 + F \xrightarrow{\text{Fast}} NO_2F$$

Hence, the above reaction must be a ***reaction of the second order.***

4. Reduction of Nitric Oxide with Hydrogen The reaction

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

The rate law equation is found to be

$$\text{Rate}\left(\frac{dx}{dt}\right) = k[NO]^2\,[H_2]$$

This suggests that the reaction is of the third order and the rate-determining step (slow step) should involve two molecules of NO and one molecule of H2. Thus, the following mechanism has been proposed:

$$2NO + H_2 \xrightarrow{\text{Slow}} N_2 + H_2O_2$$
$$H_2O_2 + H_2 \xrightarrow{\text{Fast}} 2H_2O$$

Example 27 *Order and molecularity of a reaction may not be the same. Explain.*

Solution: Order of the reaction may be defined as the sum of exponents to which the concentration terms in the rate law are raised to express the observed rate of reaction.

Molecularity, in the case of simple reactions, is the sum of molecules of the reactants as represented in the balanced equation. In complex reactions, it is the number of molecules involved in the slowest step. Order and molecularity may not be the same. Consider the hydrolysis of an ester with a mineral acid

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

This reaction has the molecularity equal to 2 while its order has been found to 1.
Consider the decomposition of acetaldehyde at 450°C.

$$CH_3CHO \xrightarrow{450°C} CH_4 + CO$$

It is a unimolecular reaction (molecularity = 1) but experimentally its order has been found to be 1.5.

7.12 METHODS FOR THE DETERMINATION OF ORDER OF A REACTION

A number of methods are available for the determination of order of a reaction. Some of them are discussed belows:

1. Integral Rate Equation Method In this method, the initial concentrations of the reactants and the concentration of any one of the reactants or the products at different instants of time are determined experimentally. Then either of the following two methods may be employed:

(a) Substitution Method (Hit and Trial Method] The appropriate values of a and x (or C_o and C_t) are substituted into the integrated forms of the rate equations for the first order, second order and third order one by one. The rate equation which gives the constant value of k gives the order of the reaction.

(b) Graphical Method In this method, a suitable function is plotted against time.

(a) If the plot of log $(a - x)$ against time is a straight line, the reaction is of the first order.

(b) If the plot of $\frac{1}{a-x}$ against time is a straight line, the reaction is of the second order.

Example 28 *Following data is obtained for the conversion of ammonium cyanate into urea.*

Time (min.)	*0*	*45*	*72*	*157*	*312*	*660*
Conc. of amm. cyanate unchanged in mol L^{-1}	*0.0916*	*0.0740*	*0.0656*	*0.512*	*0.0348*	*0.0228*

What is the order of the reaction?

Solution: Substituting the data in the first-order rate equation, if the value of k obtained is not constant the data is then substituted in the second-order rate equation, and so on. The rate equation

which gives constant value of k gives the correct order of reaction.

In the present examples,

$$a = 0.0916 \text{ mol } L^{-1}$$

Time (min.)	$(a-x)$	$k=\frac{2.303}{t}\log\frac{a}{a-x}$	$k=\frac{1}{2t}\left[\frac{1}{(a-x)}-\frac{1}{a}\right]$
45	0.0740	5.74×10^{-3}	5.77×10^{-2}
72	0.0656	4.63×10^{-3}	5.99×10^{-2}
157	0.0512	3.70×10^{-3}	5.48×10^{-2}
312	0.0348	3.08×10^{-3}	5.51×10^{-2}
600	0.0228	2.31×10^{-3}	5.49×10^{-2}

Since the value of k comes out to be almost constant by using rate equation for the second-order reaction. Therefore, it is evident that the reaction is of ***second order.***

2. Differential Rate Equation Method This method is based upon the fact that the rate of a reaction of the n^{th} order is proportional to the n^{th} power of its concentration, i.e.

$$\text{Rate of reaction}\left(\frac{dx}{dt}\right)\propto C^n$$

or
$$r = kC^n$$

where k is the rate constant for the reaction and C is the concentration at the instant of time t when the rate is r, Hence, for two different concentrations,

$$r_1 = kC_1^n \quad \text{and} \quad r_2 = kC_2^n$$

$\therefore$
$$\frac{r_1}{r_2}=\left(\frac{C_1}{C_2}\right)^n \quad \text{or} \quad \log\frac{r_1}{r_2} = n\log\frac{C_1}{C_2}$$

$$\log r_1 - \log r_2 = n(\log C_1 - \log C_2)$$

or
$$n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2}$$

Thus, to calculate the value of the order n, we require to know the values of the rates, r_1 and r_2 at two different concentrations C_1 and C_2 respectively.

Concentration of the reactant may be plotted against time and the rate at any concentration may be found from the slope of the tangent at that point.

Example 29 *For the reaction between gaseous chlorine and nitric oxide,*

$$2NO + Cl_2 \rightarrow 2NOCl$$

it is found that doubling the concentration of both reactants increases the rate eight times but doubling the chlorine concentration alone doubles the rate. What is the order of reaction with respect to nitric oxide and chlorine?

Solution: Suppose the initial concentration of NO is a moles/litre and that of Cl_2 is b moles/litre. Suppose the order of reaction w.r.t. NO is n_1 and w.r.t. Cl_2 is n_2. Then initially the rate of reaction will be given by

$$r = k(a)^{n_1}(b)^{n_2} \qquad \ldots(i)$$

In the **first case,** when the concentration of both the reactants is doubled, we will have

$$8r = k(2a)^{n_1}(2b)^{n_2} \quad \ldots(ii)$$

In the **second case,** when the concentration of only Cl_2 is doubled, we have

$$2r = k(a)^{n_1}(2b)^{n_2} \quad \ldots(iii)$$

Now to get the values of n_1 and n_2, we have to solve equations (i), (ii) and (iii). From equations (i) and (iii), we get

$$2k[a]^{n_1}[b]^{n_2} = k[a]^{n_1}[2b]^{n_2}$$

or $$2[b]^{n_2} = [2b]^{n_2}$$

or $$2 = [2]^{n_2}$$

which gives $$n_2 = 1$$

Again, from equations (ii) and (iii), we get

$$2k[2a]^{n_1}[2b]^{n_2} = 4k[a]^{n_1}[2b]^{n_2}$$

or $$[2a]^{n_1} = 4[a]^{n_1} \quad \text{or} \quad 2^{n_1} = 4 \quad \text{or} \quad n_1 = 2$$

Thus, $n_1 = 2$ and $n_2 = 1$. This means that the order of reaction w.r.t. NO is 2 and w.r.t Cl_2 is 1. The total order of reaction is, therefore, 2 + 1 = 3

Example 30 *For the reaction*

$$A + 2B \rightarrow Product$$

It is found that if the concentration of A is doubled the rate increases four times but when the concentration of B is doubled, the rate becomes doubled. What is the overall order of reaction?

Solution: Let the law expression for the reaction

$$A + 2B \rightarrow \text{Product}$$

be $$r = k(C_A)^a \cdot (C_B)^b \quad \ldots(i)$$

Case I: When the conc. of *A* alone is doubled, the rate will become 4 times. The rate is given by

$$4r = k(2C_A)^a \cdot (C_B)^b \quad \ldots(ii)$$

Case II: When the conc. of *B* alone is doubled, the rate becomes *double*. The rate is given by

$$2r = k(C_A)^a \cdot 2(C_B)^b \quad \ldots(iii)$$

Dividing (i) by (iii),

$$\frac{r}{2r} = \frac{k(C_A)^a \cdot (C_B)^b}{k(C_A)^a \cdot (2C_B)^b} \quad \text{or} \quad \left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^b$$

$\therefore$ $$b = 1$$

Order w.r.t. $$B = 1$$

Now dividing (i) by (ii), we get

$$\frac{r}{4r} = \frac{k(C_A)^a \cdot (C_B)^b}{k(2C_A)^a \cdot (C_B)^b} \quad \text{or} \quad \frac{1}{4} = \left(\frac{1}{2}\right)^a$$

or $$\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^a$$

$\therefore$ $$a = 2$$

Hence, order w.r.t $A = 2$

$\therefore$ Total order of reaction = $a + b = 2 + 1 = 3$

PROBLEMS FOR PRACTICE

1. The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \rightarrow C + D$$

Experiment	$[A]$ (mol L^{-1})	$[B]$ (mol L^{-1})	Initial rate of formation of D (mol L^{-1} min L^{-1})
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction

Ans. $$\text{Rate} = k[A]\,[B]^2$$

$$k = 6.0 \text{ mol}^{-2}\, L^2 \text{ min}^{-1}$$

3. Fractional Change (Half-life Period) Method

In general, we can say that $t_{1/2} \propto \frac{1}{a^{n-1}}$

where n is the order of the reaction.

The time taken for half the reaction to be completed is called half-life period and is represented by $t_{1/2}$.

For two different initial concentrations, we may write

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and}$$

$$(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing one equation by the other, we get

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking logarithm of both the sides, we get

$$\log (t_{1/2})_1 - \log (t_{1/2})_2 = (n-1)\,[\log a_2 - \log a_1]$$

This on simplification gives

$$n = 1 + \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log a_2 - \log a_1}$$

Example 31 *The half-life period of a substance is 50 minutes at a certain concentration. When the concentration is reduced to one half of the initial concentration, the half-life period is 25 minutes. Calculate order of the reaction.*

Solution: Suppose the initial concentration is a moles/litre

Then $(t_{1/2})_1 = 50$ minutes $\quad a_1 = a$

$(t_{1/2})_2 = 25$ minutes $\quad a_2 = a/2$

Substituting the values in the expression

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

we get $$\frac{50}{25} = \left(\frac{a/2}{a}\right)^{n-1} \quad \text{or} \quad 2 = \left(\frac{1}{2}\right)^{n-1}$$

or $$\log 2 = (n-1) \log \frac{1}{2} \quad \text{or} \quad = -(n-1) \log 2$$

$$1 = -(n-1)n = 0$$

Hence, the reaction is of the zero order.

4. Ostwald's Isolation Method This method is used to find the order of those reactions which involve two or more reactants. The method is based upon the fact that the order of a reaction does not depend upon the concentration of those reactants which are taken in excess. Turn by turn, all reactants except one are taken in excess. The order thus observed is with respect to the reactant that has been isolated from the others. The total or the overall order of the reaction is the sum of the order found with respect to the different reactants one by one by isolation.

Suppose a reaction involves three reactants *A, B* and *C*. In the first case, *B* and *C* are taken in excess (so that *A* is isolated). The order thus observed is the order with respect to *A*. Similarly, by taking *A* and *C* in excess, the order with respect to *B* can be found and by taking *A* and *B* in excess, the order with respect to *C* can be found. Suppose the orders with respect to *A, B* and *C* are found to be *a*, *b* and *c* respectively. Then the overall order of the reaction is $a + b + c$.

Example 32 *Write the units of rate constant for (a) zero order, (b) first order, (c) second order, (d) third order, and (e)* $\frac{3}{2}$ *order reactions.*

Solution: The general expression for the units of n^{th} order reaction is given by $(L^3)^{n-1}\ \text{mol}^{1-n}\ s^{-1}$

(a) For zero-order reaction $n = 0$

The units of rate constant are $(L^3)^{0-1}\ \text{mol}^{1-0}\ s^{-1}$ or $L^{-3}\ \text{mol}\ s^{-1}$

(b) For first-order reaction $n = 1$

The units of rate constant are $(L^3)^{1-1}\ \text{mol}^{1-1}\ s^{-1}$ or s^{-1}

(c) For second-order reaction $n = 2$

The units of rate constant are $(L^3)^{2-1}\ \text{mol}^{1-2}\ s^{-1}$ or $L^3\ \text{mol}^{-1}\ s^{-1}$

(d) For third-order reaction $n = 3$

The units of rate constant are $(L^3)^{3-1}\ \text{mol}^{1-2}\ s^{-1}$ or $L^6\ \text{mol}^{-2}\ s^{-1}$

(e) For 3/2 order reaction $n = 3/2$

The units of rate constant are $(L^3)^{3/2-1}\ mol^{1-3/2}\ s^{-1}$ or $L^{3/2}\ mol^{-1/2}\ s^{-1}$

7.13 COMPLICATIONS IN THE DETERMINATION OF ORDER OF REACTION

Many reactions do not occur strictly in accordance with the rate equation. These reactions generally involve two or more side reactions in addition to the main reaction. The kinetics of such reactions becomes more complicated. The overall rate of such types of reactions is the resultant of several different rate expressions. The following factors are involved in deciding the order of reactions:

1. Reversible or opposing reactions
2. Consecutive reactions
3. Side reactions or parallel reactions

1. Opposing or Reversible Reactions If in a reaction, the reactants react to form the products and the products also react to give back the original substances under the same conditions, it is called a reversible reaction. In other words, the reaction takes place not only in the forward direction but also in the backward direction (i.e. the forward reaction is opposed by the reverse reaction). Let us consider a general reversible reaction in which both the forward and the backward reactions are of the first order:

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

If the velocity constant for the backward reaction (k_b) is very small as compared to that of the forward reaction (k_f), the former can be neglected in comparison to the latter. However, if the forward and the backward reactions take place at comparable rates, the rate equation has to be modified.

Some examples of the reversible reactions whose kinetics have been studied are

(a) $2\ HI \rightleftharpoons H_2 + I_2$ (Both forward and backward reactions are of second order)

(b) $2NO + O_2 \rightleftharpoons 2NO_2$ (Forward reaction is of third order, backward reaction is of second order)

(c) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

2. Consecutive Reactions In the case of complex reactions, the order of the reaction is usually not equal to the molecularity of the reaction as observed from the stoichiometry of the equation. Such reactions are supposed to take place in a number of steps. The slow step is the rate-determining step. The various step reactions thus written for the overall reaction are called consecutive reactions.

$$2A + B \longrightarrow C$$

Suppose by experiment, the rate of reaction $\propto [A][B]$, i.e. the rate of reaction depends upon one molecule of A and one molecule of B. The slow step should, therefore, involve only one molecule of A and one molecule of B. The step reactions (or the consecutive reactions) may, therefore, be written as

(a) $A + B \xrightarrow{\text{Slow } (k_1)} D$

(b)

3. Parallel or Side Reactions If in a reaction, the reactants react to form two different products by two different paths such that one product is in large amount than the other then the reaction giving the large amount is called *main* reaction, while the other giving the smaller amount of the product is called *side* reaction or *parallel* reaction, i.e.

If the side reaction takes place only to a small extent, it can be neglected in comparison to the

main reaction. However, if the two reactions take place in comparable amounts, the rate equation has to be modified to account for this fact. A few examples of parallel or side reactions are given below:

(a) Nitration of Phenol

(b) Chlorination of Benzene

7.14 SURFACE REACTIONS

Gaseous reactions which take place exclusively on the walls of the container are called surface reactions. The rate of these reactions is affected by the following factors.

1. ***If the surface is sparsely covered*** (as in the case at high temperatures), the rate of reaction depends only upon the number of molecules colliding per unit time on the surface, i.e. on the pressure (P) of the gaseous reactants. We may write

   Hence, all reactions are kinetically the reactions of the first order. Examples of such reactions are the decomposition of phosphric on the surface of glass, silica or tungsten, and decomposition of hydrogen iodide on platinum.

2. ***If the surface is almost completely covered,*** it is found that the rate of reaction is independent of pressure, i.e.

   Such reactions are then kinetically the reactions of the zero order. Examples of such reactions are decomposition of ammonia on the surface of tungsten and decomposition of hydrogen iodide on the surface of gold.

3. ***If some of the molecules of the reactants are firmly held on the surface of the solid,*** the rate of the reaction is obviously retarted.

7.15 CHAIN REACTIONS

A reaction that takes place in steps is called a chain reaction. The following steps are involved in a chain reaction.

(i) Chain initiating Step This is the slowest step in which the reaction species are produced.

(ii) Chain propagating Step The reactive species produced in the first step reacts immediately with the other molecules of the reactants producing new reactive species and products. The new reactive species on combination with other molecules regenerates the original reactive species. In this way the reaction goes on.

(iii) Chain-terminating Step Towards the end, the reactive species left behind combine with each other and the reaction stops. The steps (ii) and (iii) are fast because they involve reactive species.

A reaction proceeding in a series of successive steps initiated by a suitable primary process is called a chain reaction.

The following two examples will illustrate:

1. Combination between Hydrogen and Bromine to form Hydrogen Bromide

$$H_2 + Br_2 \rightarrow 2HBr$$

This is an example of a reaction in which the reactive species produced in the chain-initiating step

are atoms. The various steps may be explained as follows:

(a) Chain-initiating step In the presence of light, bromine molecules dissociate to form the highly reactive bromine atoms.

(b) Chain-propagating Step The above reaction is immediately followed by the following reactions:

The bromine atom thus produced reacts with more of H_2 and the reaction goes on till whole of hydrogen or bromine present is used up.

(c) Chain-terminating Step The left-off atoms then combine with each other or with the molecule of the product and the reaction stops.

2. Thermal Decomposition of Acetaldehyde at High Temperature

$$CH_3CHO \rightarrow CH_4 + CO$$

This is an example of a reaction which proceeds through the free radical mechanism. The measured order of the reaction is 1.5 and the possible mechanism is as follows:

(a) Chain-initiating Step

(b) Chain-propagating Step

(c) Chain-terminating Step

Example 33 *The possible mechanism for the reaction*

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \text{ is}$$

(a)

(b)

Write the rate law and order for the reaction.

Solution: Rate law is derived from slow step (b).

Substituting for $[NO_3]$ in Eq. (i), we have

Example 34 *Nitric oxide reacts with H_2 to give N_2 and H_2O.*

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

The rate law for the above reaction is

Explain the mechanism of the reaction.

Solution: The following mechanism is proposed.

PROBLEM FOR PRACTICE

1. For the reaction at 500 K,

$$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$$

The proposed mechanism is as follows:

(a) $NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)

(b) $NO_3 + CO \rightarrow CO_2 + NO_2$ (fast)

What is the predicted rate law?

7.16 TEMPERATURE DEPENDENCE AND ARRHENIUS EQUATION

The effect of temperature on the rate of a reaction was studied by Arrhenius in detail. The equation, called ***Arrhenius equation*** is usually written in the form

where A is a constant called ***frequency factor*** (because it gives the frequency of collisions of the reacting molecules), E_a is called energy of activation, R is gas constant and T is the absolute temperature.

The energy of activation (E_a) is an important quantity as it is characteristic of the reaction using the above equation. Its value can be calculated as follows:

Taking logarithm of both sides of Eq. (7.45), we get

If the values of the rate constant at temperatures T_1 and T_2 are k_1 and k_2 respectively then we have

Subtracting Eq. (7.47) from Eq. (7.48), we get

Svante Arrhenimus (1859–1927) Svante Arrhenius was a Swedish scientist and one of the founders of the science of physical chemistry

Knowing the values of the rate constants k_1 and k_2 at two different temperatures T_1 and T_2, the value of E_a can be calculated. Alternatively, knowing the rate constant at any one temperature, its value at another temperature can be calculated provided the value of E_a is known for that reaction.

Equation (7.46) may be written as

Fig. 7.12 *A typical plot of log kvs*

This equation is of the form

$$y = mx + c$$

i.e. the equation of a straight line. Thus, a plot of log k vs is a straight line shown in Fig. 7.12. Further, from Eq. (7.50), we have

By measuring the slope of the line, the value of E_a can be calculated.

Example 35 *The activation energy of a reaction is 225 k cal mol^{-1} and the value of rate constant at 40°C is 1.8 × 10^{-5} s^{-1}. Calculate the frequency factor A.*

Solution: Here, we are given that

Substituting the values in the equation

Example 36 *Calculate the activation energy of a reaction whose reaction rate at 27°C gets doubled for 10°C rise in temperature.*

Solution: Here, we are given that

Substituting these values in the equation

Example 37 *ln k versus 1/T graph was plotted to calculate the activation energy of a reaction using Arrhenius equation for the effect of temperature on reaction rate. The slope of the straight line was found to be –2.55 × 10^4. Calculate the activation energy of the reaction.*

Solution: Slope of the straight-line graph is given by

Remove negative sign from both sides and put the value of R in joules.

Example 38 *Rate constant k of a reaction varies with temperature T according to the equation*

where E_a is the activation energy. When a graph is plotted for log k vs. a straight line with a slope of –4250 K is obtained. Calculate E_a for the reaction.

Solution: The equation log

Substituting the values, we have

Example 39 *The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the activation energy (E_a) of the reaction assuming that it does not change with temperature.*

(R = 8.314 J K^{-1} mol^{-1}, log 4 = 0.6021)

Solution: Use the Arrhenius equation

Substituting the values, we have

PROBLEMS FOR PRACTICE

1. The rate constant of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of activation energy for the reaction.

   Given R = 8.314 J K^{-1} mol^{-1}

   [Ans. E_a = 18.263 kJ]

2. Rate constant for a first-order reaction becomes six times when the temperature is raised from 350 K to 400 K. Calculate the activation energy for the reaction. [R = 8.314 J K^{-1} mol^{-1}]

   [Ans. 41.715 k J mol^{-1}]

3. Rate constant k of a reaction varies with temperature according to the equation: log k = constant where E_a is the energy of activation. When a graph is plotted for log k vs $1/T$, a straight line with a slope of –6670 K is obtained. Calculate the energy of activation for this reaction. State the units (R = 8.314 J K^{-1} mol^{-1})

   [Ans. 127.7 kJ mol^{-1}]

Theories of Reaction Rates

Two theories which are used to predict the rates of reactions are

1. Collision theory
2. Transition state theory or theory of absolute reaction rates or theory of activated complex formation

7.17 COLLISION THEORY OF REACTION RATES

This theory is based upon the kinetic theory of gases which assumes that molecules of a gas are continuously moving and hence colliding with each other. Since for a collision to take place, at least two molecules must be involved, therefore, the simple case to consider is that of ***bimolecular reactions.*** Hence, in the discussion that follows, we shall first discuss the collision theory for bimolecular reactions and then for unimolecular reactions.

1. Collision Theory for Bimolecular Reactions In a bimolecular reaction, in order that two molecules may react, they should not only collide but also must possess sufficient energy so that the molecules are activated. This means that all collisions are not effective. The number of effective collisions is only a fraction of the total number of collisions. Taking the specific reaction rate (k) as equal to the number of effective collisions per cc per second, if Z is the number of molecules per cc taking part in the collisions and f is the fraction of those molecules that are activated, we can write

Now, according to kinetic theory of gases, the fraction of the molecules in a gas possessing energy greater than a particular value E, is given by the equation

where ΔN = number of molecules possessing energy greater than E

and N = total number of molecules

If E corresponds to E_a, the energy of activation, then the fraction of the activated molecules will be given by

Putting the value of f from Eq. (7.52) in Eq. (7.51), we get

Fig. 7.13 *Representation of Collision theory*

Example 40 *The rate constant k_r for the second-order decomposition of N_2O follows the equation*

Calculate the energy of activation and pre-expo-nential factor with reaction.

Solution: Arrhenius equation for the reaction is

Comparing the equation with the given equation

$E_a = 29{,}000 \times 8.314 = 241.1 \text{ kJ mol}^{-1}$

The frequency factor $A = 5 \times 10^{11} \text{ L mol}^{-1} s^{-1}$

Fig. 7.14 *In moving from A to B (or reactants to products), we need to cross the hill, i.e. we need to provide the activation energy.*

7.17.1 Failure of Simple Collision Theory

The collision theory of reaction rate predicts the value of rate constant very accurately for atomic species or simple and small molecules. There are many reactions for which the predicted and the experimental value of rate constant show a wide difference. Major examples of failure of the theory are the following:

1. Polymerisation of 1,3-butadiene or combination of two molecules of ethene, the theoretical value of k_r is 10^4 times greater than the experimentally calculated value.
2. For the reaction between ethyl alcohol and acetic anhydride at 75°C, the theoretically calculated rate constant k_r is 10^5 times greater than the experimental value.
3. The theory is only applicable to homogeneous gas phase bimolecular reactions which are generally of the second order.
4. The plot of ln k_r against $1/T$ is not strictly a straight line as predicted by Arrhenius equation. This is because frequency factor is not completely independent of temperature; rather it has square-root dependence of temperature, i.e.,
5. The theory totally ignores the structure and properties of the reacting molecule. The bigger or complex molecules do not behave as rigid spheres.
6. The theory does not account for the higher rates of chain reactions.

7. The theory fails to account for the first-order kinetics of bimolecular gaseous reactions at high pressure.
8. There is no way to determine E_a from the theory itself.

7.17.2 Causes of Failure of Collision Theory

1. The main reason for the failure of collision theory for reactions involving complex or large molecule is the oversimplification in the assumption that the entire energy of the molecules is the transitional kinetic energy which is true only in case of simple molecules which behave as rigid spheres. The complex molecules do not behave as such and these molecule possess vibrational and rotational kinetic energies in addition to translational kinetic energy.
2. Another cause of the failure of collision theory is that the proper activation energy by the colliding molecules is not the only pre-requisite for the reaction to occur. For effective collision, suitable orientation of the colliding molecules is also essential for the reaction to occur.

The effect of orientation of molecules in space for a simple reaction

$$2HI \rightarrow H_2 + I_2$$

can be represented as shown in (Fig. 7.15).

It can be concluded that collisions of only properly oriented molecules possessing energy greater than E_a will result into the reaction.

Fig. 7.15 *Proper orientation of molecules during collision is necessary for the reaction to take place.*

7.17.3 Modification of the Equation of Collision Theory

A good agreement between the calculated value and the observed value is found for a number of bimolecular reactions in the gaseous phase as well as in the solution. Still there are many reactions for which the calculated value is found to be much higher than the observed value. Hence, Eq. (7.53) is modified as

where the factor p, introduced in the above equation, is called ***probability factor*** or ***steric factor.*** It accounts for the fact that all collisions between the activated molecules may not result into a reaction; only those collisions between the activated molecules result into reaction which collide with proper orientations. The value of p varies from 1 to 10^{-9}. When $P = 1$, the reaction obeys collision theory.

7.17.4 Thermodynamic Interpretation of Steric Factor

Consider a reversible reaction

$$A_2 + B_2 = 2AB$$

Rate constant k_f (for forward reaction) = $p_1 z_1 e^{-E_1/RT}$

Rate constant k_b (for backward reaction) = $p_2 z_2 e^{-E_2/RT}$

The value of equilibrium constant K is given by

Making use of thermodynamic principles,

where Δ = free energy change Δ = enthalpy change Δ = entropy change

for the activation process, i.e. in going from reactants to the activated complex state.

Comparing (7.58) and (7.59),

If the molecules A_2, B_2 and AB are of comparable dimensions then so that

The steric factor 'p' should be interpreted in terms of entropy of activation Δ rather than the probability of proper orientation of molecules.

1. When Δ is +ve, p will be large and the reaction will be fast.
2. When Δ is –ve, p will be small and the reactions will be slower than that predicted from the collision theory.

7.17.5 Collision Theory for Unimolecular Reactions (Lindemann Hypothesis)

A unimolecular reaction means a reaction of the type

$$A \rightarrow \text{Products}$$

In such reactions, only one molecule of the reactant takes part in the reaction. Consequently, the question arises:

How do molecules in a unimolecular reaction attain their energy of activation? The answer to this question was first suggested by Lindemann in 1922. He pointed out that the behaviour of unimolecular reactions can be explained on the basis of ***reaction.*** During this time, the activated molecules may either react or be deactivated to ordinary molecules. Consequently, the rate of reaction will not be proportional to all the molecules activated but only to those which remain active. This concept may be illustrated as follows:

where k_1, k_2 are k_3 are the rate constants of the different processes involved as shown above.

7.18 TRANSITION STATE THEORY OR THEORY OF ABSOLUTE REACTION RATES OF THEORY OF ACTIVATED COMPLEX FORMATION

According to this theory, it is believed that before the reacting molecules change into products, they form an intermediate, called activated complex which has higher energy than both the reactants and the products. It is for this reason that the theory is called transition state theory. The activated complex is in equilibrium with the reacting molecules and the rate of reaction is given by the rate of decomposition of the complex to form the products. Thus we may represent the situation as follows:

Making use of some fundamental properties of the reacting molecules. Eyring showed that the rate constant (k) for any reaction (irrespective of its molecularity or order) is given by

and K = Equilibrium constant for the formation of the activated complex from the reacting molecules that is

Now, from thermodynamics, we know that

where ΔG^* is the free energy of activation for the reaction $A + B \rightarrow X^*$

Substituting this value of K in equation (7.62), we get

Further substituting for $\Delta G^* = \Delta H^* - T\Delta S^*$, where ΔH^* and ΔS^* are the changes in enthalpy and entropy of activation respectively, we get

Figs. 7.16 and 7.17 illustrate the formation of activated complex for the reactions:

(i) $CO + NO_2 \rightarrow CO_2 + NO$

(ii) $CH_3Br + OH^- \rightarrow CH_3OH^- + Br^-$

Fig. 7.16 *Activated complex formation*

Consider the reaction $CO + NO_2 \rightarrow CO_2 + NO$. In this reaction, the reactant molecules absorb energy to form an activated complex after overcoming the activation energy barrier, then release energy and form the products (Fig. 7.16).

Fig. 7.17 *Reaction between bromoethane and hydroxide ion*

7.18.1 Significance of the Equation of the Transition State Theory

Equation (7.64) involves two factors, The first factor is constant at constant temperature. Hence, the rate of reaction depends only upon the second factor. This factor involves ΔG^* with a negative sign. This means that at particular temperature, ***greater the value of the free energy of activation for a reaction, the slower will be the reaction.***

Comparison with Arrhenius Equation Comparing Eq. (7.65) with the Arrhenius equation, viz. $k = Ae^{-E_a/RT}$, we observe that we should have

(i.e. enthalpy of activation is equal to the energy of activation).

Comparison with the Collision Theory Equation Comparing Eq. (7.65) with the collision theory equation, viz.

Thus, the probability factor P is related to the entropy of activation ΔS^*.

7.18.2 Advantages of Transition-State Theory over Collision Theory

The transition-state theory is better than the collision theory in a couple of ways.

For example,

1. In collision theory, the correction factor P was introduced arbitrarily whereas in the transitionstate theory, its inclusion has been justified in terms of entropy of activation ΔS^*.
2. The concept of the formation of an activated complex seems to be more appropriate than assuming that the molecules just collide together and change into products.

7.19 EXPERIMENTAL METHODS OF CHEMICAL KINETICS

The underlying principle behind kinetic studies of reactions is to follow the progress of a reaction with passage of time. We need to know how much of the reactant changes into the product at different intervals of time. The technique to be employed to make kinetic studies will depend upon the nature, medium and the physical state of the reactants and products. If the reactant and product is gaseous, the barometric method may be employed. If the reactant or product contains some acid or base, titration methods are handy to obtain the concentration of the reactants at different intervals of time. Other methods which involve the use of instruments are described below:

1. Conductometric Methods A conductometer is employed to study the progress of a reaction involving either ionic reactants or products. With the passage of time, conductance is measured at different interval of time. This gives us the concentration of reactants at different times, after which it is possible to find the rate of the reaction.

2. Polarimetrie Methods This method is employed to study reactions in which either the reactant or product or both are optically active, i.e. rotate the plane of polarised light. For example, the inversion of cane sugar (sucrose) can be studied by this method. Sucrose is dextro-rotatory. On hydrolysis, it is broken down to glucose which is dextro-rotatory and fructose which, is laevo-rotatory. But the laevo-rotation of fructose is greater than the dextro-rotation of glucose. Thus, the solution obtained after hydrolysis is found to be laevo-rotatory. The instrument used in this method is called a polarimeter.

3. Potentiometrie Methods A potentiometer is employed to study the progress of the reaction involving a redox couple in which one component gets oxidised and the other gets reduced. The emf of the redox couple is observed after different intervals of time. From these values, we can calculate the concentration of reactants after different intervals of time. This enables us to arrive at the rates of reactions.

4. Spectrophotometric Method This method is employed to study reactions which involve either coloured reactants or products. Let us say the reactant is coloured. As the reaction proceeds, the solution becomes less and less coloured because the product is colourless. The intensity of transmitted light is noted after different intervals of time. Thereafter, we can obtain the concentration of a reactant after different intervals of time and calculate the rate constant.

CHEMICAL KINETICS COMES TO RESCUE

Consumption of methanol causes headache, nausea, blindness and even death. In the liver, methanol is metabolised with the help of ADH (alcohol dehydrogenase) formaldehyde and formic acid which are responsible for the toxic effects of methanol. We can protect a victim of methanol poisoning by administering large quantities of ethanol. Now ethanol has 100 times greater affinity for ADH compared to methanol. Thus, oxidation of methanol to toxic compounds stops. Methanol is removed from the body by dialysis. This is how the relative rates of reaction find applications in the medical field.

Fig. 7.18 *Methanol poisoning*

SUMMARY

1. The branch of chemistry that deals with the rates of reactions is called chemical kinetics.
2. Rate of a reaction may be defined as the change in concentration of any one of the reactants or

products. Rate of a reaction at *any time* is defined as the change in concentration of any one of the reactants or products per unit time at that particular instant of time.

3. Factors that affect rate of a reaction are (a) nature of the reactants, (b) concentration of the reactants, (c) temperature, and (d) catalyst.
4. Rate of a reaction increases with rise of temperature. Roughly, rate of a reaction becomes nearly *double* or even *treble* for every 10°C rise in temperature.
5. An effective collision is that which results into chemical reaction. *Threshold energy* is defined as the minimum energy which the colliding molecules must possess in order that the reaction takes place.
6. The extra amount of energy that the molecules of the reactants must be provided so that their energy becomes equal to the threshold energy is called *activation energy*.
7. The number of molecules which collide simultaneously in the elementary step to bring about a chemical reaction is called *molecularity*. Molecularity of a complex reaction which takes place in a number of steps (elementary steps) has no meaning.
8. Sum of the concentration terms on which the rate of a reaction depends is called the *order* of the reaction or in other words, sum of the exponents, to which the concentration terms are raised in the rate law, is called order of the reaction.
9. A reaction is said to be of *zero* order if the rate of a reaction is independent of the concentration of the reactants.
10. A reaction is said to be first order if the rate of the reaction depends upon one concentration term only. Units of k for first order are s^{-1} or min^{-1}. Time taken for any fraction of the reaction to be completed is independent of the initial concentration. It has been found that radioactive decay follows the first-order kinetics.
11. A reaction is said to be of second order if the rate of reaction depends upon two concentration terms. The time taken for any fraction of the reaction to be completed is inversely proportional to the initial concentration.
12. A reaction is said to be of third order if the rate of reaction depends upon three concentration terms. Time taken for any fraction of the reaction to be completed is inversely proportional to the square of initial concentration.
13. A series of step reactions proposed to account for the overall reaction is called the mechanism of the reaction.
14. Order of a reaction can be determined by(a) integral rate equation, (b) differential rate equation method, (c) fractional change method, and (d) Ostwald isolation method.
15. Various complications in the determination of order of the reaction are (a) reversible reactions, (b) consecutive reactions, and (c) side reactions
16. According to collision theory for bimolecular reactions, the molecules should not only collide, but the collision must be associated with sufficient energy so that the molecules are activated.
17. According to transition-state theory, it is believed that before the molecules change into products, they form an intermediate called activated complex which has higher energy than both the reactants and products.
18. Kinetics studies can be made using conductometric, potentiometric, polarimetric and spectrophotometric methods.

KEY EQUATIONS

1. For the reaction $\alpha A + \beta B \rightarrow$ Products, Rate $\alpha [A]^{\alpha} [B]^{\beta}$ order of the reaction = $a + b$
2. For zero-order reaction,

   For first-order reaction:

For second-order reaction:

For third-order reaction

3. Half life period and order of the reaction. For a reaction of *n*th order,

Thus, for zero order, $t_{1/2} \propto a$; for first order, $t_{1/2}$ is independent of initial concentration; for second order, ; for third order,

4. General equation for the units of k for a reaction of nth order is $L^{n-1}\ mol^{1-n}\ s^{-1}$.
5. Arrhenius equation for the change of rate of reaction with temperature is given by

EXERCISES

Based on Different University Papers

Objective Questions

(A) Fill in the Blanks

1. Hydrolysis of ester in the presence of a base is a_____order reaction.
2. Temperature coefficient of most of the reactions lie between_____
3. A series of step reactions, proposed to account for the overall reaction, is called the_____of the reaction.
4. Arrhenius equation is given by_____
5. In a third-order reaction, the half-life period is inversely proportional to_____the unitial concentration.
6. It the concentration is expressed in mol dm^{-3} and time in seconds, the unit of rate constant for a second-order reaction will be_____
7. To start a reaction, a minimum amount of energy known as_____energy should be possessed by the reacting molecule.
8. Reactions of higher order are_____
9. The middle step in a chain reaction is known as chain_____step.
10. Two theories to explain reaction rates are (a)_____(b) Transition state theory

(B) Multiple Choice Questions

1. The rate of a reaction, on increasing concentration of the reactants
   (a) increases
   (b) decreases
   (c) remains unaltered
   (d) none of these
2. According to activated complex theory, the rate of a reaction depends on:
   (a) the intensity of collision
   (b) initial velocity of molecules
   (c) energy of activation of the molecules
   (d) the velocity of molecules with which they cross the energy barrier.
3. The rate constant of a reaction is equal to its rate constant at constant temperature when the

concentration of the reactants is

(a) unity

(b) zero

(c) two

(d) three

4. According to the collision theory, the rate of a reaction depends on

(a) the average collision of molecules

(b) the total number of molecules

(c) the number of colliding molecules per ml per unit time.

(d) none of these

5. The half-life period of a reaction is independent of the initial concentration of the reactants. The reaction is of

(a) first order

(b) zero order

(c) second order

(d) third order

6. The one which is a unimolecular reaction is

(a) $2HI \rightarrow H_2 + I_2$

(b) $N_2O_5 \rightarrow N_2O_5 + (1/2)O_2$

(c) $H_2 + Cl_2 \rightarrow 2HCl$

(d) $PCl_3 + Cl_2 \rightarrow PCl_5$

7. On increasing temperature, rate of a reaction increases, because

(a) the number of activated molecules increases

(b) the number of activated molecules decreases

(c) the number of activated molecules becomes zero

(d) the activated molecules move with a low speed

8. The half-life period $t_{1/2}$ of a reaction varies with the initial concentration of a reaction as . The order of the reaction is

(a) 0

(b) 1

(c) 2

(d) none of these

9. The ratio of the velocity constant for a reaction at two temperatures differing by 10°C is called its

(a) rate constant

(b) temperature coefficient

(c) activation energy

(d) specific reaction rate

10. The essential condition for a reaction to occur, according to collision theory is that the

(a) molecules should dissociate after collision

(b) molecules should acquire activation energy

(c) molecules should become deactivated

(d) volume of molecules should decrease

11. The specific rate constant of a first-order reaction depends on

(a) concentration of the reactants

(b) time

(c) concentration of the products

(d) temperature

12. The rate equation of a reaction is $dx/dt = k[A]^a [B]^b$ for which the order of the reaction is

(a) a + b

(b) a – b

(c) a

(d) b

13. For the chemical change $A \rightarrow B$, it is found that the rate reaction doubles when the concentration is increased four times. The order in A for this reaction is

(a) two

(b) one

(c) zero

(d) half

14. The statement which is true in respect of order of a reaction is

(a) it is always a whole number

(b) it is always a fraction

(c) it may be zero, a whole number or a fraction

(d) it can never be a fraction

15. The equation which expresses the effect of temperature on the velocity constant of reaction is

(a) Faraday

(b) Arrhenius equation

(c) Avogadro's equation

(d) none of these

16. The rate at which a substance reacts is proportional to its

(a) active mass

(b) concentration in g/litre

(c) mole fraction

(d) none of these

17. In a first-order reaction, the conc. of reactant decreases from 1.0 M to 0.25 M in 20 minutes. The value of k is

(a) 0.6932

(b) 6.932

(c) 0.06932

(d) none of these

18. The half-life period of a first-order reaction is 10 minutes. The time required for the concentration of the reactant to change from 0.08 M to 0.02 M is
    (a) 10 minutes
    (b) 20 minutes
    (c) 30 minutes
    (d) 40 minutes
19. If the concentration is expressed moles/litre, the unit of rate constant for a first-order reaction is
    (a) mole litre^{-1} s^{-1}
    (b) mole litre^{-1}
    (c) s^{-1}
    (d) mole^{-1}
20. The rate of a reaction usually
    (a) increases with increase in temperature
    (b) decreases with increase in temperature
    (c) remains unaffected with increase in temperature
    (d) none of these

Answers

(A) Fill in the Blanks

1. Second
2. 2 and 3
3. mechanism
4. $k = Ae^{-Ea/RT}$
5. Square
6. dm^3 mol^{-1} s^{-1}
7. threshold
8. rare
9. propagating
10. collision theory

(B) Multiple-Choice Questions

1. (a)
2. (a)
3. (a)
4. (c)
5. (a)
6. (b)
7. (b)
8. (d)

9. (b)
10. (a)
11. (d)
12. (a)
13. (d)
14. (c)
15. (b)
16. (a)
17. (c)
18. (c)
19. (c)
20. (a)

GENERAL QUESTIONS

1. Discuss the importance of chemical kinetics in the study of mechanism of reactions. Illustrate your answer by giving suitable examples.
2. (a) How does the value of the rate constant of a second-order reaction depend upon the units of concentrations of the reaction?

   (b) What do you understand by the terms:

   (i) Order of reaction

   (ii) Molecularity of a reaction?

   Explain with examples.
3. Explain the term rate of a reaction. How can it be determined? Why cannot the rate of a reaction be measured by giving the total time taken? How can we express the rate of a reaction?
4. (a) Deduce the expression for the specific rate constant for a second-order reaction of the type: $2A \rightarrow$ Product

   (b) In a reaction, $2R \rightarrow$ Product
   the concentration of the reactant R after time t seconds was A moles/litre. Derive an expression for the rate constant if the initial concentration was A_o moles/litre. What will be the units of the rate constant?
5. Define chemical kinetics. "What is meant by rate of chemical reaction differing from one another?
6. (a) What is meant by pseudo-unimolecular reactions? Explain with examples.

   (b) Derive an expression for the time required for completion of one third of a first-order reaction.
7. (a) On what factors does the rate of a chemical reaction depend? Explain with examples.

   (b) What is meant by the term molecularity of a reaction? Why does the molecularity of a reaction seldom exceed three?
8. (a) Why are the reactions of higher order rare?

   (b) A first-order reaction is 40% complete at the end of 50 minutes. What is the value of rate constant in s^{-1}? In how many minutes will the reaction be 80% complete?

[Ans. 1.7×10^{-4} s^{-1}, 157.8 min]

9. (a) Give a brief account of the methods for determining the order of a reaction.

   (b) The optical rotation of sucrose in 1 N HCl at various times was given below:

   (i) Show that inversion of sucrose is a first-order reaction.

   (ii) When is the solution optically inactive?

[Ans. 109 minutes]

10. (a) Show that for a first-order reaction the half-life period is independent of the initial concentration

    (b) Give two examples of zero-order reaction.

11. (a) What is meant by the term rate law and rate constant?

    (b) Distinguish between order of a reaction and molecularity of a reaction.

12. (a) Derive the mathematical expression for the rate constant of a second-order reaction.

$$A + B \rightarrow \text{Product}$$

    (b) Derive the mathematical expression for half-life period of a second-order reaction

13. (a) Write two examples in which the order of a reaction is fractional.

    (b) Give two examples of first-order reactions.

    (c) Write down the units of specific rate constant for first-order reactions.

14. (a) Define and explain the term order of reaction and rate constant of a reaction.

    (b) Differentiate between rate constant and rate of a reaction.

15. (a) Give a brief account of temperature dependence of reaction rates.

16. (a) Name the methods used for the determination of order of a reaction.

    (b) Discuss one method in detail.

    (c) How will you show experimentally the hydrolysis of ethyl acetate by alkali when alkali is not used in excess in a bimolecular reaction?

17. (a) The rate constant of a certain reaction increases two-fold with increase in temperature by 10 degrees. Explain clearly.

    (b) What is meant by activation energy? How can it be determined?

18. (a) Discuss the kinetics of the first-order parallel reaction.

    Explain how the values of k_1 and k_2 can be determined separately. Show that the reaction as a whole is of first order.

19. (a) What is a second-order reaction? Derive an equation given the velocity constant of a second-order reaction.

    (b) Show that:

    (i) For a first order reaction,

    (ii) For a second order reaction,

    (iii) For a third order reaction,

20. (a) What are consecutive reactions? Discuss the kinetics of the first-order consecutive reaction:

Show graphically the variation of concentration of A, B and C with time.

21. (a) Comment on the statement:

The molecularity of the slowest step in a chemical reaction gives the order of the overall reactions.

(b) Discuss various methods for the determination of order of a reaction.

22. (a) The magnitude of the activation energy depends upon the nature of the reacting species. Support this statement with suitable examples.

(b) Explain activation energy, potential energy barrier and Arrhenius law.

23. (a) State and explain rate law. How does it differ from law of mass action?

(b) What are psuedo-unimolecular reactions? Give two examples in support of your answer.

24. (a) Explain the term energy of activation. How is the activation energy of a reaction determined?

(b) The values of the rate constant observed for the reaction

$$2HI \rightarrow H_2 + I_2$$

at 356°C and 443°C are 3.02×10^{-5} mol^{-1} dm^2 mol^{-1} and 2.53×10^{-3} mol^{-1} dm^3 s^{-1} respectively. Calculate the energy of activation for the forward and backward reaction. ΔH = 16.32 kJ mol^{-1}

[Ans. $E_{(forward)}$ = 190.613 kJ: $E_{a(Backward)}$ = 174.293kJ]

25. (a) What is activation energy? On the basis of the concept of activation energy, explain why the reaction having the same concentration of the reactants differ so much in their rates.

(b) Derive the mathematical expression for the rate constant of a reaction

$$A + B \rightarrow \text{Products}$$

(c) Show that in case of a first-order reaction, the time required for 99.9% of the reaction to take place is about ten times than that required for half the reaction.

26. Explain why

(a) (i) Rate constant of a reaction is generally doubled for 10°C rise in temperature.

(ii) Reactions of higher molecularity are rare.

(b) With a suitable example show how chemical kinetics helps in determining the mechanism of reactions.

(c) A second-order reaction in which initial concentration of both the reactants is same, is complete in 20 minutes. How long will it take for the reactions to complete to 75%?

[Ans. 180 minutes]

27. Discuss clearly the kinetics of the first-order reaction

Show how the values of k_1 and k_2 are determined in reversible reactions.

28. Discuss the kinetics of hydrogen-bromine reaction.

29. Give an account of Arrhenius equation for temperature dependence of the reaction rates. Show how it is possible to determine the value of activation energy of the reaction.

30. Write short notes on the following:

(a) Order of a reaction.

(b) Molecularity of a reaction.

(c) Collision theory of reaction rate

31. Derive the expression for the time required for completion of 1/3 of a first-order reaction and write down the units of specific rate constant and also show that in a first-order reaction,

    (a) Half-life period is independent of the initial concentration of the reactants.

    (b) The rate constant is independent of the change of concentration units.

32. (a) Derive the expression for the velocity constant of the reaction

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

    when alkali is used in large excess.

    (b) The half-life period of a substance is an hour at a certain concentration. When the concentration is reduced to one half of the initial concentration, the half-life period is half an hour. Calculate the order of a reaction.

33. (a) Deduce the expression for the rate constant of a second-order reaction of the type

$$2A \rightarrow \text{Product}$$

    (b) A second-order reaction in which the initial concentration of both the reactants are same is 25%. complete in 600 seconds. How long will it take for the reaction to go to 70% completion?

[Ans. 5400 seconds]

34. (a) At 298.4°C, azomethane decomposes mainly according to the reaction

$$CH_3 - N == N - CH_3(g) \rightarrow C_2H_6(g) + N_2(g)$$

    If this be the only reaction obeying first-order kinetics with a rare constant k as $2.50 \times 10^{-4}\ s^{-1}$, what will be the partial pressure of reactants and products when azomethane initially at 200 mm Hg decomposes for 30.0 min?

    (b) Deduce a general rate equation for a second-order bimolecular reaction when the initial concentrations of the reactants are different.

35. (a) Give the units of specific rate constant for second-order reactions.

    (b) What is energy of activation? Justify the statement that for a fast reaction, energy has a low value whereas for a slow reaction, it has a high value.

    (c) In a second order reaction, half-life period is 60 minutes when the initial is 0.02 mole per litre. Calculate the value of specific reaction rate.

    (d) What is the order of the reaction

[Ans. $0.8333\ mol^{-1}\ Lt\ min^{-1}$]

36. (a) What are initial and instantaneous rates? How do they differ from average rate?

    (b) The optical rotation of sucrose in 0.5 M. HCl at various intervals are given below:

    Show that the reaction is of first order.

37. (a) What is the order of a reaction? Comment on the statement that order of a reaction is an experimental quantity. Describe the half-life period method for determining the order of a reaction.

    (b) What are chain reactions? Study the rate law for the chain reaction between hydrogen and bromine.

    (c) The half-life period of a first-order reaction $A \rightarrow B$ is 10 minutes. What percentage of A remains after 1 hour?

38. (a) Explain any one of the methods used for the determination of the order of a reaction.

(b) Give an example of the chemical reaction where order and molecularities are different.

(c) Why do reaction rates vary from reaction to reaction even if the concentrations of reactants and the temperatures are kept constant?

(d) Explain how will you determine the activation energy of a reaction by using Arrhenius equations.

39. (a) Explain the concept of energy of activation and potential energy barrier. Discuss the effect of temperature on the rate of a reaction.

(b) What are the advantages of transition state-theory over the collision theory?

40. Write briefly on the following:

(a) Explosive reactions

(b) Influence of temperature on rates of reactions

41. What are consecutive and parallel reactions? Discuss the kinetics of the first-order consecutive reaction

Represent graphically the concentration changes in case of A and B with time.

42. (a) What is the order of a reaction? Describe the half-life period method for determining the order of a reaction.

(b) What are chain reactions? Study the rate law for the chain reaction between hydrogen and bromine.

43. (a) What is the difference between energy of activation and threshold energy?

(b) Explain Arrhenius equation.

(c) An artificially produced radio isotope decomposes according to the first-order law with a half-life period of 15 minutes. In what time will 80% of the sample be decomposed?

44. (a) The activation energy of a non-catalysed reaction at 37°C is 200 kcal mol^{-1} and the activation energy of the same reaction when catalysed by an enzyme is 6.0 kcal mol^{-1}. Calculate the ratio of the rate constants of the catalysed and non-catalysed reactions. Assume frequency factor to be the same in both the cases.

(b) Calculate the activation energy of a reaction whose rate constant doubles when the temperature is raised from 22°C to 32°C.

45. (a) What is energy of activation? Justify the statement:
For a fast reaction, energy of activation for the reaction has a low value whereas for a slow reaction, it has a high value.

(b) In a second-order reaction, half-life period is 60 minutes. When the initial concentration is 0.02 mole per litre. Calculate the value of specific reaction rate.

[Ans. (a) $N_2(g) + O_2(g) \rightarrow 2NO(g)$]

Express the rate of this reaction in terms of reactants and products. What are the units of rate?

(b) The rate of a reaction depends upon concentration of reactants. Explain.

(c) Show that for a first-order reaction,

where the symbols have their usual meanings.

(d) A second-order reaction in which the initial concentration of both the reactants is 0.01 mol/dm^3 is 25%. complete in 300 seconds. How long does it take for the reaction to go to 75% completion?

46. (a) Differentiate order and molecularity of a reaction.

(b) Define a second-order reaction and deduce the expression for the rate constant of second-order reaction of the type

$$2A \rightarrow \text{Product}$$

(c) Hydrolysis of ethyl acetate in the presence of H^+ ions is of ... order (Fill in the blanks)

(d) Optical rotation of sucrose in 1 N HCl at various times was given as shown below:

Show that inversion of sucrose is a first-order reaction

47. (a) Write a note on stationary state hypothesis.

(b) Calculate the activation energy of a reaction whose reaction rate at 27°C gets doubled for 10°C rise in temperature.

(c) Discuss the kinetic of the first-order consecutive reaction:

Deduce expression for the concentration of *A*, *B* and *C* at any time. Show graphically the variation of concentration of A, *B* and *C* with time.

48. (a) Derive a second-order rate equation for the reaction

$$2A \rightarrow \text{Products}$$

(b) Explain that half-life period in a second-order reaction depends upon the initial concentration of the reactions.

(c) Explain the following:

(i) Some reactions take place at higher temperature but not at room temperature.

(ii) Rate of forward reaction is greater than the rate of reverse reaction in case of an endothermic reaction.

(d) Why are reactions of higher order rare?

49. (a) Derive the equation:

For a first-order reaction, what are the units of k?

(b) State and explain the following:

(i) Consecutive reactions

(ii) Parallel reactions



Catalysis 8

LEARNING OBJECTIVES

- Define the phenomenon of catalysis and classify into positive and negative catalysis
- Explain the principle of catalysis using the concept of activation energy
- Understand the action of promotors, activators and inhibitors (poisons)
- Describe the general characteristics of catalysed reaction
- Understand intermediate compound formation theory and adsorption theory to explain the phenomenon of catalysis
- Understand activity and selectivity of solid catalysis
- Have an elementary idea of shape-selective catalysis by zeolites
- Study the examples, mechanism and kinetics of homogenous and heterogeneous catalysis
- Learn enzyme catalysis and its mechanism (Michaelis-Menten equation)
- Learn autocatalysis with examples

8.1 INTRODUCTION

There are certain reactions which are not complete even after long periods of time, may be hours, days or even months. But these reactions are completed in seconds and minutes if carried out in the presence of a very small quantity of a foreign substance. This foreign substance is called a *catalyst.* For example, thermodynamic principles say that hydrogen can react with oxygen to form water. However, an actual experiment shows that no appreciable quantity of water is formed. However, when we carry out the reaction in the presence of platinum the progress of the reaction is very fast.

It was Berzelius who discovered in 1836 that there are some substances which increase the rate of a reaction without themselves getting consumed. He named such substances *catalysts* (Greek ***kata*** = wholly, ***lein*** = to loosen). He assumed that catalysts functioned by loosening the bonds in reacting molecules.

A catalyst is a substance that changes (usually increases) the rate of a reaction but is recovered chemically unchanged at the end of the reaction and the phenomenon is called catalysis.

Positive and Negative Catalysis If a catalyst increases the rate of a reaction, it is called a positive catalyst and the phenomenon is called positive catalysis.

A few examples of positive catalysis are:

(a) Oxidation of SO_2 to SO_3 using NO as catalyst

$$SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{NO(g)} SO_3(g)$$

(b) Decomposition of potassium chlorate in presence of MnO_2 as catalyst

$$2KCl\,O_3(s) \xrightarrow{MnO_2(s)} 2\,KCl(s) + 3O_2(g)$$

(c) Manufacture of ammonia by Haber's process using finely divided iron as catalyst

$$N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3(g)$$

If a catalyst decreases the rate of a reaction, it is called a negative catalyst and the phenomenon is called negative catalysis. A few examples of negative catalysis are

(a) Decomposition of H_2O_2 is retarded in the presence of traces of acetanilide

$$2H_2O_2 \xrightarrow{\text{Acetanilide}} 2H_2O + O_2$$

(b) Oxidation of chloroform is retarded in the presence of a small quantity of ethyl alcohol

$$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \xrightarrow{C_2H_5OH} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

8.1.1 Activation Energy Diagram for Catalysed and Uncatalysed Reactions

Mechanism of Catalysis A catalyst decreases the activation energy of the reactants. It lowers the energy barrier and thus makes the reaction faster, as shown in Fig. 8.1. However, in a reversible reaction, the catalyst decreases the activation energy of the forward reaction as well as that of the backward reaction by the same amount. Thus, both the forward and the backward reactions are accelerated to the same extent. As a result, the equilibrium is attained quickly but does not change position.

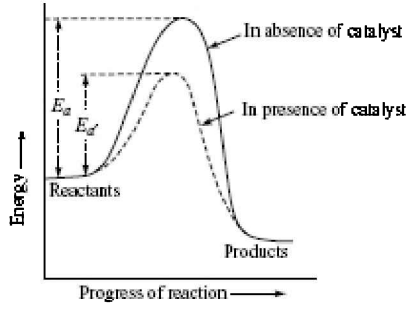


Fig. 8.1 *Activation energy diagram uncatalysed and catalysed reactions.*

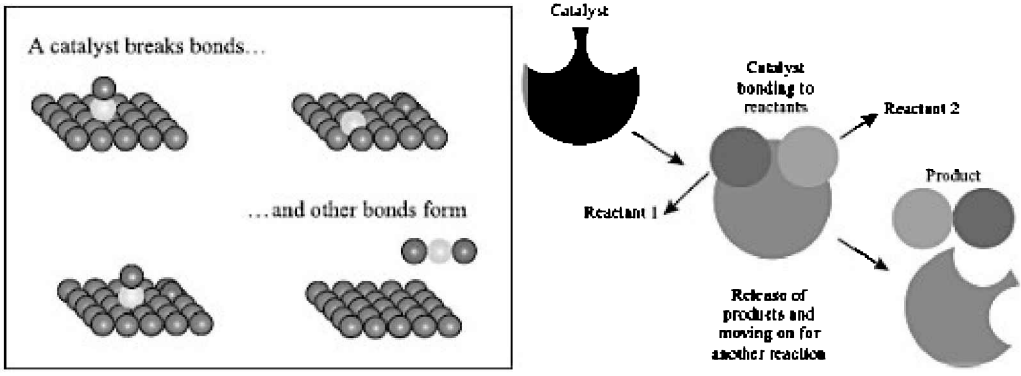


Fig. 8.2 *Function of a catalyst*

The function of the catalyst is to break the bonds in the reactant molecules and form new bonds to give the products through lowering of activation energy.

8.1.2 Promoters or Activators

Sometimes, the presence of some other substances which are not themselves catalysts but increases the efficiency of a catalyst. Such substances, thus, act as catalyst for the catalyst and are called ***promoters*** or ***activators.*** Molybdenum acts as a promoter for the iron catalyst in the manufacture of ammonia by Haber's process.

Explanation of Promoter Action There is ambiguity about the promoter action. It is assumed that the following changes take place on adding the promoter to the catalyst.

(a) Increase of Active Sites The number of peaks and cracks on the catalyst surface is increased on addition of a promoter to the catalyst. This increases the concentration of reactants (based on adsorption theory) and rate of the reaction.

(b) Change in Lattice Spacing The lattice spacing is increased, thus enhancing the space between the catalyst particles. The bonds between the molecules of the reactants (say, H_2) are weakened and cleaved. This makes the reaction go faster (Fig. 8.3)

This explains how Mo acts as a promoter in the manufacture of NH_3 with Fe as catalyst in the Haber's process.

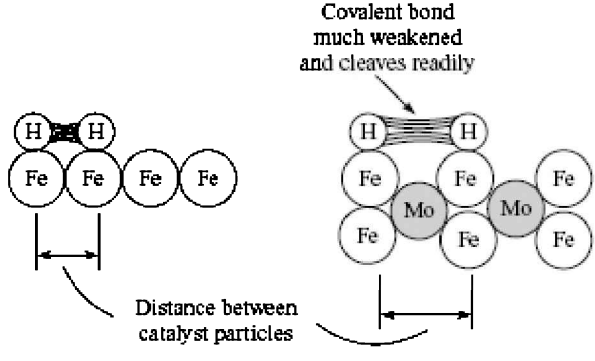


Fig. 8.3 *Increase of crystal lattice spacing of catalyst makes the reaction go faster.*

8.1.3 Inhibitors (Catalytic Poisons)

It has been observed in some cases that the presence of small quantities of impurities in the reacting substances makes the catalyst inactive. Such substances are called ***catalytic poisons*** or ***inhibitors.*** Catalytic poisons are usually also poisonous to organisms. Arsenious oxide and hydrogen cyanide are two of the most powerful catalytic poisons. Arsenious oxide poisons plantinized asbestos used as a catalyst in the manufacture of H_2SO_4 by contact process.

Similarly, platinum catalyst used in the oxidation of H_2 is poisoned by CO.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O \text{ (Poisoned by the presence of CO)}$$

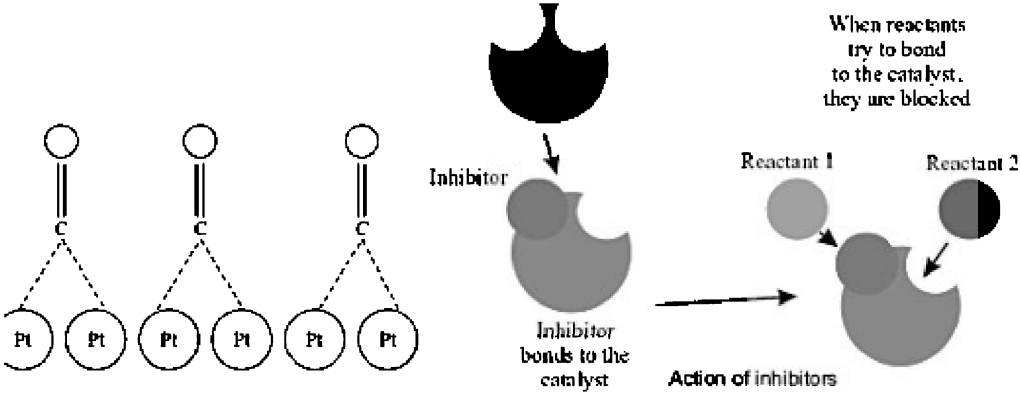


Fig. 8.4 *Poisoning of platinum catalyst by carbon monoxide*

Explanation of the Action of Inhibitors (Poisoning)

1. The catalyst may combine chemically with the poison. Poisoning of iron by H_2S falls in this category (Fe is a catalyst in the manufacture of NH_3 by Haber's process):

$$Fe + H_2S \rightarrow FeS + H_2$$

2. The poison is adsorbed on the catalyst surface in preference to the reactants. The surface of the catalyst becomes unavailable to the reactant and the rate of reaction falls. Poisoning by As_2O_3 or CO appears to be of this kind (Fig. 8.4).

8.2 GENERAL CHARACTERISTICS OF CATALYSED REACTIONS

Some characteristic properties of catalysed reactions are discussed as under:

1. Only a Small Quantity of the Catalyst is Needed for Carrying out the Reaction

There are reactions where a very small amount of catalyst is required to convert very large amounts of reac-tants into the products. For example,

one gram of platinum is quite sufficient for the decomposition of 10^8 litres of hydrogen peroxide. However, there are some reactions, especially homogenous catalysed, where the rate increases with the increase in concentration of the catalyst. In the inversion of cane sugar in the

presence of dilute HCl as a catalyst, the rate of the reaction increases with the increase in concentration of HCl. On the other, hand there are reactions in which the rate of the reaction increases proportionally with the increase in the surface area of the catalyst.

2. Catalyst Remains Unchanged Chemically at the End of the Reaction The amount of catalyst recovered at the end of the reaction is found to be the same as the amount taken at the beginning of the reaction. Thus, a catalyst does not undergo any chemical change although its physical state such as size, colour, etc., may change. For example, MnO_2 which is used as a catalyst in the decomposition of $KClO_3$, changes its physical state from coarse powder to fine powder at the end of the reaction.

A smooth platinum gauze which is used for the oxidation of NH_3 may turn rough at the end of the reaction.

3. Catalyst does not Initiate a Reaction, it Simply Increases or Decreases the Speed of the Reaction However, this is not always the case because there are a large number of reactions which are initiated in the presence of a catalyst. The function of the catalyst is to follow an alternative path for the reaction which requires lower activation energy.

4. A Catalyst does not Affect the State of Equilibrium in a Reversible Reaction It does not alter the value of the equilibrium constant. From the thermodynamic point of view, for a reversible reaction whether it occurs in the presence or absence of a catalyst, the free energy of the process is the same. A catalyst accelerates both the forward and backward reaction and helps to attain the equilibrium quickly (Fig. 8.5).

The figure indicates that the equilibrium for the reaction between $A + b \rightarrow C + D$ is attained in a shorter time in the presence of a catalyst.

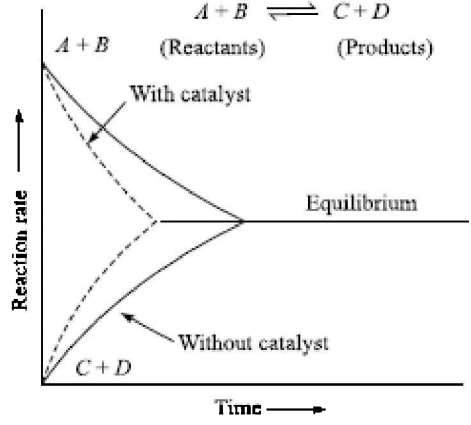


Fig. 8.5 *Effect of a catalyst on the time required for the equilibrium to be established.*

5. Activity of a Catalyst is Increased by the Presence of a Substance Known as Promoter For example, in the manufacture of ammonia by Haber's process, finely divided iron is supported over molybdenum. Here, molybdenum (*Mo*) acts as a promoter for the catalyst iron.

6. A Catalyst is Specific in its Action A given catalyst can catalyse only a specific reaction. For example, MnO_2 can catalyse the decomposition of $KClO_3$ but fails for other

reactions. Similarly, enzymes are also specific in their action.

7. A Catalyst is Poisoned by the Presence of Certain Substances Even in Small Amounts Called Catalystic Poisons Some powerful catalytic poisons are As_2O_3, HCN, CO, etc. Presence of these substances makes the catalyst inactive.

8. A Catalyst has an Optimum Temperature A catalyst can act effectively at a particular temperature for a specified reaction. This temperature is known as optimum temperature, for example, the optimum temperature for the oxidation of SO_2 to SO_3 in the presence of Pt catalyst is 400° to 500°C.

8.3 THEORIES OF CATALYSIS

Different mechanisms have been proposed by which catalysts can act. The major requirement for such type of reactions to occur is that the reactants must acquire some minimum amount of energy, called threshold energy. ***The energy required to activate the reactant species to the level of threshold energy is known as activation energy.***

In the presence of a catalyst, the magnitude of activation energy required is less than in the uncatalysed reaction because the reaction follows a different path which has low activation energy. Due to lower value of activation energy of the catalysed reaction, a greater number of reactant species participate in the reaction and thereby the rate of the reaction is increased.

Two main theories which explain the role of a catalyst in the catalytic reactions are discussed below:

8.3.1 Intermediate Compound Formation Theory

According to this theory, a catalyst must chemically combine with one or more of the reactants to form an unstable ***intermediate product.*** It decomposers or combines later with the other reactant to form the product and the catalyst is regenerated. The catalyst reacts further with more of reactants.

Consider a reaction

$$A + B \xrightarrow{X} AB \ (X \text{ is a catalyst})$$

The reaction is supposed to occur by the following steps:

(i) $A + X \rightarrow A X$ (unstable intermediate)

(ii) $AX + B \rightarrow AB + X$

OR

(i) $A + B + X \rightarrow ABX$ (unstable intermediate)

(ii) $AB X \rightarrow AB + X$

In many cases, the intermediates have been isolated. Some examples are given below.

1. In the formation of diethyl ether by the action of conc. H_2SO_4 on ethyl alcohol, an intermediate ethyl hydrogen sulphate is formed which reacts with other molecules of ethyl alcohol to form diethyl ether and H_2SO_4 is regenerated.

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

(Reactant) (Catalyst) (Ethyl hydrogen sulphate)

$$C_2H_5HSO_4 + C_2H_5OH \xrightarrow{140^\circ} C_2H_5-O-C_2H_5 + H_2SO_4$$

(Intermediate) (Product) Catalyst

2. During the manufacture of sulphuric acid by lead chamber process, an intermediate compound, nitrososulphuric acid ($HOSO_2NO_2$), is actually formed if the amount of water vapour is small.

$$2SO_2 + H_2O + \underbrace{NO + NO_2}_{\text{Catalyst}} + O_2 \rightarrow \underset{\text{Nitrosulphuric acid}}{2HO - SO_2 - NO_2}$$

$$2HO - SO_2 - NO_2 + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$$

Nitrososulphuric acid (Intermediate) Catalyst

The intermediate compound formation theory satisfactorily accounts for homogeneous catalysis but fails to explain the gaseous reaction taking place on the surface of solids, i.e. heterogeneous catalysis. Also, this theory does not explain deactivation by a catalyst poison and activation by catalyst promoter.

8.3.2 Adsorption Theory

Heterogeneous reactions generally occur through adsorption of the reactants on the surface of the catalyst. The catalytic action of a surface depends on the extent of adsorption of the reactants. The molecules of the reacting gases are adsorbed at different sites on the surface of a catalyst. These adsorbed molecules may then combine to form ***adsorbed activated*** *complex* which then decomposes to form the products which are desorbed from the surface. Following steps are involved in the whole process, in the given order:

1. Diffusion of reactants to the surface
2. Adsorption of reactants molecules on to the surface.
3. Chemical reaction on the surface
4. Desorption of products from the surface
5. Diffusion of products away from the surface

In general, Step (3) determines the rate of reaction as it is the slowest step.

The stronger forces are operative in chemisorption which tend to bring about a partial loosening of the bonds in the adsorbed reacting molecules and a very small amount of energy is required to form the activated complex for the reaction.

Adsorption takes place on ***active centres*** on the surface of a catalyst. *X*-ray studies of the catalyst reveal that there are free valencies present on the surface of a catalyst because of a number of edges, corners, cracks and peaks on the rough surface of the catalyst. ***The surface atoms at these sites have free valencies which can be used to attach molecules. The reacting gas molecules are adsorbed at these sites to form surface activated complex. These sites are called active centres.***

This explains how the catalytic activity of the finely divided catalyst is increased.

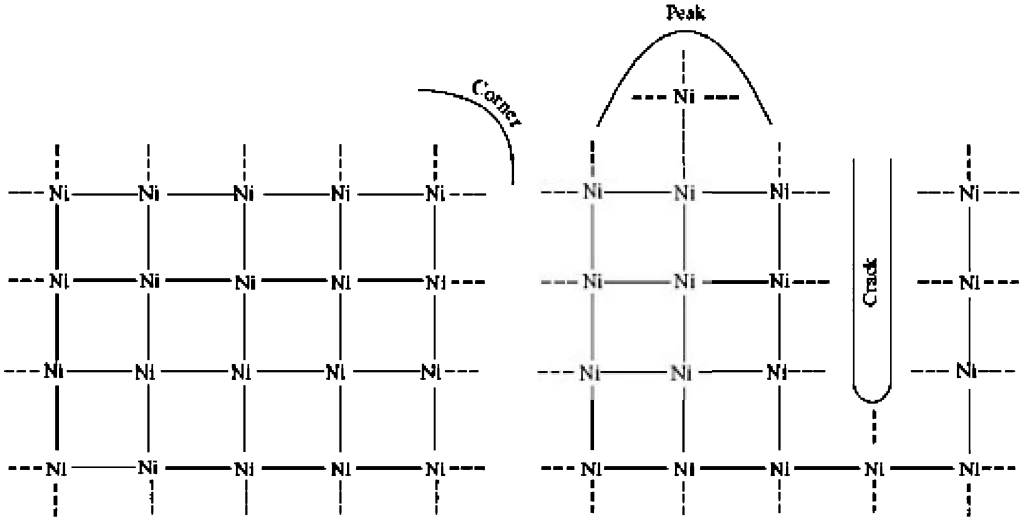


Fig. 8.6 *Active centres on a catalyst surface*

The surface of nickel crystal may be represented in Fig. 8.6. The dotted lines represent free valencies of nickel atoms. At the peak, there will be a greater number of unsatisfied valencies. Isolated nickel atoms would be the centres of great activity.

8.3.3 Function of Surface in Heterogeneous Catalysis

A molecule is activated when it gets adsorbed on two or more active sites. Molecules can react with more probability when they are held side by side on the surface than during the collisions in the bulk of the gas. Hence, spacing of the active sites and the mode of attachment of the gas molecules are most important.

This is illustrated with the help of the following examples:

When alcohol vapours are passed over reduced copper at 623 K, the alcohol undergoes dehydroge-nation while it gets dehydrated on alumina.

The possible orientation of the molecules are shown below in Fig. 8.7.

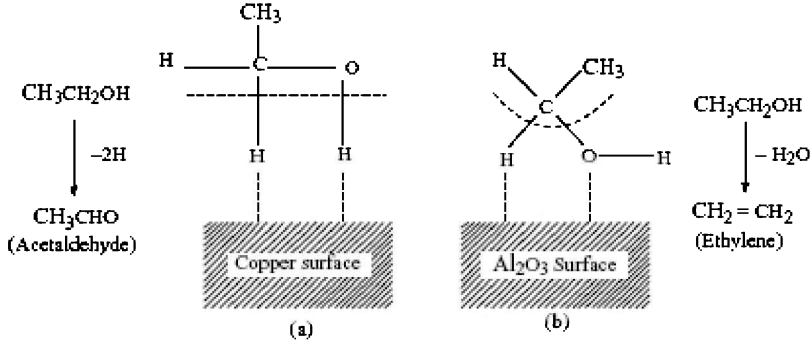


Fig. 8.7 *Adsorption of C_2H_5OH molecule on different catalytic surfaces.*

In Fig. 8.7(a), the C–H and O–H bonds get weakened and dehydrogenation is favoured. In Fig. 8.7(b), C–O and C–H bonds get weakened or stretched and dehydration is favoured.

8.4 IMPORTANT FEATURES OF SOLID CATALYSTS

Activity and selectivity are two important features of solid catalysts. These are discussed separately as under:

1. Activity We estimate the activity of a catalyst by the strength of chemisorption. The reactants must get adsorbed on the surface. But at the same time, they must leave the surface after the reaction is complete in order to make space for the adsorption of other reactant molecules. Activity of the metals increases along the period in *d*-block elements. For example, in hydrogenation reactions, the catalytic activity increases from Group 5 to Group 11 metals with the maximum activity shown by groups 7-9 elements. Thus, Pt acts as catalyst for the combination of H_2 and O_2 to give H_2O.

2. Selectivity By selectivity of a catalyst, we mean its ability to form a particular product. For example, combination of H_2 and CO yields different products with different catalysts as given below:

(a) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

(b) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO - Cr_2O_3} CH_3OH(g)$

(c) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

We can, therefore, say that action of a catalyst is highly selective in nature. That is, a given substance can catalyse only one particular reaction. A substance which is used for a reaction may not work for another reaction.

8.5 SHAPE-SELECTIVE CATALYSIS BY ZEOLITES

The catalytic activity that depends on the pore structure of the catalyst, size of the reactant and product molecules is called ***shape-selective catalysis.*** Examples of shape selective catalysts are zeolites which have honeycomb-like structures. They are microporous (small pores) aluminosilicates having three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms. The catalytic reaction that takes place depends upon the pore size and cavities in zeolites. Zeolites find extensive use in petrochemical industry for cracking of hydrocarbons and isomerisation. The zeolite ZSM-5 converts alcohols directly into gasoline which is a mixture of different hydrocarbons. Similarly, Al-MCM-68 zeolite catalyst at 450-600°C brings about cracking of hexane into smaller hydrocarbons (Fig. 8.8).

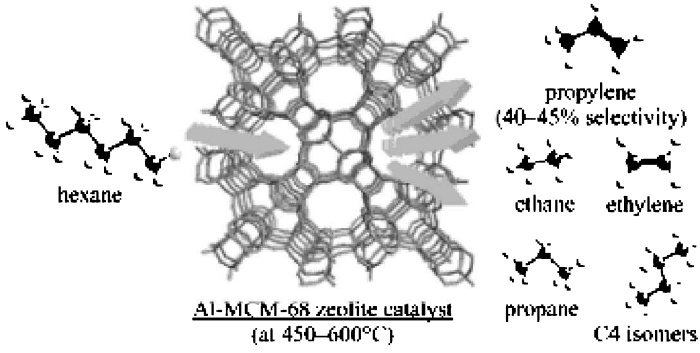


Fig. 8.8 *Zeolite Catalyst*

8.6 HOMOGENEOUS CATALYSIS

When in a reaction, the catalyst is present in the same phase as the reactants, it is called homogeneous catalysis.

Examples of homogeneous catalysis are given below:

1. Gaseous Phase

(a) Decomposition of acetaldehyde in the presence of iodine vapours

$$CH_3CHO(g) \xrightarrow{I_2(g)} CH_4(g) + CO(g)$$

(b) Decomposition of ozone in presence of NO or N_2O_5

$$2O_3(g) \xrightarrow{NO(g)} 3O_2(g)$$

(c) Reaction between SO_2 and O_2 to form SO_3 in presence of nitric oxide (NO)

$$2SO_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(d) Decomposition of vapours of N_2O at 1000 K in presence of traces of chlorine gas

$$2N_2O(g) \xrightarrow[1000\ K]{Cl_2(g)} 2N_2(g) + O_2(g)$$

2. Liquid Phase

(a) Decomposition of H_2O_2 in the presence of I^- ion or Br_2

$$2H_2O_2(aq) \xrightarrow[or\ Br_2]{I^-(aq)} 2H_2O(l) + O_2(g)$$

(b) Acid-Base Catalysis

(i) Hydrolysis of cane sugar (sucrose) in the presence of a mineral acid (inversion of cane sugar)

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H^+(aq)} \underset{Glucose}{C_6H_{12}O_6(aq)} + \underset{Fructose}{C_6H_{12}O_6(aq)}$$

(ii) Hydrolysis of methyl acetate by an acid or a base

$$CH_3COOCH_3(aq) + H_2O(l) \xrightarrow[\text{or } OH^-(aq)]{H^+(aq)} CH_3COOH(aq) + CH_3OH(aq)$$

(iii) Hydrolysis of starch to glucose in presence of an acid

$$(C_6H_{10}O_5)n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$

Starch Glucose

8.6.1 Mechanism of Homogeneous Catalytic Reactions

A homogeneous catalytic reaction usually involves the following two steps:

1st Step: The catalyst (C) reacts with the reactant (A) to form an intermediate complex:

$$A + C \rightarrow AC$$

2nd Step: The complex then decomposes to form the product regenerating the catalyst or reacts with a second reactant (B) to give the product and regenerating the catalyst, i.e.,

$$AC \rightarrow \text{Product} + C$$

$$AC + B \rightarrow \text{Product} + C$$

or

This is illustrated with examples given below:

1. **Mechanism of the reaction** $CH_3CHO \xrightarrow{I_2} CH_4 + CO$

   1st step: $CH_3CHO + I_2 \rightarrow CH_31 + HI + CO$

   2nd step: $CH_3I + HI \rightarrow CH_4 + I_2$

2. **Mechanism of the reaction** $2O_3 \xrightarrow{N_2O_5} 3O_2$

   1st step: $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

   2nd step: $N_2O_4 + O_3 \rightarrow N_2O_5 + O_2$

3. **Mechanism of the reaction** $2SO_2 + O_2 \xrightarrow{NO} 2SO_3$

   1st step: $2NO + O_2 \rightarrow 2NO_2$

   2nd step: $2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$

4. **Mechanism of the reaction** $2H_2O_2 \rightarrow 2H_2O + O_2$

   1st step: $H_2O_2 + I^- \rightarrow H_2O + KT$

   2nd step: $H_2O_2 + KT \rightarrow H_2O + O_2 + \Gamma$

5. **Mechanism of the reaction** $2N_2O \xrightarrow{Cl_2} 2N_2 + O_2$

   1st step: $Cl_2 \rightarrow 2Cl$

   2nd step: $N_2O + Cl \rightarrow N_2 + ClO$

   3rd step: $2ClO \rightarrow Cl_2 + O_2$

8.6.2 Kinetics of Homogenous Catalytic Reactions

The rate equation in the presence of a catalyst is obtained experimentally. This tells the type and number of the different molecules taking part in the rate-determining step (slowest step), which then helps to write the probable mechanism of the reaction. This is illustrated with the help of following examples.

1. Kinetics of the Dehydration of Tert-butyl Alcohol in the Presence of HBr The dehydration of tert-butyl alcohol takes place as

$$\underset{\text{Tert-butyl alcohol}}{(CH_3)_3C-OH} \longrightarrow \underset{\text{2-methyl propene}}{(CH_3)_2C=CH_2} + H_2O$$

In the absence of a catalyst, the alcohol does not decompose at any appreciable rate upto about 700 K. On adding a small amount of HBr, rapid decomposition occurs at 500 K. The rate equation for the uncatalysed reaction is

$$\text{Rate} = -\frac{d[t\text{-BuOH}]}{dt} = k_1[t\text{-BuOH}]$$

i.e., it is a first-order reaction with very low value of k_1.

In the presence of HBr, the rate equation is observed to be

$$\text{Rate} = -\frac{d[t\text{-BuOH}]}{dt} = k_2[t\text{-BuOH}][HBr]$$

i.e. it is a second-order reaction with high value of k_2. This suggests that a possible mechanism for the catalysed reaction is

$$(CH_3)_3C-OH + HBr \xrightarrow{\text{slow}} (CH_3)_3C-Br + H_2O \ldots \text{Rate-determining step}$$

$$(CH_3)_3C-Br \xrightarrow{\text{fast}} (CH_3)_2C=CH_2 + HBr$$

2. Kinetics of the decomposition of acetaldehyde in presence of iodine vapours as catalyst The decomposition of acetaldehyde takes place as

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

The observed rate equation for this reaction is found to be

$$\text{Rate} = \frac{d[CH_3CHO]}{dt} = k_1[CH_3CHO]^2$$

Which suggests the mechanism as follows

$$CH_3CHO + CH_3CHO \rightarrow 2CH_4 + 2CO$$

In the presence of iodine vapors (as catalyst), the rate equation is observed to be

$$\text{Rate} = \frac{d[CH_3CHO]}{dt} = k_1[CH_3CHO][I_2]$$

This suggests the probable mechanism of the catalysed reaction as follows.

$$CH_3CHO + I_2 \xrightarrow{\text{slow}} CH_3I + HI + CO \text{ Rate determining step}$$

$$CH_3I + HI \xrightarrow{\text{fast}} CH_4 + I_2$$

8.6.3 Rate of an Acid Catalysed Reaction

In an ***acid catalysed reaction,*** the first step is the transfer of a proton (H^+ ion) from the acid HA to the substrate S (one of the reactants).

$$S + HA \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^- \qquad \ldots(8.1)$$

This is then followed by one of the two possibilities, i.e., either proton transfer to the solvent

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+ \text{ (P = Product)} \qquad \ldots(8.2)$$

or proton transfer to the base A^-, i.e.

$$SH^+ + A^- \rightarrow P + HA \qquad \ldots(8.3)$$

Taking the reaction (8.1) as the first step and reaction (8.2) as the second step, then taking the latter as the rate-determining step, the reaction rate is given by

$$= \frac{-d[S]}{dt} = k_2[SH^+] \qquad \ldots(8.4)$$

But the reaction of $[SH^+]$ with time is given by

$$\frac{d[SH^+]}{dt} = \text{Rate of formation of } SH^+ \text{ from S and } HA^+ - \text{Rate of reaction of } SH^+ \text{ with } H_2O$$

$$= k_1[S][HA] - k_1'[SH^+][A^-]\} - \{k_2[SH^+]\}$$

But steady-state condition implies that the rate of change of concentration of $[SH^+]$ with time should be zero,

i.e. $$\frac{d[SH^+]}{dt} = 0$$

Thus, $$k_1[S][HA] - k_1'[SH^+][A^-] - k_2[SH^+] = 0$$

or $$[SH^+]\{k_1'[A^-] + k_2\} = k_1[S][HA]$$

or $$[SH^+] = \frac{k_1[S][HA]}{k_1'[A^-] + k_2} \qquad \ldots(8.5)$$

Putting this value in Eq. (8.4), we get,

$$-\frac{d[S]}{dt} = k_1 k_2 \times \frac{[S][HA]}{k_1'[A^-] + k_2} \qquad \ldots(8.6)$$

If $k_2 << k'_1 [A^-]$, Eq. (8.6) becomes

$$-\frac{d[s]}{dt} = \frac{k_1 k_2 [S][HA]}{k_1'[A^-]} \qquad \ldots(8.7)$$

8.7 HETEROGENEOUS CATALYIS

If the catalyst is present in a different phase from that of the rectants in a reaction, it is called heterogeneous catalysis. The catalysts are usually solids whereas the reactants could be gaseous or liquid. The reactions occur at the surface of the catalyst. That is why this type of catalysis is also called ***surface catalysis*** or ***contact catalysis.*** Evidently, greater the surface area of the catalyst, greater is the efficiency of the catalyst. For this reason, finely divided solids are generally used as catalysts.

8.7.1 Examples of Heterogeneous Catalytic Reactions

1. Formation of SO_3 from SO_2 and O_2 in contact process, using finely divided platinum or vanadium pentoxide as catalyst for manufacture of sulphuric acid

$$2SO_2(g) + O_2(g) \xrightarrow[\text{or } V_2O_5]{Pt} 2SO_3(g)$$

2. Manufacture of methyl alcohol from CO and H_2 using ZnO and Cr_2O_3 as catalysis

$$CO(g) + 2H_2(g) \xrightarrow{ZnO/Cr_2O_3} CH_3OH(g)$$

3. Manufacture of ammonia from nitrogen and hydrogen using finely divided iron as catalyst

$$N_2(g) + 3H_2(g) \xrightarrow[\text{divided Fe}]{\text{finely}} 2NH_3(g)$$

8.7.2 Heterogeneous Catalysis is Surface Catalysis

Consider the bromination of ethylene

$$CH_2 = CH_2(g) + Br_2(g) \longrightarrow BrCH_2 - CH_2Br(g)$$

This reaction takes place readily in a glass vessel at 470 K. It was considered an ordinary homogeneous catalytic reaction. However, it was observed that the rate is higher in a smaller reaction vessel or in a vessel packed with glass beads but the rate is reduced when the vessel is coated on the inside with paraffin wax. This shows that the reaction is not occurring in the gas phase but is occurring on the glass surface of the vessel. The glass acts as a catalyst.

8.7.3 Heterogeneous Catalysts are Specific

Consider the decomposition of formic acid. If the acid vapour is passed through a heated glass tube the reaction is about 50% dehydration and 50% dehydrogenation, i.e.

(a) $HCOOH \rightarrow H_2O + CO$

(b) $HCOOH \rightarrow H_2 + CO_2$

If the tube is packed with Al_2O_3, only the reaction (a) occurs but if it is packed with ZnO, only the reaction (b) occurs. This illustrates specificity of a heterogeneous catalyst.

8.7.4 Mechanism of Heterogeneous Catalytic Reactions

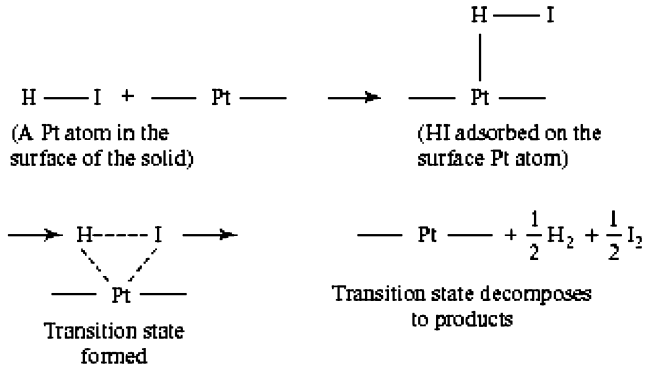
A heterogeneous catalytic reaction takes place through the following sequence of steps (see Fig. 8.9).

1. Diffusion of the reactant molecules towards the surface of the catalyst.
2. Adsorption of the reactant molecules on the surface of the solid.
3. Chemical reaction of the absorbed molecules with the surface of the catalyst resulting into stretching and weakening of bonds forming an activated complex with the catalyst which then decomposes or even breaking of the bonds of reactant molecules.
   Step (2) and (3) are jointly called chemisorption.
4. Desorption of the products from the surface.
   Diffusion of the products away from the surface.
   The various steps are illustrated with the following examples:

1. Decomposition of HI in the Presence of Platinum

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

The mechanism of this reaction may be represented as follows:



2. Hydrogénation of Ethylene in Presence of Finely Divided Ni, Pt or Pd.

It is illustrated as under:

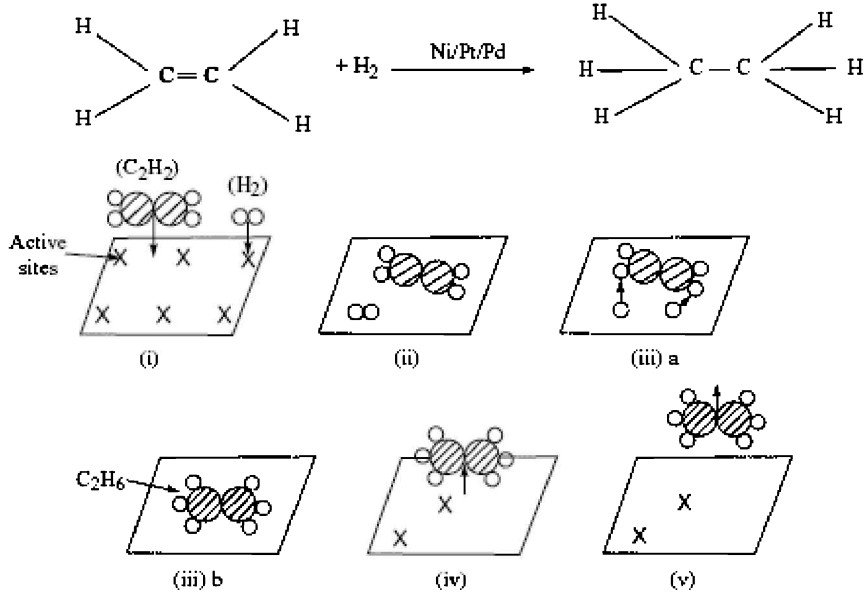


Fig. 8.9 *Mechanism for the reaction between ethylene and hydrogen on a catalytic surface*

(i) Diffusion of C_2H_4 and H_2 towards the surface

(ii) Adsorption of C_2H_4 and H_2 at the active sites.

(iii) • Dissociation of H_2 into H atoms

• Linking of the H-atoms to C_2H_4 to form C_2H_6

(iv) Desorption of C_2H_6 from the surface

(v) Diffusion of C_2H_6 away the surface

8.7.5 Kinetics of Heterogeneous (Surface) Catalytic Reactions

A heterogeneous catalytic reaction takes place in a number of consecutive steps. Although any of these steps may be slowest and hence rate determining, yet from the point of view of the study of the kinetics of these reactions, the reaction of the adsorbed molecules is considered to be the rate of determining.

Further, the rate of reaction is supposed to be proportional to the fraction θ of the surface covered by the reactant molecules.

Thus, the two assumptions in the study of kinetics of the surface reactions are

1. The rate of reaction is proportional to the fraction θ of the surface covered by the reactant molecules.
2. The rate-determining step of the surface reaction is the reaction of the adsorbed molecules with the surface of the catalyst.

To understand the kinetics of surface reactions, we consider here the simplest case involving only one ***gaseous reactant*** decomposing on the surface of a solid catalyst according to the reaction.

$$A \longrightarrow \text{Products}$$

Then if θ_A is the fraction of the surface covered by A at any time t when the pressure of the gas is P, then according to the assumption (1), the rate of reaction would be

$$\text{Rate} = k' \theta_A \qquad \ldots(8.8)$$

where k' is a proportionality constant.

The fraction θ is related to the presence of the gas according to the Langmuir equation, viz.

$$\theta = \frac{bP}{1 + bP} \qquad \ldots(8.9)$$

where b is a constant.

Substituting this value in Eq. (8.8), we get

$$\text{Rate} = -\frac{dP}{dt} = k' \frac{bP}{1 + bP}$$

Heterogeneous catalysis finds use in catalytic converters in automobiles. There is high temperature in the car engine which makes N_2 and O_2 of air to combine to form NO (Fig. 8.10)

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

NO gas formed rapidly combines with the atmospheric oxygen to form NO_2 which is a major cause of air pollution. These days, cars are fitted with converters which serve two purposes:

1. Complete conversion of CO formed due to incomplete combustion of the fuel to CO_2. It may be remembered that CO is a harmful gas while CO_2 is not.
2. Dissociation of NO and NO_2 gases into $N_2 + O_2$. The catalyst used in these converters is either CuO or Cr_2O_3

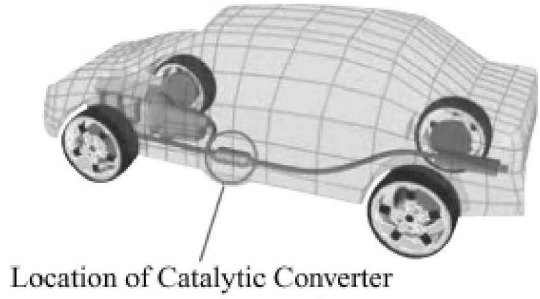

Location of Catalytic Converter

Fig. 8.10

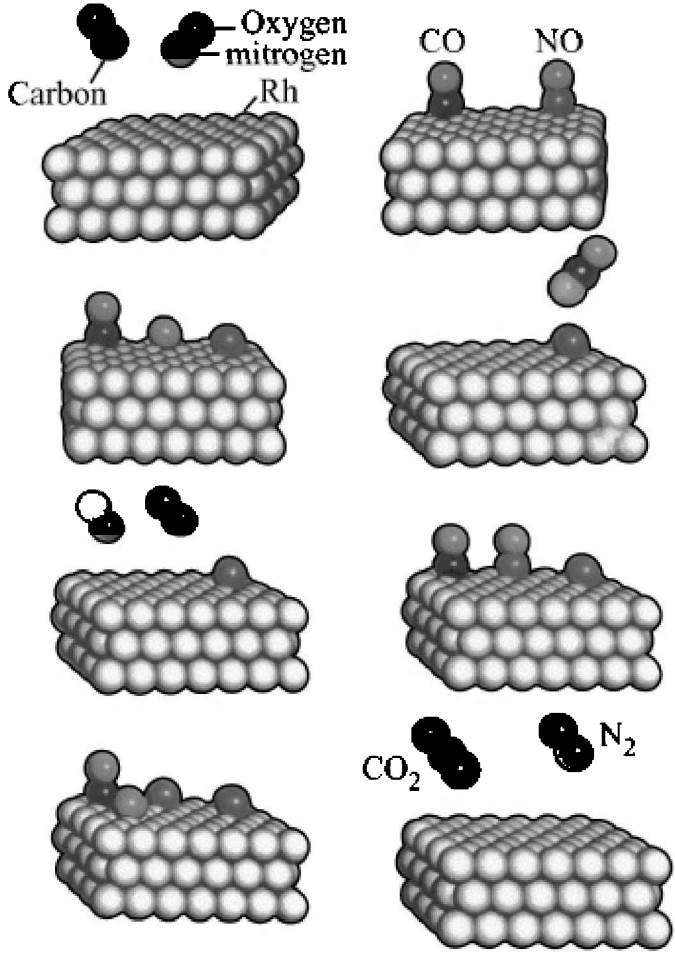

Oxygen
mitrogen
Carbon
Rh
CO
NO
CO_2
N_2

Fig. 8.11 *Conversion of CO and NO into CO_2 and N_2*

Figure 8.11 depicts how the gases CO and NO produced in the automobiles are converted to CO_2 (harmless) and N_2 in different steps in the presence of rhodium (*Rh*)

8.8 ENZYME CATALYSIS

Enzymes are protein molecules present in the living system. Their molecular masses range from $10^4 - 10^6$ g/mol. They are highly efficient biological catalysts which catalyse the reactions taking place in the living cells and also help in controlling the reaction rates.

The reaction in enzyme catalysis occurs at a specific site on the protein molecule. This is called the ***active site.*** The reactants in an enzyme reaction are referred to as ***substrates.***

A few examples of enzyme-catalysed laboratory reactions are given below:

1. $\text{Starch} \xrightarrow{\text{Diastase}} \text{Maltose} \xrightarrow{\text{Maltase}} \text{Glucose} \xrightarrow{\text{Zymase}} \text{Alcohol} + CO_2$

2. $\text{Cane sugar} \xrightarrow[+H_2O]{\text{Invertase}} \underset{\text{(Glucose + Fructose)}}{\text{Invert sugar}} \xrightarrow{\text{Zymase}} \text{Alcohol} + CO_2$

The names of the enzymes are written on the arrows.

Table 8.1 *Enzymes, their source and the enzymatic reaction*

Enzyme	Source	Enzymatic Reaction
Invertase	Yeast	Sucrose → Glucose + Fructose
Zymase	Yeast	Glucose → Ethyl alcohol + Carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Unease	Soyabean	Urea → Ammonia + Carbon dioxide
Pepsin	Stomach	Protein → Amino acids

Enzymes possess certain characteristics which are different from other types of catalysts. A few of these are briefly described below:

1. ***They are highly specific in their catalytic action*** for example, urease, even in very low concentrations, catalyses the hydrolysis of urea but it has no detectable effect on the hydrolysis rate of substituted ureas such as methyl urea. There are many such examples to quote. However, there are some exceptions to this generalisation.
2. ***They are highly sensitive to the acidity or basicity of the solution.*** It is found that the enzymes show a sharp change in activity if the pH of the solution is changed.
3. ***Their efficiency is very high,*** i.e., many of them are so powerful catalysts that they increase the rate of a reaction by many orders of magnitude even at quite low concentration.
4. ***They are highly sensitive to temperature.*** The activity of an enzyme is usually found to be maximum at the normal temperature of the organism in which the enzyme is found. Above this temperature, usually the activity is first found to increase temporarily and then drops to zero when the protein is denatured.

5. ***Their activity increases in the presence of activators and co-enzymes.*** Presence of certain substance called co-enzymes increases enzymatic activity. When a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is considerably increased. Activators are generally metal ions such as Na^+, Mn^{2+}, Cu^{2+}, etc. These metal ions, when bonded to enzyme molecules, increase their catalytic activity.
6. ***Inhibitors and poisons affect the activity.*** The inhibitors or poisons interact with the active functional group or the enzyme surface and result into reduction of catalytic activity of the enzyme. Drugs act as enzyme inhibitors in the body.

Mechanism of Enzyme Reactions (Michaelis-Menten Equation)

The mechanism of an enzyme reaction as proposed by Michaelis and Menten is as follows:

The long chains of the enzyme (protein) molecules are coiled to make a rigid colloidal particle with cavities on its surface. These cavities, which are of characteristic shape and rich in active groups ($–NH_2$, –COOH, –SH, –OH), are termed ***active centres.*** The molecules of substrates which have complementary shapes fit into these cavities just as a key fits into a lock (lock-and-key theory). With the help of active groups, the enzyme forms an activated complex with the substrate which decomposes to yield the products. Thus, the substrate molecule enters the cavities, forms a complex and reacts and the products move out of the cavities (Fig. 8.12).

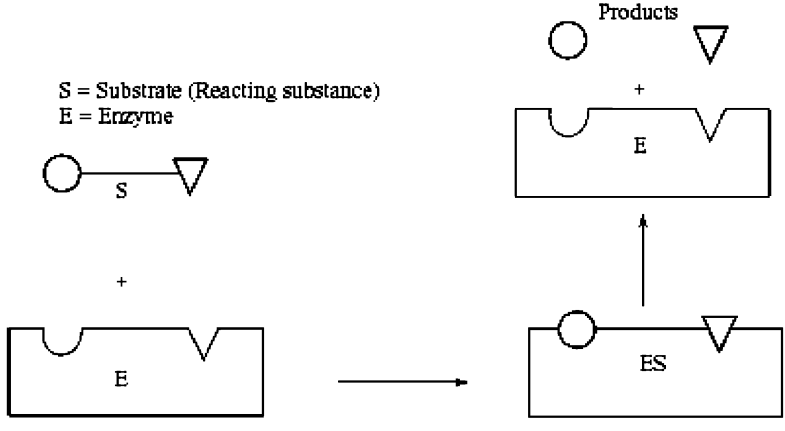


Fig. 8.12 *Illustration of the lock-and-key model of enzyme catalysis*

The first reaction in the enzyme reaction is the reaction between the enzyme E (at the active site) and the substrate S (i.e. reactants of the enzyme reaction) to form the complex ES.

$$E + S \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} ES \qquad \ldots(8.10)$$

This reaction is very fast and the equilibrium is quickly established.

The complex then dissociates forming one or more product P and the enzyme is regenerated.

$$ES \underset{k'_2}{\overset{k_2}{\rightleftharpoons}} E + P \qquad \ldots(8.11)$$

This reaction usually goes to completion, so the rate coefficient k'_2 is effectively zero. The steps (8.10) and (8.11) can be written together as

$$E + S \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} ES \underset{k'_2}{\overset{k_2}{\rightleftharpoons}} E + P \qquad \ldots(8.12)$$

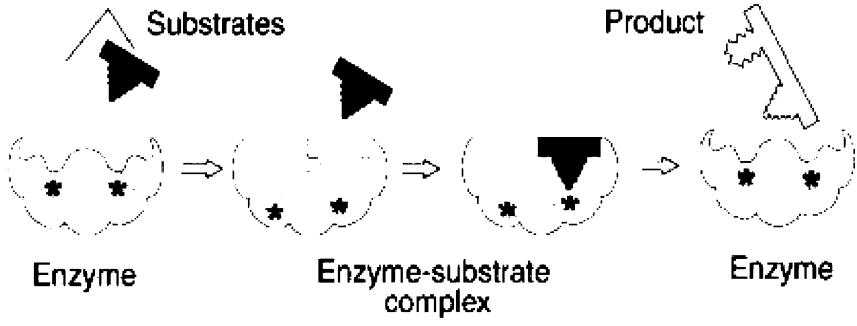


Fig. 8.13 *Illustration of enzyme catalysis*

Thus, the enzyme-substrate complex, ES, is an intermediate and the net reaction is S → P. As a result, the rate of appearance of the product must be equal to the rate of disappearance of the substrate S, i.e.,

$$\frac{d[P]}{dt} = -\frac{d[S]}{dt}$$

This implies that the concentration of the complex ES, represented by [ES] must be in a ***steady state"***.

In other words, the rate of change of concentration of ES with time must be equal to zero. But rate of change of concentration of ES with time will be given by

$$\frac{d[ES]}{dt} = \text{Rate of formation of ES from E and S} - \text{Rate of decomposition of ES into E and P}$$

$$= \{k_1[E][S] - k_1'[ES]\} - \{k_2[ES]\} \quad \ldots(8.13)$$

For steady-state condition, $d[ES]/dt = 0$.

Hence $$k_1[E][S] - k_1'[ES] - k_2[ES] = 0$$

or $$[ES]\{k_1' + k_2\} = k_1[E][S]$$

or $$[ES] = \frac{k_1[E][S]}{k_1' + k_2} \quad \ldots(8.14)$$

This expression gives the steady-state concentration [ES].

Putting $\frac{k_1' + k_2}{k_1} = k_m$, called ***Michaelis constant,*** the expression (8.14) can be written as

$$[ES] = \frac{[E][S]}{K_m} \quad \ldots(8.15)$$

Since [ES] is a steady state, we must have rate of disappearance of S = Rate of disappearance of ES.

i.e., $$-\frac{d[S]}{dt} = k_2[ES] \quad \ldots(8.16)$$

But rate of disappearance of S means the rate of the enzyme catalysed reaction, usually represented by v. Hence,

$$v = -\frac{d[s]}{dt} = k_2 [ES] \quad \ldots(8.17)$$

Substituting the value of [ES] from Eq. (8.15) in Eq. (8.17), we get

$$\boxed{v = -\frac{d[S]}{dt} = k_2 [ES] = k_2 \frac{[E][S]}{k_m}} \quad \ldots(8.18)$$

The equation is, however, not useful in this from since it includes the concentration of free enzyme [E] whereas the experimentally measurable quantity is $[E_o]$, the total concentration of the enzyme, i.e., free as well as combined in the complex ES. But we have

So that

$$[E_o] = [E] + [ES]$$

$$[E] = [E_o] - [ES]$$

Substituting this value in Eq. (8.15), we get

$$[ES] = \frac{\{[E_o] - [ES]\}[S]}{K_m}$$

or $$K_m [ES] - [E_o][S] - [ES][S]$$

or $$K_m [ES] + [ES][S] = [E_o][S]$$

$$[ES]\{K_m + [S]\} = [E_o][S]$$

or $$[ES] = \frac{\{[E_o][S]\}}{K_m + [S]} \quad \ldots(8.19)$$

Substituting this value in Eq. (8.17), we get

$$v = -\frac{d[S]}{dt} = k_2 [ES] = \frac{k_2 [E_o][S]}{k_m + [S]} \quad \ldots(8.20)$$

This equation is known as ***Michaelis–Menten equation*** which contains the measurable quantities, $[E^o]$ and [S].

Equation (8.20) is usually written in terms of maximum velocity v_m of the enzyme-catalysed reaction which is reached when [S] becomes so large that [S] >> K_m so that K_m can be neglected in comparison to [S]. Then Eq. (8.20) takes the form

$$v_m = k_2 [E_o] \quad \ldots(8.21)$$

Hence

$$\frac{v}{v_m} = \frac{[S]}{K_m + [S]} \quad \ldots(8.22)$$

From this equation, we find that

when

$$[S] = K_m, \quad \frac{v}{v_m} = \frac{1}{2}$$

i.e., $$v = \frac{1}{2} v_m$$

Thus, the Michaelis constant is equal to that concentration of the substrate at which the rate

of the enzyme catalysed reaction falls to one half of its maximum value. Thus, the values of v_m and k_m can be obtained by plotting the rate of reaction, v versus the concentration of the substrate *S*.

8.9 AUTOCATALYSIS

When one of the products in the reaction acts as a catalyst for that reaction, the phenomenon is known as autocatalysis.

Examples of Autocatalysis

I. Hydrolysis of an Ester Hydrolysis of ethyl acetate forms acetic acid and ethanol. Acetic acid acts as a catalyst for the reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow[\text{Catalyst}]{H^+} CH_3COOH + C_2H_5OH$$

2. Oxidation of Oxalic Acid When oxalic acid is oxidised by acidified potassium permanganate, manganous sulphate or Mn^{2+} ions produced during the reaction *act as a catalyst* for the reaction

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$$

Whenever autocatalysis occurs, the initial rate of reaction rises as the catalytic product is formed unlike in a normal reaction where the rate of reaction decreases with the passage of time. The curve shown in Fig. 8.14 shows a maximum when the reaction is complete.

Example 1 *The activity of a catalyst increases on decrease in particle size. Explain.*

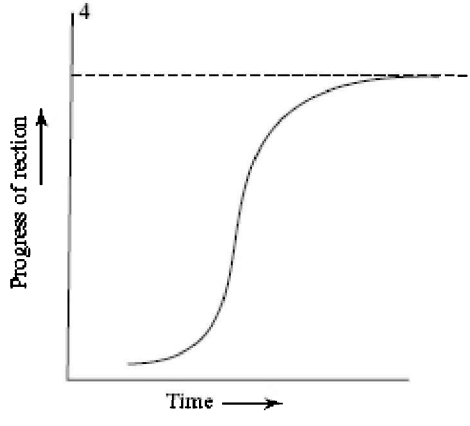


Fig. 8.14 *Curve showing the rise of rate of reaction with time.*

Solution:It has been observed that catalysts in fine powder are more effective than in lump form. This is because the free valencies, which are responsible for catalytic activity increase as the particle size decreases. This is illustrated in Fig. 8.15

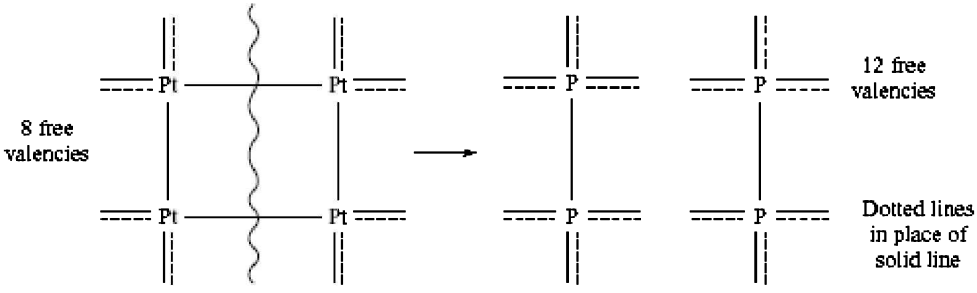


Fig. 8.15 *Subdivision of a catalyst makes it more efficient due to increase of free valence bonds.*

One big particle of Pt. catalyst has 8 free valencies. On division into two smaller particles the number of free valencies increases to 2. The number of free valencies will go on increasing on further subdivision of the catalyst particles.

Example 2 *Write down important features (criteria) of a catalyst.*

Solution:Important features (also known as criteria) of a catalyst are listed as under:

(i) A small quantity of catalyst is generally sufficient to complete a reaction.
It has been observed that in most of the reactions, only a very small amount of the catalyst can produce huge quantities of the products. Only in exceptional cases, like in Friedel Crafts reaction, we require large quantities of the catalyst to obtain good yield.

(ii) A catalyst is specific in action.
A catalyst which works for a reaction may not work for another reaction. The same reactant may yield different products with different catalysts. For example,

$$2C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O \qquad C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2$$

Ethene Ethanal

(iii) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.
Qualitative and quantitative analysis of the catalyst shows that it undergoes no change in mass or chemical nature. It might undergo a physical change.

(iv) A catalyst is more effective when finely divided and powdered than in the coarse state.
Finely divided nickel is a better catalyst than lumps of solid nickel.

SUMMARY

1. A catalyst is a substance that changes (usually increase) the rate of a reaction but is recovered chemically unchanged at the end of the reaction. This phenomenon is called *catalysis.*
2. If the catalyst decreases the rate of the reaction, it is called a negative catalyst or a catalytic poison.
3. There is always an energy barrier that the reactants have to cross in order to change into products. The function of the catalyst is to lower the activation energy so that the reaction takes place faster.
4. There are certain substances which are not catalysts by themselves, but they increase the

efficiency of the catalyst. Such substances are called promoters or activators. They work by increasing the active sites and by changing lattice spacing.

5. Presence of small quantities of certain substances in the reactants makes the catalyst unreactive. Such substances are called poisons or negative catalysts.
6. Some of the characteristics of catalysed reactions are
   (a) only a small quantity of the catalyst is needed
   (b) the catalyst remains unchanged at the end of the reactions
   (c) a catalyst does not initiate the reaction, it simply increases or decreases the rate of the reaction
   (d) a catalyst does not change the equilibrium point
   (e) activity of a catalyst is increased by the presence of promoters and decreased by the presence of poisons
   (f) a catalyst is specific in action and has an optimum temperature
7. According to ***intermediate compound formation theory,*** a catalyst must combine with one or more of the reactants to form an ***unstable intermediate compound.*** It decomposes or combines further with other reactants to give the final products. The catalyst is regenerated.
8. According to ***adsorption theory,*** the molecules of reactants are adsorbed on the surface of the catalyst. These adsorbed molecules may then combine to form ***adsorbed activated complex*** which then decompose into the products.
9. Catalysis performed by living organism is called ***enzyme catalysis.*** Proteins are highly efficient biological catalysts which catalyse the reactions taking place in the living cells and also help in controlling the reaction rates.
10. According to mechanism proposed by ***Michaelis and Menten,*** long chains of enzyme (proteins) molecules are wiled to make a rigid colloidal particle with cavities on its surface. These cavities which are of characteristic shape and rich in active groups like – NH_2, –COOH, –SH, – OH are termed ***active centres.*** The molecules of the substrate which have complementary shape fit into these cavities just as a key first into a lock **(lock-and-key theory)**
11. When one of the products in the reaction acts as a catalyst for that reaction, the phenomenon is called autocatalysis.

KEY RELATIONS

Michealis-Menten Equation

1. $v = -\frac{d[S]}{dt} = k_2\,[\mathrm{ES}] = \frac{k_2[E_0][S]}{k_m + [S]}$

The terms E and S stand for the enzyme and substrate respectively

υ = Rate of the enzyme catalysed reaction

E_0 = Total concentration of the enzyme, i.e. free as well as combined

2. $v = \frac{1}{2}v_m$ where υ_m = Maximum velocity of the enzyme-catalysed reaction

EXERCISES

Objective Questions

(A) Fill in the Blanks

1. A_____ remains unchanged in mass and chemical composition at the end of the reaction.
2. _____ theory explains the mechanism of enzyme reactions.
3. If the catalyst is present in a different phase from that of the reactants, it is called_____ catalyst.
4. A catalyst does not_____ a reaction, it simply increases or decreases the rate of the reaction.
5. The promoter changes the_____ in the catalyst which help in weakening the bond between reactant molecules.
6. Subdivision of a catalyst makes it more efficient due to increase of_____
7. When one of the products of a reaction act as a catalyst for that reaction, the phenomenon is known as _____
8. The enzyme_____ converts glucose into alcohol.
9. Hydrolysis of cane sugar in the presence of a mineral acid is an example of_____catalysis.
10. Platinum catalyst used in the oxidation of H_2 is poisoned by_____

(B) Multiple-Choice Questions

1. Which of the following are most efficient catalysts?
   (a) Transition metals
   (b) Alkali metals
   (c) Radioactive metals
   (d) Alkaline earth metals
2. The name catalyst was proposed by
   (a) Rutherford
   (b) Langmuir
   (c) Graham
   (d) Berzelius
3. Efficiency of a catalyst depends upon
   (a) molecular mass
   (b) room temperature
   (c) absolute temperature
   (d) optimum temperature
4. Which is not an example of homogeneous catalyst?
   (a) Formation of SO_3 in chamber process

(b) Formation of SO_3 contact process

(c) Hydrolysis of methyl acetate in the presence of an acid

(d) Decomposition of $KClO_3$ in the presence of MnO_2

5. A catalyst is a substance which
   (a) increases the equilibrium concentration of the products
   (b) changes the equilibrium constant of the reaction
   (c) shortens time to reach equilibrium
   (d) supplies energy to the reaction
6. Which of the following statements is not correct?
   (a) Catalyst action is specific.
   (b) A catalyst does not alter the equilibrium.
   (c) A small amount of catalyst is sufficient to catalyse a reaction.
   (d) The catalyst initiates the reaction
7. In the reaction $KMnO_4 + H_2SO_4 + H_2C_2O_4 \rightarrow$ Products, Mn^{2+} ions act as a/an
   (a) positive catalyst
   (b) negative catalyst
   (c) auto catalyst
   (d) enzyme catalyst
8. A substance which decreases the rate of a reaction is a/an
   (a) inhibitor
   (b) poison
   (c) moderator
   (d) promoter

Answers

(A) Fill in the Blanks

1. Catalyst
2. Lock and key
3. Heterogeneous
4. Initiate
5. Lattice spacing
6. Free valence bonds
7. Autocatalysis
8. Zymase
9. Homogeneous
10. CO

(B) Multiple-Choice Questions

1. (a)
2. (d)
3. (d)
4. (b)
5. (c)
6. (d)
7. (c)
8. (a)

SHORT-ANSWER QUESTIONS

1. What is meant by positive and negative catalysis? Give one example each.
2. What are promoters? Explain its action
3. Explain:
   (a) The catalyst does not affect the state of equilibrium.
   (b) The catalyst remains unchanged at the end of the reaction.
4. What is intermediate compound formation theory? What are the different steps involved?
5. What are the different catalysts involved in the conversion of ethyl alcohol to acetaldehyde and ethylene respectively. Illustrate by using the bonds formed with the surface.
6. Give two examples each of homogenous catalysis in gaseous phase and liquid phase.
7. Prove that heterogeneous catalysis is surface catalysis.
8. What is meant by activity and selectivity of a catalyst?
9. What is enzyme catalysis? Give two examples of reactions catalysed by enzymes. i0. What is autocatalysis? Give two examples.

GENERAL QUESTIONS

1. Explain giving examples:
   (a) Catalytic poisons
   (b) Action of promoters
   (c) Active centres
   (d) The specific nature of catalyst
2. What are catalytic inhibitors?
3. What do you mean by the term *catalysis?* What are the general characteristics of a catalysed reaction?
4. Discuss the characteristics of a catalysed reaction. What are catalytic inhibitors?
5. For the reaction:

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_3} E + P$$

where E is enzyme, S is substrate, ES is enzyme substrate complex and P is product. Following the Michaelis-Menten mechanism, deduce the equation for rate of the reaction.

6. Define acid base catalysis. Explain acid base catalysis by giving suitable examples.
7. What are enzymes? How do they act as catalysts? Explain in terms of Michaelis-Menten mechanism.
8. (a) What is a catalyst? How does it work?

   (b) Write short notes on the following:

   (i) Acid-base catalysis

   (ii) Enzyme catalysis

   (c) Explain the application of adsorption in catalysis.
9. (a) Discuss the mechanism of an enzyme reaction as proposed by the Michaelis-Menten equation.

   (b) Derive a general expression for the rate of reaction of an acid catalysed reaction.
10. Discuss the mechanism of enzyme-catalysed reactions. Deduce Michaelis-Menten equation and give conditions under which an enzyme catalyst changes its order.
11. Differentiate clearly between homogeneous and heterogeneous catalysis with suitable examples.
12. Write short notes on the following:

    (a) Intermediate compound formation theory

    (b) Adsorption theory for heterogeneous catalysis
13. Show that for a unimolecular surface tension,

$$v = \frac{k_1 k_2 P_A}{k_1 P_A + k_{-1} + k_2}$$

where P_A is the partial pressure of the reactant A,

k_1 = Rate constant for adsorption process

k_{-1} = Rate constant for desorption

k_2 = Rate constant for decomposition

14. What is enzyme catalysis? How will you account for the fact that enzyme-catalysed reactions have maximum activity at a definite pH. Give the mechanism of an enzyme catalysed reaction.
15. What are enzymes? How do they act as catalysts?
16. Give the kinetics of unimolecular surface reaction.
17. What is Michaelis constant? How can it be determined?



Thermodynamics-I

9

LEARNING OBJECTIVES

- Learn the objectives and limitations of thermodynamics
- Define the terms used in thermodynamics
- Understand internal energy and change in internal energy
- Derive an expression for work of expansion against constant pressure.
- Follow zeroth law of thermodynamics
- State the first law in different forms and derive its mathematical formulation
- Understand the terms: enthalpy, enthalpy change and heat capacity
- Derive the relation between C_P and C_V
- Understand Joule's law and Joule-Thomson effect
- Calculate Joule-Thomson coefficient and inversion temperature
- Correlate Joule-Thomson coefficient with other thermodynamic quantities
- Derive the expression for work done in isothermal reversible expansion of a gas
- Obtain the values of q, w, ΔU and ΔH in the case of isothermal and adiabatic expansion of a gas
- Correlate pressure, volume and temperature in adiabatic expansion of a real gas
- Compare isothermal and adiabatic expansion of a real gas

9.1 INTRODUCTION

Most of the generalisations in physical chemistry like van't Hoff law of dilute solutions, Raoult's law, distribution law, phase rule and law of chemical equilibrium are deducible from the laws of thermodynamics. Thus, study of thermodynamics is of great importance in physical chemistry. The laws of thermodynamics are applicable only to bulk matter and not to individual atoms or molecules.

The meaning of the word thermodynamics can be understood like this:

Thermo means heat and ***dynamics*** means motion or mechanical work. Hence, thermodynamics means that branch of science which deals with the conversion of heat into mechanical work and vice versa. In a wide sense, ***thermodynamics is a branch of science that deals with quantitative relationships between heat and other forms of energy.*** Study of thermodynamics is based on three laws, viz. first, second and third law of thermodynamics. There is no theoretical proof of the laws, but nothing contrary to the laws has been reported so far.

Using the principles of thermodynamics, we can predict the feasibility or spontaneity of a reaction although it does not tell us about the rate at which the reaction or process will take place. For example, hydrogen and oxygen are expected to form water on thermodynamic consideration. However, the reaction is extremely slow unless we add a catalyst.



Fig. 9.1 *Scientists who laid the foundation of thermodynamics*

9.1.1 Objectives of Thermodynamics

Study of thermodynamics is vital to understanding scientific principles. Its main objectives are the following:

(a) To predict the Feasibility of a Process Whether or not, a process will occur under the given set of conditions, can be predicted by applying the principles of thermodynamics.

(b) To Estimate the Yield of the Products Thermodynamics relations help to predict the yield of the products obtainable in a process or a reaction. It is possible to know the extent up to which the reaction takes place before attaining equilibrium.

(c) To Deduce some Important Relationships in Physical Chemistry It has been possible to deduce some important and useful results such as Raoult's law of lowering of vapour pressure and expressions for depression in freezing point, elevation in boiling point, distribution law and phase rule from the study of thermodynamics.

9.1.2 Limitations of Thermodynamics

In spite of its great usefulness, thermodynamics suffers from certain limitations. These are the following:

1. It helps to predict the feasibility of a process but does not tell anything about the time taken for

the process to complete or the rate at which the process would proceed.

2. It concerns itself only with the initial and final states of a system and is not concerned with the path by which the change is brought about, i.e. it does not reveal the mechanism of a process.
3. It deals with the properties like temperature pressure, etc., of the matter in bulk, i.e. with macroscopic quantities and not with the microscopic quantities. Thus, it deals with large groups of atoms, molecules and ions rather than individual atoms, molecules or ions.

9.1.3 Definitions of Certain Thermodynamics Terms

1. System and Surroundings

The part of the universe chosen for thermodynamic consideration (i.e. to study the effect of temperature, pressure, etc.) is called a system.

The remaining portion of the universe, excluding the system, is called surroundings. (Fig 9.2)

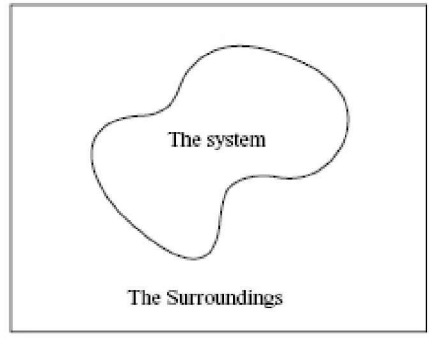


Fig. 9.2 *The system and the surroundings*

2. Open, Closed and Isolated Systems

(a) Open System ***A system is said to be an open system if it can exchange both matter and energy with the surroundings.*** For example, if some water is kept in an open vessel (Fig. 9.3), exchange of both matter and energy takes place between the system and the surroundings.

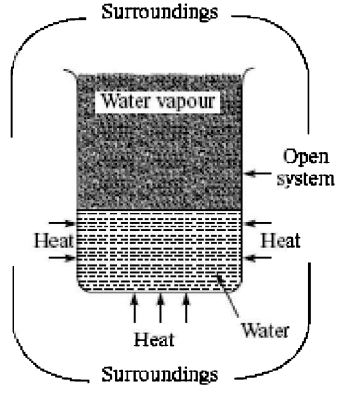


Fig. 9.3 *Example of open system: Water kept in an open vessel*

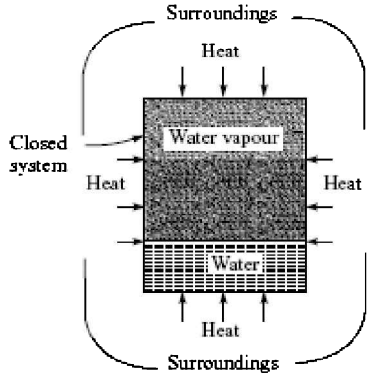


Fig. 9.4 *Water placed in a closed vessel*

(b) Closed System ***If a system can exchange only energy with the surroundings but not matter, it is called a closed system.*** For example, if some water is placed in a closed metallic vessel (Fig. 9.4) then as the vessel is closed, no exchange of matter between the system and the surroundings can take place. But, as the vessel has conducting walls, exchange of energy can take place between the system and the surroundings. Heat can flow in and out of the vessel.

(c) Isolated System ***If a system can exchange neither matter nor energy with the surroundings, it is called an isolated system.*** For example, if water is placed in a vessel which is closed as well as insulated, no exchange of matter or energy is possible between the system and the surroundings. This constitutes an isolated system (Fig. 9.5).

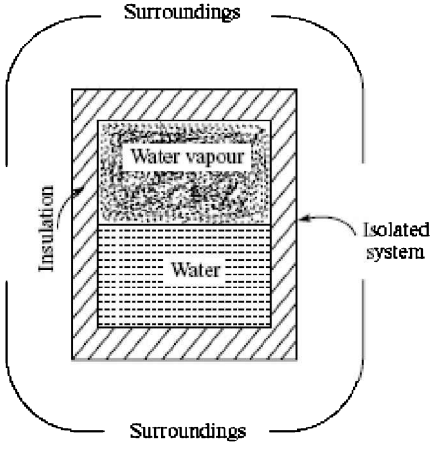


Fig. 9.5 *An example of an isolated system*

3. Homogeneous System A system is said to be homogeneous if it is uniform throughout. For example, a gas or a mixture of gases or a pure liquid or a pure solid or a solution of a solid in a liquid are all homogeneous systems. Such a system consists of one phase only.

4. Heterogeneous System If a system is not uniform throughout, it is said to be heterogeneous. It then consists of two or more phases which are separated from each other by definite bounding surfaces. A few common examples of the heterogeneous systems are (a) a system consisting of a liquid and its

vapour, (b) two or more immiscible liquids, and (c) a mixture of two or more solids.

5. Macroscopic System Macroscopic system means a system containing a large amount of the substance, In other words, a macroscopic system is one in which there are a large number of particles, i.e. atoms, ions or molecules.

6. Macroscopic Properties A property associated with the collective behaviour of particles in a macroscopic system is called a macroscopic property. A few examples of these properties are pressure, volume, temperature, surface tension, viscosity, density refractive index, etc.

7. State of the System The state of a system means a condition of the system when the various macroscopic properties like pressure, volume, temperature, etc., of the system have definite values. The first and the last state of the system are called initial state and final state respectively.

State Variables Macroscopic properties are known as state variables. The four most common macroscopic properties which are sufficient to define the state of a system are ***composition, pressure, volume*** and ***temperature.*** If these properties are fixed, all other physical properties of the system are automatically fixed.

State Functions, and Exact and Inexact Differentials

State function is a property of a thermodynamic system which depends upon the initial and final states of a system and is independent of the path by which the state has been attained. The differential of a state function is an exact *differential*. Thus, au and ah are state functions and ΔU and ΔH are exact differentials.

The quantities q and w are not state functions. They depend upon the path taken by the system to undergo the change. If a gas expands against a pressure P, $w = P\Delta V$ and if the expansion is against vacuum, $w = 0$. We know $\Delta U = q + w$ and ΔU is a state function. If w is not a state function, then q is also not a state function. Hence, dq and dw are ***inexact*** differentials.

8. Thermodynamic Equilibrium A system is said to be in thermodynamic equilibrium if the macroscopic properties of the system in various phases do not undergo any change with time. In fact, the thermodynamic equilibrium denotes that three different types of equilibria which must exist simultaneously. These are the following:

(a) *Thermal Equilibrium.* This equilibrium implies that there should be no flow of ***heat*** from one portion of the system to another. This can happen if the temperature of the system remains constant.

(b) *Mechanical Equilibrium.* This equilibrium implies that no work should be done by one part of the system over another, i.e. no macroscopic movement of matter should occur within the system or of the system with respect to its surroundings. This is possible if the pressure of the system remains constant.

(c) *Chemical Equilibrium.* This equilibrium implies that no change in composition should take place in any part of the system with passage of time.

9. Extensive and Intensive Properties

(a) Extensive Properties These are the properties which depend upon the quantity of matter contained in the system. Examples of extensive properties are ***mass, volume, energy, heat capacity,*** etc. The total value of an extensive property is equal to the sum of the values for the separate parts into which the system may be divided for the sake of convenience.

(b) Intensive Properties These are those properties which depend only upon the nature of the substance and are independent of the amount of the substance present in the system. The common examples of these properties are temperature, pressure, refractive index, viscosity, density, surface

tension, specific heat, etc. It is because pressure and temperature are intensive properties independent of the matter present that they are frequently used as variables to describe the state of a system.

Interestingly, an extensive property may become an intensive property by specifying unit amount of the substance concerned. Thus, mass and volume are extensive properties but density is an intensive property, heat capacity is an extensive property but specific heat is intensive.

10. Thermodynamic Processes

(a) Isothermal Process ***When a process is carried out in such a manner that the temperature remains constant throughout the process, it is called an isothermal process.*** Obviously, when such a process occurs, heat can flow from the system to the surroundings and vice versa in order to keep the temperature of the system constant

(b) Adiabatic Process ***When a process is carried out in such a manner that no heat can flow from the system to the surroundings or vice versa, i.e. the system is completely insulated from the surroundings, it is called an adiabatic process.*** Temperature of the system might change in on adiabatic process.

(c) Isochoric Process ***It is a process during which the volume of the system is kept constant.***

(d) Isobaric Process ***It is a process during which the pressure of the system is kept constant.***

A ***reversible process*** is one which is carried out infinitesimally slowly so that all changes occurring in the direct process can be exactly reversed and the system remains almost in a state of equilibrium at all times. In other words, a reversible process may be defined as a process which is conducted in such a manner that at every stage, the driving force is only infinitesimally greater than the opposing force and which can be reversed by increasing the opposing force by an infinitesimal amount.

Strictly speaking, a reversible process is almost impossible as it would require an infinite time for completion. A process can be made very nearly reversible in some cases. For example, if an opposing emf is applied to a cell then no current flows if the opposing emf is exactly equal to that of the cell. If the opposing E.M.F. is very slightly (infini-tesimally) smaller than that of the cell, a very small current is given out by the cell. If the opposing emf is slightly greater than that of the cell, a very small current flows in the opposite direction.

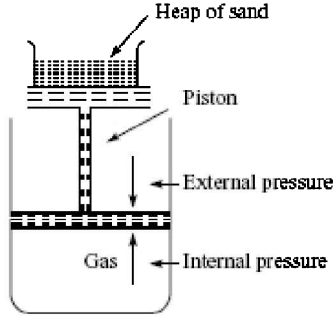


Fig. 9.6 *Demonstration of a reversible process*

A reversible process can also be demonstrated with the help of the following experiment as shown in Fig. 9.6.

Take a cylinder and fit a frictionless piston into it as shown. The cylinder contains a gas at a moderate pressure, due to which the piston will start rising upwards. Balance it by placing a petri disk containing fines and over the piston. In the balance position, the piston will be static.

Now if we add a very small sand grain to the petri dish, the piston will start moving downwards very slowly. On the other hand, if we take out a very small sand grain from the petri dish, the piston will start moving upwards very slowly. In both cases, it demonstrates reversible process.

A process which does not meet the above requirements is called an ***irreversible process.*** In other words, an irreversible process is defined as that process which is not carried out infinitesimally slowly (instead, it is carried out rapidly) such that the successive steps of the direct process cannot be retraced and any change in the external conditions distrubs the equilibrium.

It is interesting to note that naturally occuring processes like the flow of water down a hill or the flow of heat from a hot end to a cold end of an iron bar or flow of electricity from higher to lower potential are thermodynamically irreversible.

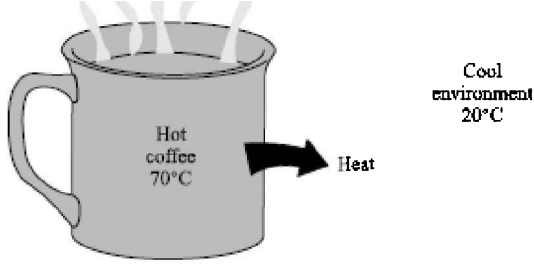


Fig. 9.7 *Heat flow in the direction of decreasing temperature. That is why your cup of coffee becomes cold, say in 5 minutes.*



Fig. 9.8 *An irreversible process in nature. Flow of water down a hill is an interesting example of an irreversible process*

9.1.4 Internal Energy and Change in Internal Energy

1. Internal Energy The evolution or absorption of energy in different processes clearly shows that every substance must be associated with some definite amount of energy, the actual value of which depends upon the nature of the substances (i.e., arrangement of atoms and electrons within the molecules) and the conditions of temperature, pressure, volume and composition. The energy associated with a substance is called its internal energy and is usually denoted by the symbol E or U.

2. Change of Internal Energy It is not possible to find the absolute value of internal energy of a substance because it involves certain quantities (like translational, vibrational and rotational kinetic energies) which cannot be measured.

However, it is not required to know the absolute value of internal energy possessed by any

substance (or a system). What is required in different processess is simply the ***change of internal energy*** when the reactants change into products or when the system changes from initial state to the final state. This is easily measurable and is represented by ΔE (or ΔU). Thus, if the internal energy of a system in the initial state is E_1 (or U_1) and in the final state, it is E_2 (or U_2) then the change of internal energy (ΔE or ΔU) may be given by

$$\Delta E \text{ (or } \Delta U) = E_2 - E_1 \text{ (or } U_2 - U_1)$$

Similarly, in a chemical reaction, if E_R is the internal energy of the reactants and E_p is the internal energy of the products then energy change accompanying the process would be

$$\Delta E = E_P - E_R \quad \text{or} \quad \Delta U = U_P - U_R$$

9.1.5 Internal Energy *U* is a State Function

A state function is one whose value depends upon the state of the system and not upon the manner in which it has been attained. We can prove that internal energy is a state function as under:

Let us bring about a change in the internal energy of the system by doing some work. Let the initial state be represented as state a and its temperature at T_A. Let the internal energy of the system in state A be represented as U_A. We can bring about a change in internal energy in two different ways: The system in this case is a definite amount of water taken in an insulated vessel.

1. First Way We do some mechanical work say equivalent to i kJ by rotating a set of peddles which churn water and raise its temperature. Let the temperature measured in the new state B be T_b. The change in temperature of the system ΔT is thus $T_B - T_A$.

2. Second Way We perform a different kind of work, say electrical work, again say 1 kJ, by dipping an immersion rod. Again note down the temperature after performing 1 kJ electrical work (we can calculate the time for which the immersion rod will be kept on if we know the wattage of the rod). We observe the same rise in temperature of the system.

Since the rise in temperature and final temperature is the same in the two cases, we can say that increase in internal energy ΔU and the final internal energy itself is the same (U_B) in the two cases. Therefore, internal energy is a state function. Its value depends upon the state of the system and not on the matter in which that state has been attained.

3. Sign Conventions in Energy Obviously, if $E_1 > E_2$ or ($E_R > E_P$), the extra energy possessed by the system in the initial state (or the reactants) would be given out, and ΔE will be negative according to the above equations. Similarly, if $E_1 < E_2$ (or $E_R < E_P$), energy will be absorbed in the process and ΔE will be positive. Hence, ΔE (or ΔU) is **negative if energy is evolved** and ΔE (or ΔU) is **positive if energy is absorbed** in units of U. The unit of energy is erg or joule.

$$1 \text{ joule} = 10^7 \text{ ergs}$$

Units of work, energy and heat in SI units are joule.

$$1 \text{ caloric} = 4.184 \text{ joules} = 4.184 \times 10^7 \text{ ergs}$$

9.1.6 Expression for Work of Expansion Against Constant Pressure

The expression for work of expansion against constant pressure is derived as under:

Consider a gas enclosed in a cylinder fitted with a frictionless piston (Fig. 9.9).

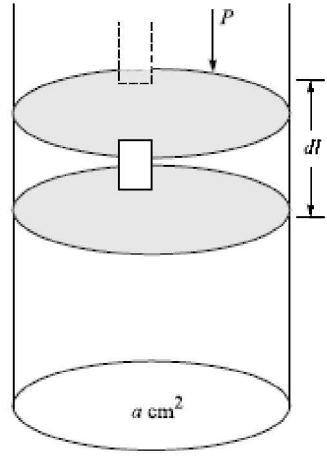


Fig. 9.9 *Expansion of a gas*

Area of cross section of the cylinder = a sq. cm.

Pressure on the piston (which is slightly less than internal pressure of the gas so that the gas can expand) = P

Distance through which gas expands = dl cm

As pressure is force per unit area, force (f) acting on the piston will be

$$f = P \times a$$

$\therefore$ work done by the gas (i.e. the system)

$$= \text{Force} \times \text{Distance}$$
$$= f \times dl$$
$$= P \times a \times dl$$

But $a \times dl = dV$ is a small increase in the volume of the gas.

Hence, the small amount of work (δW) done by the gas can be written as

$$\delta W = P dV$$

If the gas expands from initial volume V_1 to the final volume V_2 then the total work done (w) will be given by

$$w = \int_{V_2}^{V_1} P dV$$

If the external pressure P against which the gas expands remains almost constant throughout the process, the above result may be written as

$$w = P \int_{V_2}^{V_1} P dV = P(V_2 - V_1)$$
$$= P \Delta V$$

where $\Delta V = (V_2 - V_1)$ is the total change in the volume of the gas.

If the external pressure (P) is slightly more than the pressure of the gas, the gas will contract, i.e. the work will be done by the surroundings on the system. However, the same formulae will apply for the work done. It may be mentioned here that P is the ***external pressure*** and, hence, is sometimes written as

P_{ext} so that

$$w = P_{ext} \times \Delta V$$

According to the latest SI conventions of sign, w is taken as positive if work is done on the system (i.e. $w_{contraction}$ is positive) and it is taken as negative if work is done by the system (i.e. $w_{expansion}$ is negative). Thus,

$$w_{exp} = -P\Delta V$$

And

$$w_{contraction} = +P\Delta V$$

1. Nature of Work and Heat James Joule in 1850 showed that there is a definite relationship between mechanical work done, W and heat produced, H.

$$W \propto \text{H or } W = JH$$

J = Mechanical equivalent of heat, its numerical value is taken as 4.184×10^7 ergs or 4.184 joules. Thus, when 4.184 joules of mechanical energy is used, 1 calorie of heat is produced. *As mentioned earlier, now we use the same unit of joule for work, energy and heat.*

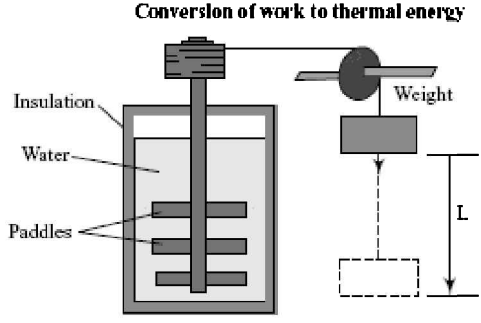


Fig. 9.10 *Falling weight spins paddles converting mechanical energy to internal thermal energy in water*



Fig. 9.11 *James Prescott Joule FRS was an English physicist and brewer, born in Lancashire. Joule studied the nature of heat and discovered its relationship to mechanical work*

2. Electrical Work The electrical work done is expressed as under:

Electrical work done = Electromotive force (emf) × Quantity of electricity

3. Gravitational Work Gravitational work done when an object of mass (m) moves against the gravitional force *(g)* and the displacement of the object is h, is given by

Work done = $m \times g \times h$

9.1.7 Work Done in a Reversible Process is the Maximum Work Obtainable

The work done by a system is the maximum work if the process is carried out under reversible conditions. This may be proved as follows. We know that work done by the system = $P_{ext} \times \Delta V$. Thus, for a given increase in volume (ΔV), the work done can be maximum if P_{ext} is maximum. But in order that the expansion may take place (i.e. the work may be done by the system), the external pressure should always be less than the internal pressure of the gas. Thus, the maximum value that P_{ext} can have is that it should be **infinitesimally smaller** than the internal pressure of the gas. But these are the conditions of a reversible process. Hence, the maximum work is done in a process only when it is carried out under reversible conditions. Hence, in a reversible process, w is sometimes replaced by w_{max}.

9.1.8 Heat

Heat is a mode of energy exchange between the system and the surroundings as a result of the difference of temperature between them. It is usually represented by the letter q.

Sign of 'q' When heat is given by the system to the surroundings, it is *given a negative* sign. When heat is absorbed by the system from the surroundings, it is given a *positive* sign.

Units of 'q' Heat is usually measured in terms of calories. A calorie is defined as the quantity of heat required to raise the temperature of one gram of water through 1°C.

In SI units, heat is expressed in terms of ***joules.*** The two units are related to each other as under

1 calorie = 4.184 joules

There are four laws of thermodynamics, namely zeroth law, first law, second law and third law. These are described separately as under:

9.1.9 Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states: ***When two bodies have equality of temperature with a third body, they in turn have equality of temperature with each other.***

We are so familiar with this fact that we do not need any further experiments for its support. However, since this fact is not derivable from other laws and since it logically proceeds the first and the second law of thermodynamics, it has been called the zeroth law of thermodynamics.

If B and C have equality of temperature with A then B and C have equality of temperature with each other.

9.1.10 First Law of Thermodynamics

The first law of thermodynamics can be stated in a number of ways.

1. Energy can neither be created nor destroyed although it may be converted from one form to another.
2. Whenever a certain quantity of some form of energy disappears, an exactly equivalent amount of some other form of energy must be produced.
3. The total energy of an isolated system remains constant, although it may undergo transformation from one form to the other.
4. It is impossible to construct a perpetual motion machine, i.e. a machine which would produce work continuously without consuming energy.

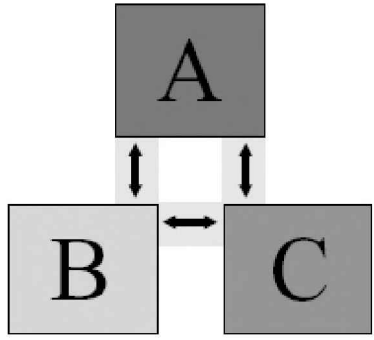


Fig. 9.12 *illustration of zeroth law of thermodynamic. It B and C have equality of temperature with A, then B and C have equality of temperature with each other.*

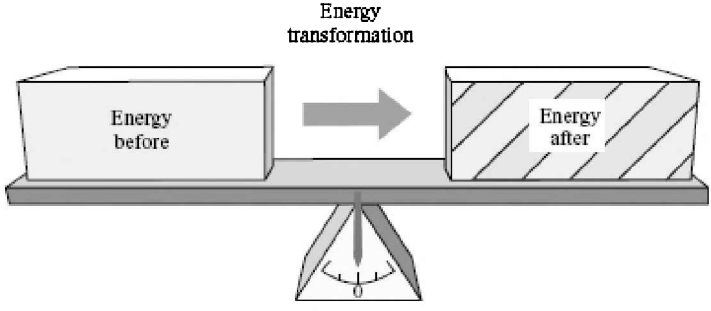


Fig. 9.13 *Energy transformation*

Einstein in 1905 showed that energy could be created by the destruction of mass. The energy produced (E) by the destruction of mass m is given by the equation

$$E = mc^2 \text{ (called Einstein equation)}$$

where c is the velocity of light. In the light of this idea, the law of conservation of energy has been modified and now it is called ***law of conservation of mass and energy.*** It may be stated as follows: ***The total mass of the energy of an isolated system remains constant*** in chemical thermodynamics.

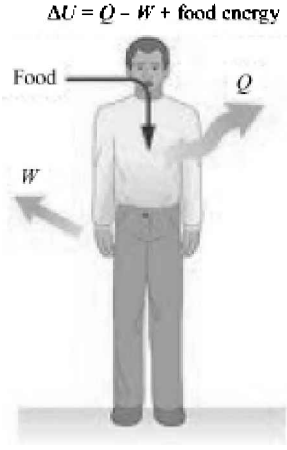


Fig. 9.14 *Illustration of first law of thermodynamics*

9.1.11 Mathematical Formulation of the First Law of Thermodynamics

If heat q is supplied to a system, it may be used up partly to increase the internal energy of the system and partly to do some mechanical work. If ΔU is the increase in internal energy of the system and w is the work done by the system then we have

$$\Delta U = q + w \qquad \ldots(9.1)$$

If the work done is work of expansion,

$$w = -P\Delta V$$

or

$$q = \Delta U + P\Delta V \qquad \ldots(9.2)$$

If the changes are very small, it may be written as

$$\delta q = dU + PdV \qquad \ldots(9.3)$$

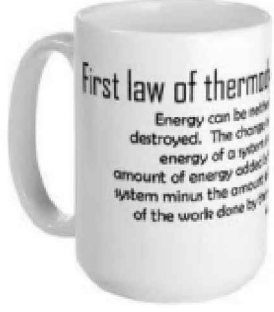


Fig. 9.15 *Statement of first law of thermodynamics*

9.1.12 Internal Energy is a State Function but Work and Heat are Not

1. Internal Energy The internal energy is a state function, that is, when a process occurs, the

change in its value depends only upon its value in the initial state and that in the final state and is independent of the path by which the change is brought about. For example, consider a system having a particular pressure, volume and temperature represented by the point A in Fig. 9.16. Suppose the pressure, volume and temperature are changed in such a way that the system is brought to the point B by path I. If the system is returned to the point A by path II then the energy change involved in path I must be equal in magnitude to that involved in path II. If the energy changes involved in path I and II are not the same then suppose that the increase in internal energy by path I is greater than the decrease in internal energy along path II. Thus, by carrying out the process $A \rightarrow B$ by path I and the reverse process $B \rightarrow A$ by path II, though the original state has been restored, some energy would have been created. This is contrary to the first law of thermodynamics. Thus, it may be inferred that the energy change involved in the process $A \rightarrow B$ must be equal in magnitude to that involved in the reverse process $B \rightarrow A$ by path II. In other words, the energy change accompanying a process is independent of the path followed and depends only upon the initial and the final states. Thus, if U_A is the internal energy of the system in the initial state and U_B that in the final state then the change in internal energy accompanying the process would be given by

$$\Delta U = U_B - U_A \qquad \ldots(9.4)$$

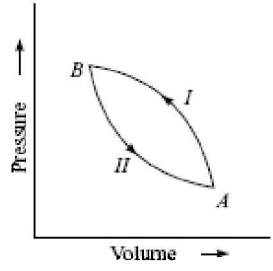


Fig. 9.16 *Energy changes in direct and reverse paths.*

2. Work and Heat Unlike internal energy, the work done during a process does not depend merely upon the initial and the final states of the system but it also depends upon the path followed. Hence work is not a state function but a path function. This is explained as under:

Suppose we want to change the system from state A to state B. This may be done by following different paths as shown in the different figures below (Fig. 9.17). Confining ourselves to the work of expansion only, we know that the work done for a small change in volume dV is PdV where P is the external pressure. Thus, the total work done is the sum of PdV terms and this is equivalent to the area under the curve in the P-V diagrams. From the figures given below, it is obvious that the areas under the curves are different and hence the work is different when different paths are followed.

That heat is also not a state function follows directly from the mathematical formulation of the first law of thermodynamics, viz.

$$q = \Delta U - W \qquad \ldots(9.5)$$

Thus, the heat q is the sum of two quantities, i.e. the internal energy change, ΔU and the work done, w. Now ΔU is state function whereas w is not. Now since w depends upon the path followed, therefore, q will also depend upon the path followed. In other words, q is also not a state function but is a path function.

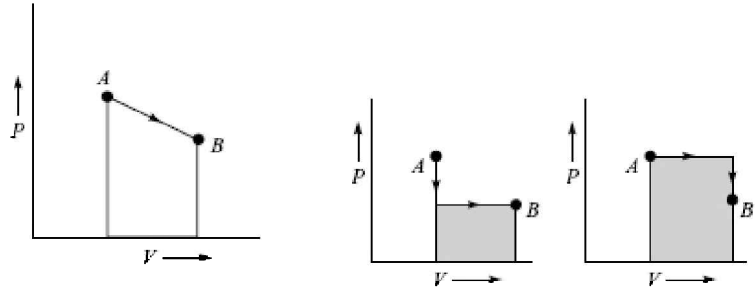


Fig. 9.17 *Different paths followed in going from state A to state B*

If the process is carried out at constant volume, $\Delta V = 0$, the equation $q = \Delta U - P\Delta V$ reduces to $q_v = \Delta U$. Thus, heat absorbed at constant volume is equal to change in internal energy.

9.1.13 Enthalpy or Heat Content

Most chemical reactions are carried out not at constant volumes, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

If a process is carried out at constant pressure, the work of expansion is given by

$$w = -P\Delta V \qquad \ldots(9.6)$$

where ΔV is the increase in volume and P is the constant pressure.

According to first law of thermodynamics, we know that

$$q = \Delta U - w \qquad \ldots(9.7)$$

where q is the heat absorbed by the system, ΔU is the increase in internal energy of the system and w is the work done by the system. Under conditions of constant pressure, putting $w = -P\Delta V$ and representing the heat absorbed by q_P, we get

$$q_p = \Delta U + P\Delta V \qquad \ldots(9.8)$$

Let us suppose when the system absorbs q_P calories of heat, its internal energy increases from U_1 to U_2 and the volume increases from V_1 to V_2. Then we have

$$\Delta U = U_2 - U_1 \qquad \ldots(9.9)$$

and

$$\Delta V = V_2 - V_1 \qquad \ldots(9.10)$$

Putting these values in Eq. (9.8) above, we get

$$q_p = (U_2 - U_1) + P(V_2 - V_1)$$

$$q_p = (U_2 + PV_2) - (U_1 + PV_1) \qquad \ldots(9.11)$$

Now as U, P and V are the functions of state, therefore, the quantity $U + PV$ must also be a state function. The thermodynamic quantity $U + PV$ is called the ***heat content*** or ***enthalpy*** of the system and is represented by the symbol H, i.e., the enthalpy may be defined mathematically by the equation

$$H = U + PV$$

Thus, if H_2 is the enthalpy of the system in the final state and H_1 is the value in the initial state then

$$H_2 = U_2 + PV_2$$

and

$$H_1 = U_1 + PV_1$$

Putting these values in Eq. (9.11), we get

$$q_p = H_2 - H_1$$

or $$q_p = \Delta H \quad \ldots(9.12)$$

where $\Delta H = H_2 \rightarrow H_1$ is the enthalpy change of the system. Hence, ***enthalpy change*** of a system is equal to the heat absorbed by the system at constant pressure.

Further, putting the value of q_p, from Eq. (9.12) in Eq. (9.8) we get

$$\Delta H = \Delta U + P\Delta V \quad \ldots(9.13)$$

Hence, ***the enthalpy change accompanying a process*** may also be defined as the sum of the increase in internal energy of the system and the pressure-volume work done, i.e. the work of expansion At constant volume $\Delta V = 0$ and $\Delta U = q_V$, so that Eq. (9.13) becomes

$$\Delta H = \Delta U = q_v$$

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and/or liquids. Solids and liquids do not usually undergo volume changes on heating. But the difference becomes significant when substances in the gaseous phase are involved.

If V_A represents the total volume of the gaseous reactants and V_B, the total volume of the gaseous products, n_A the number of moles of the gaseous reactants and n_B the number of moles of the gaseous products, all at constant pressure and temperature then using the gas law equation, we can write

$$PV_A = n_A RT$$

$$PV_B = n_B RT$$

Thus, $$PV_B - PV_A = n_B RT - n_A RT = (n_B - n_A)RT$$

or $$P(V_B - V_A) = (n_B - n_A)RT$$

or $$P\Delta V = \Delta n_g RT$$

Here, Δn_g = Total number of moles of gaseous products – Total number of moles of gaseous reactants

Equation (9.13) can, therefore, be written as $\Delta H = \Delta U + \Delta n_g RT$ ... (9.14)

Equation (9.14) is useful for calculating ΔH from ΔU and **vice versa.**

Example 1 *If water vapour is assumed to be a perfect gas, molar enthalpy change for vaporisation of 1 mol of water at 1 bar and 100°C is 41 kJ mol^{-1}, calculate the internal energy change when*

(a) 1 mol of water is vaporised at 1 bar pressure and 100°C

(b) 1 mol of water is converted into ice

Solution:

(a) The change H_2O (*l*) — H_2O (g)

$$\Delta H = \Delta U + \Delta n_g RT$$

or $$\Delta U = \Delta H - \Delta n_g RT$$

Substituting the values, we get

$$\Delta U = 41.00 \text{ kJ mol}^{-1} - 1 \times 8.3 \text{ J mol}^{-1} \text{ K}^{-1} \times 373 \text{ K}$$

$$= 41.00 \text{ kJ mol}^{-1} - 3.096 \text{ kJ mol}^{-1} = 37.904 \text{ kJ mol}^{-1}$$

(b) For the change H_2O (l) $\rightarrow$ H_2O (s), there is negligible change in volume.

$\therefore$ $$P\Delta V = \Delta n_g RT = 0$$

Hence $$\Delta H = \Delta U$$

or $$\Delta U = 41.00 \text{ kJ mol}^{-1}$$

Example 2 *The heat of formation of methane at 27°C is –19.3 kcal when the measurements are made at constant pressure. What will be the heat of formation at constant volume?*

Solution: Apply the relationship

$$\Delta H = \Delta U + \Delta n \cdot RT \quad \ldots(i)$$

ΔH is the heat of reaction at constant pressure whereas ΔU is the heat of reaction at constant volume.

$$\Delta H = -19.3 \text{ kcal}$$

For the reaction

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

Number of moles of the gaseous reactants = 2

Number of moles of the gaseous products = 1

Thus, $\Delta n = 1 - 2 = -1$

Substituting the values in Eq. (i) above

$$-19.3 \times 1000 \text{ cal} = \Delta U + (-1) \times (1.987 \text{ cal}) \times 300$$

or

$$\Delta U = -19300 - 5961 \text{ cal}$$

$$\Delta U = -13339 \text{ cal or } -13.339 \text{ kcal}$$

9.1.14 Heat Capacity

Heat capacity of a system is defined as the amount of heat required to raise the temperature of the system through 1°C. If q is the amount of heat supplied to a system to raise the temperature from T_1 to T_2 then the heat capacity of the system is given by

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \quad \ldots(9.15)$$

The value of C has to be considered in a narrow range because the heat capacity varies with the temperature.

If δq is the small amount of heat absorbed by a system which raises the temperature of the system by a small amount dT then the heat capacity of the system is given by

$$C = \frac{\delta q}{\delta T} \quad \ldots(9.16)$$

There are two types of heat capacities, viz.

1. Heat capacity at constant volume *(Cv)*
2. Heat capacity at constant pressure *(Cp)*

1. Heat Capacity at Constant Volume (C_V) According to the first law of thermodynamics,

$$\delta q = dU + PdV \quad \ldots(9.17)$$

Substituting for δq from Eq (9.17) into Eq (9.16),

$$C = \frac{dU + PdV}{dT} \quad \ldots(9.18)$$

When the volume is kept $dV = 0$ and Eq. (9.18) becomes

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \ldots(9.19)$$

Or for an ideal gas, this equation may simply be written as

$$C_V = \frac{dU}{dT} \quad \ldots(9.20)$$

C_V is the heat capacity at constant volume. Thus, ***the heat capacity at constant volume may be defined as the rate of change of internal energy with temperature at constant volume.***

2. Heat Capacity at Constant Pressure, C_p When the pressure is kept constant during the absorption of heat, Eq. (9.18) becomes

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(9.21)$$

We know that the heat content or enthalpy of a system is given by

$$H = U + PV$$

Differentiating w.r.t T at constant P, we get

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(9.22)$$

Combining equations (9.21) and (9.22), we get

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \ldots(9.23)$$

Or for any ideal gas, this equation may simply be put in the form

$$C_P = \frac{\partial H}{\partial T}$$

C_P is the heat capacity at constant pressure. Thus, ***the heat capacity at constant pressure may be defined as the rate of change of enthalpy with temperature at constant pressure.***

9.1.15 Relation between C_P and C_V

Relation between C_P and C_V can be obtained as under:

If the volume of the system is kept constant when heat is supplied to a system then no work is done by the system. Thus, the heat absorbed by the system is used up completely to increase the internal energy of the system. And if the pressure of the system is kept constant when the heat is supplied to the system then some work of expansion is also done by the system in addition to the increase in internal energy. Thus, if at constant pressure, the temperature of the system is to be raised through the same value as at constant volume then some extra heat is required for doing the work of expansion Thus, $C_P > C_V$

We have the following equations for C_V and C_P.

$$C_V = \frac{dU}{dT} \qquad \ldots(9.24)$$

$$C_P = \frac{dH}{dT} \qquad \ldots(9.25)$$

The difference between the heat capacities of an ideal gas can be obtained by subtracting Eq. (9.24) from Eq. (9.25). So we have

$$C_P - C_V = \frac{dH}{dT} - \frac{dU}{dT} \qquad \ldots(9.26)$$

$H = U + PV$ (by definition)

$PV = RT$ (for 1 mole of an ideal gas)

$\therefore \quad H = U + RT$

Differentiating this equation w.r.t T we get

$$\frac{dH}{dT} = \frac{dU}{dT} + R \qquad \ldots(9.27)$$

or
$$\frac{dH}{dT} - \frac{dU}{dT} = R \qquad \ldots(9.28)$$

Combining equations (9.26) and (9.28),

$$C_P - C_V = R \text{ (for 1 mole of an ideal gas)}$$

Thus, C_P is greater then C_V by the gas constant R, i.e. approximately 2 calories or 8.314 joules. The ratio of specfic heats (C_p/C_v) is represented by γ.

Thus,
$$\gamma = \frac{C_P}{C_V}$$

It is found that the value of γ comes out to be about 1.67 for monoatomic gases, 1.40 for diatomic gases and 1.30 for triatomic gases.

9.2 JOULE'S LAW

The law can be stated as: ***The change of internal energy of an ideal gas with volume at constant temperature is zero.***

$$\text{Mathematically, } \left(\frac{\partial U}{\partial V}\right)_T = 0$$

This result has been obtained from the Joule-Thomson experiment as described below:

A combination of bulbs *A* and *B* connected through a stopcock *S* is immersed in water taken in a trough (Fig. 9.18). Bulb *A* contains an ideal gas at certain pressure with the stopcock closed. There is complete vacuum in the flask *B*. The bulbs reach a thermal equilibrium after some time. The temperature of water is noted.

The stopcock *S* is now opened and the gas is allowed to move to the bulb *B*. The bulbs reach a thermal equilibrium after some time. The temperature of water is again noted.

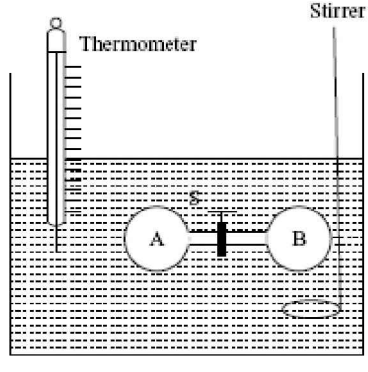


Fig. 9.18 *Joule-Thomson experiment (Expansion of real gas through a porous plug)*

We find that there is no change in temperature. On opening the stopcock, the gas from the bulb *A* expands into the evacuated bulb *B*, i.e. the opposing force $P_{opposing} = 0$. Thus, work of expansion

$$dW = -P_{opposing}\, dV = 0$$

From the first law of thermodynamics,

$$dU = dq + dw$$

As $dW = 0$, we have $dU = dq$

As the temperature of water has not changed,

$$dq = 0$$

Hence, $$dU = 0$$

The mathematical form of Joule's law is derived as under:

Taking U as a function of volume and temperature,

$$U = f(V, T)$$

Differentiating,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \ldots(9.29)$$

We have found earlier that in such a situation, $dU = 0$ and $dT = 0$

Substituting for dU and dT in Eq (9.29) above, we have

$$\left(\frac{\partial U}{\partial V}\right)_T dV = 0 \quad \text{but} \quad dV \neq 0$$

$\therefore$ $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

9.2.1 Joule-Thomson Effect

It was observed by Joule and Thomson that ***when a real gas at a certain pressure expands adiabatically through a porous plug or a fine hole into a region of low pressure, it is accompanied by cooling (except for hydrogen and helium which get warmed up). This phenomenon is known as Joule-Thomson effect.***

Figure 9.19 shows the set-up of Joule-Thomson experiment.

A thoroughly insulated tube is fitted with a porous plug in the middle and pistons on either side as shown in the figure. The pressures of the gas are kept different on the two sides of the plug, being P_1 on the left side and P_2 on the right side where $P_1 > P_2$. By applying pressure on the piston on the left slowly enough (so as not to change the pressure P_1), a volume of the gas equal to V_1 is forced slowly through the porous plug and then allowed to expand to the pressure P_2 and volume V_2 by moving the piston on the right outward. When the process is being carried out as above, the temperature on the two sides of the porous plug is recorded accurately. The experiment is repeated with different gases. It is observed that a fall in temperature of the gas takes place in case of all gases except hydrogen and helium when the experiments are carried out at ordinary temperature, i.e. at room temperature.

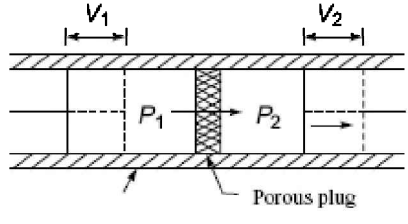


Fig. 9.19 *Joule-Thomson experiment (expansion of real gas through a porous plug)*

As the process is carried out adiabatically,

$$q = 0$$

$\therefore$ but the first law of thermodynamics, viz.

$$\Delta U = q + w$$

$$\Delta U = w$$

or
$$w = \Delta U \qquad \ldots(9.30)$$

From the above relation, we can say that the work done during the expansion of the gas under adiabatic conditions, is at of the cost of internal energy. In other words, the work of expansion is done adiabatically, the internal energy of the gas decreases and hence the temperature decreases. In fact, part of the internal energy is used up to overcome the forces of attraction existing among the molecules (van der Waals' forces).

In the Joule-Thomson experiment, which is an example of adiabatic process, on the left side of the plug, the work is done ***on*** the system whereas on the right side of the plug, the work is done ***by*** the system.

Work done on the system on the left side = P_1V_1

Work done by the system on the right side = $-P_2 \cdot V_2$

$\therefore$ net work done by the system is

$$w = P_1V_1 - P_2V_2 \qquad \ldots(9.31)$$

Putting the value in Eq. (9.30), we get

$$\Delta U = P_1V_1 - P_2V_2$$

Further putting

$$\Delta U = U_2 - U_1$$

we get
$$U_2 - U_1 = P_1V_1 - P_2V_2$$

or
$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

i.e.
$$\Delta H = H_2 - H_1 = 0$$

Thus, it leads to the conclusion that ***when the expansion of a gas takes place adiabatically through a porous plug of a fine hole, the enthalpy of the system remains constant.***

Thus, the Joule-Thomson expansion of a real gas occurs not with constant internal energy but with constant enthalpy. It is, therefore, an *isoenthalpic process*.

As H is a state function, dH is a complete differential. Taking H as a function of P and T_1, we have

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

But
$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$\therefore$
$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT$$

For an adiabic expansion $\Delta H = 0$, hence

$$\left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT = 0$$

or
$$\frac{dT}{dP} = -\frac{(\partial H/\partial P)_T}{C_P}$$

or
$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \times \frac{1}{C_P} \qquad \ldots(9.32)$$

The quantity $\left(\frac{\partial T}{\partial P}\right)_H$ is called Joule-Thomson coefficient and is denoted by μ.

9.2.2 Joule-Thomson Coefficient

The Joule-Thomson coefficient μ may be defined as the temperature change in degrees produced by a drop of one atmospheric pressure when the gas expands under conditions of constant enthalpy. It is expressed as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

1. For cooling, μ will be positive (because dT and dP both will be negative).
2. For heating μ will be negative (because dT is positive while dP is negative).
3. If $\mu = 0$, the gas gets neither heated up not cooled on adiabatic expansion (because $\mu = 0$, only if $dT = 0$ for any value of dP).

9.2.3 Inversion Temperature

Every gas has a definite temperature (at a particular pressure) at which $\mu = 0$. Below this temperature, μ is positive and above this temperature, μ is negative. ***This temperature (at a particular pressure) at which $\mu = 0$, i.e. the gas neither cools down nor heats up upon adiabatic expansion is called the inversion temperature.***

9.2.4 Calculation of Joule-Thomson coefficient and Inversion Temperature

We may use van der Waals equation to calculate Joule – Thomson coefficient, μ. Simplifying the van der Waals equation and neglecting the term ab/V^2, as it would be very negligible, we have

$$PV = RT - \frac{a}{V} + bP \qquad \ldots(9.33)$$

Replacing V by RT/P, we are making the approximation here by taking the equation of an ideal gas

$$PV = RT \text{ or } V = RT/P$$

$$PV = RT - \frac{aP}{RT} + bP \qquad \ldots(9.34a)$$

or

$$V = \frac{RT}{P} - \frac{a}{RT} + b \qquad \ldots(9.34b)$$

Differentiating w.r.t T at constant P, we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} \qquad \ldots(9.35)$$

Rearranging Eq. (9.34a) we have

$$RT = P(V - b) + \frac{aP}{RT} \qquad \ldots(9.36)$$

Dividing both sides by PT,

$$\frac{R}{P} = \frac{V - b}{T} + \frac{a}{RT^2} \qquad \ldots(9.37)$$

Substituting for R/P from Eq. (9.37) in Eq. (9.35), we get

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} - \frac{b}{T} + \frac{2a}{RT^2} \quad \ldots(9.38)$$

or
$$T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b \quad \ldots(9.39)$$

Using the thermodynamic relation,

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \frac{\partial H}{\partial P} \quad \ldots(9.40)$$

Equation (9.39) can be written as

$$-\left(\frac{\partial H}{\partial P}\right)_T = \frac{2a}{RT} - b \quad \ldots(9.41)$$

From Eq. (9.32), Art and Eq. (9.41) above, we get.

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \quad \ldots(9.42)$$

Thus Joule-Thomson coefficient will be positive as long as $2a/RT$ is greater than b. It becomes equal to zero when $2a/RT$ is equal to b and negative if $2a/RT$ is less than b at the inversion temperature $\mu = 0$. Therefore, from Eq. (9.42). we have

$$\frac{2a}{RT_i} = b \quad \text{or} \quad T_i = \frac{2a}{Rb}$$

Here, T_i represents the inversion temperature. We can, therefore, say that the inversion temperature depends upon the values of van der Waals constants a and b of the real gas

Example 3 *Calculate the inversion temperature of hydrogen gas given that the values of a and b in dm^3 atm units are 0.24 and 2.7 × 10^{-2} respectively.*

Solution: Apply the relation

$$T_i = \frac{2a}{Rb}$$

Substituting the values of a, b and R, we have

$$T_i = \frac{2 \times 0.24 \text{ dm}^6 \text{ atm mol}^{-2}}{(0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(0.027 \text{ dm}^3 \text{ mol}^{-1})}$$

$$= 216.8 \text{ K} \quad \text{or} \quad -56°\text{C}$$

9.2.5 Helium and Hydrogen show Heating on Adiabatic Expansion in Joule-Thomson Experiment

The inversion temperature of most gases are very high (much higher than the room temperature). That is why these gases undergo cooling on adiabatic expansion under ordinary conditions of temperature. On the other hand, the inversion temperatures of hydrogen and helium are very low (being much below 0°C). Hence, these gases undergo heating on adiabatic expansion under ordinary conditions of temperature. But, if these gases are first cooled to temperatures below their inversion temperatures and then allowed to expand adiabatically, these gases also show cooling effect.

Relationship of Joule-Thomson Coefficient μ with other Thermodynamic Quantities

Enthalpy H is a state function. Taking temperature T and pressure P as independent variables,

$$H = f(T, P) \qquad \ldots(9.43)$$

$$\therefore \quad dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \qquad \ldots(9.44)$$

In Joule-Thomson effect, the enthalpy of the system remains constant, i.e.

$$dH = 0$$

Putting this value in the above equation, we get

$$\left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT = 0 \qquad \ldots(9.45)$$

Dividing this equation throughout by dP and imposing the condition of constant enthalpy, we get

$$\left(\frac{\partial H}{\partial P}\right)_T + \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = 0 \qquad \ldots(9.46)$$

But $$\left(\frac{\partial H}{\partial T}\right)_P = C_P, \text{ heat capacity at constant pressure,} \qquad \ldots(9.47a)$$

and $$\left(\frac{\partial T}{\partial P}\right)_H = \mu, \text{ Joule – Thomson coefficient} \qquad \ldots(9.47b)$$

Putting these values in Eq. (9.46), we get

$$\left(\frac{\partial H}{\partial P}\right)_T + \mu C_P = 0$$

or $$\mu = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \qquad \ldots(9.48)$$

Thus, μ can be calculated from $\left(\frac{\partial H}{\partial P}\right)_T$ and ***vice versa.***

Example 4 *Explain why an ideal gas shows neither heating nor cooling in the Joule-Thomson experiment.*

or

Why is Joule-Thomson coefficient of an ideal gas zero?

Solution: An ideal gas undergoes neither cooling nor heating on adiabatic expansion in Joule Thomson experiment. This is expected as explained below:

The intermolecular forces of attraction (i.e. van der Waals forces) in an ideal gas are negligible. Hence, no energy is used up in overcoming the forces of attraction when the gas expands adiabatically. Thus, the internal energy of the gas does not fall and, therefore, the temperature also does not fall.

9.2.6 Expression for Work Done in Isothermal Reversible Expansion of a Gas

A general expression for the work of expression in an isothermal reversible process may be derived as under:

Let P be the pressure of the gas within a system undergoing an isothermal expansion by a reversible process. Then in order that the expansion may take place very slowly (i.e. reversibly) the external pressure should be $P - dP$, where dP is very small quantity. The small amount of work (δw) done by the system when its volume increases by an infinitesimal amount, dV, is equal to the product of the external pressure and the volume change, i.e.

$$\delta w = -(P - dP)dV \qquad \ldots(9.49)$$

Neglecting the term $dP \times dV$ which is very small (being the product of two very small quantities) Eq. (9.48) becomes

$$\delta w = -P \cdot dV \qquad \ldots(9.50)$$

Hence, the total work (w) done by the system when its volume increases from V_1 to V_2 will be given by

$$w = -\int_{V_1}^{V_2} P dV \qquad \ldots(9.51)$$

Now, for n moles of an ideal gas, the equation of state is

$$PV = nRT$$

so that

$$P = \frac{nRT}{V} \qquad \ldots(9.52)$$

Substituting this value in Eq. (9.51), we get

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV \qquad \ldots(9.53)$$

For an isothermal process, T is constant. Also, n and R are constant quantities. Hence, Eq. (9.52) may be written as

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= -nRT \ln \frac{V_2}{V_1} \qquad \ldots(9.54a)$$

or

$$w = -2.303\, nRT \log \frac{V_2}{V_1} \qquad \ldots(9.54b)$$

A relation can also be obtained in terms of pressure. As the process is isothermal, i.e. the temperature remains constant, therefore, by Boyle's law

$$P_1V_1 = P_2V_2 \qquad \ldots(9.55)$$

where P_1V_1 are the initial pressure and volume and $P_2\,V_2$ are the final pressure and volume of the system.

Equation (9.55) can be written as

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Substituting this value in Eq. (9.54), we get

$$w = -2.303\, nRT \log \frac{P_1}{P_2} \qquad \ldots(9.56)$$

Work done in a ***reversible process*** is the maximum work obtainable from a system.

Hence, w in equations (9.54) and (9.56) may thus be written as

$$w_{max} = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -2.303\, nRT \log \frac{P_1}{P_2}$$

Internal energy of a system is a function of temperature. As the temperature remains constant in an

isothermal process, internal energy does not change or $\Delta U = 0$

Expression for *q* (Heat Absorbed) According to first law of thermodynamics,

$$q = \Delta U - w$$

But $\Delta U = 0$ (as explained above)

$$q = -w$$

Thus, all the heat absorbed is used up completely in doing the work of expression only. Hence, the expressions for the heat absorbed in an isothermal reversible expansion of an ideal gas are same as the work done, i.e.

$$q = -w = 2.303\, nRT \log \frac{V_2}{V_1} = 2.303\, nRT \log \frac{P_1}{P_2}$$

9.2.7 Values for ΔU and ΔH in an Isothermal Expansion Process

Expression for ΔU Internal energy of an ideal gas is a function of temperature only. Therefore, in an isothermal process as the temperature remains constant, the internal energy of the system (containing an ideal gas) remains constant,

i.e. $$\Delta U = 0$$

Expression for ΔH

$$\begin{aligned} \Delta H &= \Delta(U + PV) \\ &= \Delta U + \Delta(PV) \\ &= \Delta U + \Delta(nRT) \\ &= 0 + 0 \end{aligned}$$

$\begin{cases} \Delta U = 0 \text{ as explained above} \\ \Delta T = 0 \text{ as the process is isothermal} \end{cases}$

i.e., $$\Delta H = 0$$

Values of q, w, ΔU and ΔH in case of isothermal irreversible expansion when

(i) Opposing pressure is zero

(ii) Opposing pressure is constant and less then P_2 but greater than zero. The expression for w, q, ΔU and ΔH for the above expansion may be obtained as follows:

(a) For Free Expansion

Here, $$P_{opp} = 0$$

$\therefore$ $$w = -\int P_{opp}\, dV = 0$$

Hence, $$q = w = 0$$

$$\Delta U = \Delta H = 0$$

(as the gas is ***ideal*** and expansion is ***isothermal***)

(b) For Intermediate Expansion Here, P_{opp} = Constant and lies in the range $O < P_{opp} < P_2$. Hence

$$w = -\int_{V_1}^{V_2} P_{opp}\, dV = -P_{opp}(V_2 - V_1)$$

$\therefore$ $$q = -w = P_{opp}(V_2 - V_1)$$

$$\Delta U = \Delta H = 0$$ (as the gas is ***ideal*** and expansion is ***isothermal***)

Quite clearly, the work done in this process will be less than the work done in the reversible

process.

Example 5 *One mole of ideal gas is heated at constant pressure from 0°C to 100°C. (a) Calculate the work involved. (b) If the gas were expanded isothermally and reversibly at 0°C from 1 atmosphere to some other pressure P, what must be the final pressure if the isothermal work is equal to the work in (a)?*

Solution : Work involved when the gas is heated at constant pressure from 0°C to 100°C is obtained as follows:

(a) $w = -P\Delta V = -P(V_2 - V_1)$

$= -(PV_2 - PV_1) = -(nRT_2 - nRT_1)$

$= -nR(T_2 - T_1) = 1 \times 8.314\ (373 - 273)$

$= 831.4$ J

(b) Final pressure if the process is carried out isothermally involving the work as in Step (a) is obtained as under:

$$w = -2.303\, nRT \log \frac{P_1}{P_2}$$

Put $P_1 = 1$ atm, $T = 273$ K, $R = 8.314$ JK^{-1} and n = 1

This on solving gives

$$P = 0.6933 \text{ atm}$$

Example 6 *Calculate the pressure-volume work performed by the system during reversible isothermal expansion of two moles of an ideal gas from 2 litres to 10 litres at 20°C.*

Solution: Here, we are given that

$n = 2$ moles $V_1 = 2$ litres $V_2 = 10$ litres $T = (20 + 273)$K $= 293$ K

Taking $R = 8.314$ joules degree^{-1} mor^{-1},

$$W_{max} = -2.303\, nRT \log \frac{V_2}{V_1} = -2.303 \times 2 \times 8.314 \times 293 \times \log \frac{10}{2}$$

$$= -11220.2 \times \log 5$$

$$= 7842.9 \text{ joules}$$

Example 7 *Ten moles of an ideal gas at the initial pressure of one atmosphere at 0°C were expanded reversibly under isothermal conditions to a final pressure of 0.1 atmosphere. Calculate the work done by the gas, the change in internal energy and the heat absorbed by the system ($R = 8.314$ JK^{-1} log^{-1} mol^{-1}).*

Solution: Here, we are given that

$n = 10$ moles $P_1 = 1$ atm $P_2 = 0.1$ atm $T = 0°C = 273$ K $R = 8.314$ JK^{-1} mol^{-1}

$$\therefore \quad W_{max} = -2.303\, nRT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 10 \times 8.314 \times 273 \times \log \frac{1}{0.1} \qquad (\because \log 10 = 1.0)$$

$$= -52271.7 \text{ J}$$

For an ideal gas during isothermal process,

$$\Delta U = 0$$

$\therefore$ by the first law of thermodynamics ($q = \Delta U - w$),

$$q = -W_{max} = 52271.7 \text{ J}$$

PROBLEMS FOR PRACTICE

1. Calculate the work done during isothermal expansion of one mole of an ideal gas from 10 atmospheres to 1 atmosphere at 27°C

[Ans. –5.74 kJ]

2. Calculate the work done by 10 litres of an ideal gas at 0°C and 10 atm in an isothermal reversible expansion to a final pressure of 1 atm (R = 8.314 joules).

[Hint (i) Reduce the given volume to volume at STP]

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{or} \quad \frac{10 \times 10}{273} = \frac{1 \times V_2}{273}$$

or V_2 = 100 litres at S.T.P.

(ii) Calculate the number of moles as follows:

22.4 litres at S.T.P = 1 mole

100 litres at S.T.P = 4.46 moles

$$w = -2.303\, nRT \log \frac{P_1}{P_2} \quad \text{or} \quad w = -23.3 \text{ kJ}$$

3. Estimate the work done in joules when the volume of 16.0 g of oxygen at 300 K changes isothermally from 5.0 to 25.0 litres.

[R = 8.3143 Jk^{-1} mol^{-1}]

[Ans. –2007.6 J]

4. Calculate the value of w, ΔU and ΔH in the isothermal and reversible expansion of 64 grams of oxygen at 410 K from an initial volume of 20 litres to a final volume of 60 litres. Assume oxygen behaves ideally.

[Ans. w = –7490.8 J, $\Delta H = \Delta U = 0$]

5. One mole of an ideal gas is heated at constant pressure from 0°C to 100°C.

(a) Calculate the work involved. (b) If the gas were expanded isothermally and reversibly at 0°C from 1 atmosphere to some other pressure P, what must be the final pressure if the isothermal work is equal to the work involved in (a)?

[*Hint*: (i) $w = -P\Delta V = -P(V_2 - V_1) = (PV_2 - PV_1) = -(nRT_2 - nRT_1)$

$= -nR(T_2 - T_1) = -1 \times 8.314\,(373 - 273) = -831.4$ J]

(ii) $w = 2.303\, nRT \log \frac{P_1}{P_2}$. Put P_1 = 1 atm, T = 273 K, R = 8.314 JK^{-1} mol^{-1}, n =1

On solving, we get P_2 = 0.6933 atm]

6. Find the work required to compress reversible 1 mole of a perfect gas from 1 to 100 atmosphere at 27°C.

[Ans. 11488 J]

7. Ten moles of an ideal gas are compressed isothermally and reversibly at i00°C from a pressure of i atmosphere to a pressure of i0 atmosphere. Calculate the following quantities: w and ΔH.

[Ans. = 71419 J, $\Delta H = 0$]

8. Estimate the maximum work which can be obtained by the isothermal expansion of 1 mole of an

ideal gas from 2.24 litres to 22.4 litres at 273 K(R = 8.3143 JK^{-1} mol^{-1})

[Ans. –5227.4 J]

9. Calculate the maximum work per mole when 5 moles of an ideal gas expand isothermally and reversibly from 20 litres to 100 litres at 27°C. [$R = 8.314 \times 10^7$ ergs mol^{-1} deg^{-1}]

[Ans. -200.76×10^5 ergs]

9.3 CALCULATION OF VALUES OF w, q, ΔU AND ΔH IN ADIABATIC EXPANSION OF AN IDEAL GAS

An adiabatic process is one in which no heat enters or leaves the system of any stage. For every infinitesimal change of the process,

$$\delta q = 0$$

Putting this value in the equation of the first law, viz.

$$dU = \delta q + \delta w, \text{ we get}$$
$$dU = \delta w \qquad \ldots(9.57)$$

If the work involved is the work of expansion only, then if dV is the small increase in volume an P is the pressure of the gas, then

$$\delta w = -PdV \qquad \ldots(9.58)$$

Putting this value in equation (9.57), we get

$$dU = -PdV \qquad \ldots(9.59)$$

For an ideal gas

$$C_V = \frac{dU}{dT}$$

or

$$dU = C_V dT$$

Putting this value in equation (9.59) we get

$$C_V dT = -PdV \qquad \ldots(9.60)$$

Also

$$\begin{aligned} \Delta H &= \Delta(U + P\Delta V) = \Delta U + \Delta(PV) \\ &= \Delta U + \Delta(RT) = \Delta U + R\Delta T \\ &= C_V \Delta T + R\Delta T = (C_V + R)\Delta T \\ &= (C_V + R)(T_2 - T_1) \\ &= C_P(T_2 - T_1) \end{aligned} \qquad \ldots(9.61)$$

In a Nutshell For any type of adiabatic process (reversible or irreversible)

$$q = 0$$
$$w = \Delta U$$
$$\Delta U = C_V \Delta T = C_V (T_2 - T_1)$$
$$\Delta H = C_P \Delta T = C_P (T_2 - T_1)$$

9.3.1 Reversible Adiabatic Expansion

We derive here under the relationships *between temperature and volume, between temperature and pressure* and *between pressure and volume* in reversible adiabatic expansion.

1. Relationship Between Temperature and Volume Consider 1 mol of the ideal gas. Then according to the gas equation

$$PV = RT$$

or
$$P = \frac{RT}{V} \qquad \ldots(9.62)$$

Also
$$C_V dT = -PdV \qquad \ldots(9.63)$$

Substituting for P from Eq. (9.62) in (9.63)

$$C_V dT = -\frac{RT}{V} dV$$

or
$$C_V \frac{dT}{T} = -R\frac{dV}{V} \qquad \ldots(9.64)$$

Now suppose the volume of the gas changes from V_1 to V_2 when the temperature changes from T_1 to T_2. Then assuming C_V to be independent of temperature and integrating Eq. (9.64) between the limits T_1, T_2 and V_1, V_2, we get

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \quad \text{or} \quad C_V [\ln T]_{T_1}^{T_2} = -R [\ln V]_{V_1}^{V_2} \quad \text{or} \quad C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

or
$$C_V \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2} \qquad \ldots(9.64a)$$

For 1 mol of an ideal gas, we know that

$$C_P - C_V = R$$

Putting this value of R in equation (9.64a) we get

$$C_V \ln \frac{T_2}{T_1} = (C_P - C_V) \ln \frac{V_1}{V_2}$$

Dividing throughout by C_V, we get

$$\ln \frac{T_2}{T_1} = \left[\frac{C_P}{C_V} - 1\right] \ln \frac{V_1}{V_2}$$

Putting $\frac{C_P}{C_V} = \gamma$, the ratio of the two heat capacities, we get

$$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{V_2} \quad \text{or} \quad \ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

Taking antilogarithm of both sides, we get

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

or
$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$$

or
$$\boxed{TV^{\gamma - 1} = \text{Constant}}$$

2. Relationship Between Temperature and Pressure For an ideal gas,

$$P_1V_1 = RT_1 \quad \text{and} \quad P_2V_2 = RT_2$$

i.e. $$V_1 = \frac{RT_1}{P_1} \quad \text{and} \quad V_2 = \frac{RT_2}{P_2}$$

$\therefore$ $$\frac{V_1}{V_2} = \frac{P_1}{RT_2} = \frac{T_1 P_2}{T_2 P_1} \qquad \ldots(9.65)$$

Also, $$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \ldots(9.66)$$

(The relation between T and V in case of adiabatic expansion)
From (9.65) and (9.66)

$$\frac{T_2}{T_1} = \left(\frac{T_1 P_2}{T_2 P_1}\right)^{\gamma - 1} \quad \text{or} \quad \frac{T_2}{T} \times \left(\frac{T_2}{T_1}\right)^{\gamma - 1} = \left(\frac{P_2}{P_1}\right)^{\gamma - 1}$$

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma - 1} \quad \text{or} \quad \left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{1 - \gamma}$$

Taking the γth root of both sides, we get

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{(1-\gamma)/\gamma} \quad \text{or} \quad T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}$$

or $$\boxed{TP^{(1-\gamma)/\gamma} = \text{Constant}}$$

3. Relationship Between Pressure and Volume Consider the relations between temperature and volume and temperature and pressure.

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \ldots(9.67)$$

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2}\right)^{(1-\gamma)/\gamma} \qquad \ldots(9.68)$$

From (9.67) and (9.68),

$$\left(\frac{P_1}{P_2}\right)^{(1-\gamma)/\gamma} = \left(\frac{V_1}{V_2}\right)^{1-\gamma} \quad \text{or} \quad \left(\frac{P_1}{P_2}\right)^{(1-\gamma)/\gamma} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

Taking $(1 - \gamma^{\text{th}}$ root of both sides, we have

$$\left(\frac{P_1}{P_2}\right)^{1/\gamma} = \frac{V_2}{V_1}$$

Raising both sides to the power γ, we have

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

or $$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$PV^{\gamma} = \text{Constant}$$

4. Work done in an Adiabatic Reversible Expansion of an Ideal Gas The expression for the work done in an adiabatic reversible expansion of an ideal gas is obtained as under:

For adiabatic process, we have

$$PV^{\gamma} = \text{Constant}$$

Differentiating this equation, we get

$$P(\gamma V^{\gamma-1})dV + V^{\gamma}dP = 0$$

or $$\gamma P V^{\gamma-1} dV + V^{\gamma} dP = 0$$

Dividing throughout by $V^{\gamma-1}$, we get

$$\gamma P dV + V dP = 0$$

or $$V dP = -\gamma P dV \quad \ldots(9.69)$$

For n moles of an ideal gas, $PV = nRT$

Differentiating this equation completely, we get

$$P dV + V dP = nR dT \quad \ldots(9.70)$$

Substituting for VdP from Eq. (9.69) in this equation, we get

$$P dV - \gamma P dV = nR dT$$

or $$(1 - \gamma) P dV = nR dT$$

or $$P dV = \frac{nR dT}{1 - \gamma} \quad \ldots(9.71)$$

Work done in the adiabatic process is given by the general equation

$$w = -\int_{V_1}^{V_2} P dV \quad \ldots(9.72)$$

Substituting for PdV from Eq. (9.71) in this equation, and changing the limits from volumes to temperatures, we get

$$w = -\int_{T_1}^{T_2} \frac{nR dT}{1 - \gamma} = -\frac{nR}{1 - \gamma} \int_{T_1}^{T_2} dT$$

$$= -\frac{nR}{1 - \gamma}(T_2 - T_1) \quad \ldots(9.73)$$

Hence, $$w = -\frac{nR(T_2 - T_1)}{1 - \gamma}$$

Expression for work done may be obtained in a different form.

Putting $R = C_P - C_V$ and $\gamma = C_P/C_V$, Eq. (9.73) becomes

$$w = -\frac{n(C_P - C_V)(T_2 - T_1)}{1 - \frac{C_P}{C_V}}$$

$$= -\frac{n(C_P - C_V)(T_2 - T_1)}{\frac{(C_V - C_P)}{C_P}} = -\frac{n(C_P - C_V)(T_2 - T_1)}{-\frac{(C_P - C_V)}{C_V}}$$

$= nC_V(T_2 - T_1)$, (for n moles of the ideal gas)

$= C_V(T_2 - T_1)$, (for 1 mol of the ideal gas) ...(9.74)

For n moles of an ideal gas,

$$P_1V_1 = nRT_1 \text{ (for the initial state)}$$

and $$P_2V_2 = nRT_2 \text{ (for the final state)}$$

Substituting these values in Eq. (9.73), we get

$$w = \frac{P_2V_2 - P_1V_1}{1 - \gamma} \quad \ldots(9.75)$$

Example 8 *Three moles of a perfect gas with C_V = 5.0 cal/mol/degree at 1.0 atmosphere is to be compressed adiabatically and reversibly from a volume of 75 litres at 1.0 atmosphere to a pressure of 100 atmospheres. Predict (a) the final volume of the gas, and (b) the final temperature of the gas.*

Solution: Here, we are given that

n = 3 moles C_V = 5.0 cal/mol/degree P_1 = 1.0 atm P_2 = 100 atm V_1 = 75 litres

For a perfect gas,

$$C_P = C_V + R = 5.0 + 2.0 = 7.0 \text{ cal } (R \cong 2 \text{ cal})$$

$\therefore$ $$\gamma = \frac{C_P}{C_V} = \frac{7.0}{5.0} = 1.4$$

(a) To calculate the final volume

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

or $$\left(\frac{V_1}{V_2}\right)^{\gamma} = \frac{P_2}{P_1} \quad \text{or} \quad \left(\frac{75}{V_2}\right)^{1.4} = \frac{100}{1.0} = 100$$

$\therefore$ $$1.4[\log 75 - \log V_2] = \log 100$$

or $$1.4(1.8751 - \log V_2) = 2$$

or $1.4 \log V_2 = 0.62514$ $\log V_2 = 0.4465$ $V_2 = \text{antilog}(0.4465) = 2.796$ litres

(b) To calculate the final temperature for a perfect gas,

$$PV = nRT$$

When

P = 100 atm

V = 2.796 litres (calculated above)

n = 3 moles (given)

R = 0.0821 litre atm deg^{-1} mol^{-1}

$$T = \frac{PV}{nR} = \frac{100 \times 2.796}{3 \times 0.0821} = 1135.2 \text{ K}$$

Example 9 *A dry gas at NTP is expanded adiabatically from 1 litre to 5 litres. Calculate the final temperature assuming ideal behaviour (C_P/C_V = 1.4).*

Solution: Applying the relation $TV^{\gamma-1}$ = Constant

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad \text{or} \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$T_1 = 273\ \text{K},\ T_2 = ?\ V_1 = 1\ \text{litre}\ V_2 = 5\ \text{litre}$$

Substituting the values in the equation above,

$$\frac{273}{T_2} = 5^{1.4-1} \quad \text{or} \quad \frac{273}{T_2} = 5^{0.4}$$

Taking logarithm of both sides

$$\log 273 - \log T_2 = 0.4 \log 5$$

or $$\log T_2 = \log 273 - 0.4 \log 5$$

or $$\log T_2 = 2.4362 - (0.4 \times 0.6990) = 2.1566$$

or $$T_2 = 143.4\ \text{K}$$

Example 10 *For a certain gas, C_P = 8.58 J. Two moles of the gas are expanded adiabatically from an initial temperature of 20°C to a final temperature of-45.4°C. Calculate the work done in the above case.*

Solution: C_P = 8.58 J, C_V = 8.58 –2 = 6.58 J

Therefore, $$r = \frac{C_P}{C_V} = \frac{8.58}{6.58} = 1.3$$

$$n = 2, R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Work done $$w = -\frac{nR(T_2 - T_1)}{1-\gamma}$$

$$= -\frac{2 \times 8.314 \times (-65.4)}{(1-1.3)}$$

$$= -\frac{2 \times 8.314 \times 65.4}{0.3}\ \text{J}$$

$$= -3624.9\ \text{J}$$

Example 11 *Two moles of H_2 are compressed adiabatically from STP conditions to occupy a volume of 4.48 litres. Calculate the final temperature. ($\gamma$for H_2 = 1.41).*

Solution: We are given that n = 2

$$V_1 = 2 \times 22.4 = 44.8\ \text{litres at STP}$$

So that $$T_1 = 273\ \text{K} \quad V_2 = 4.48\ \text{litres} \quad T_2 = ?$$
$$\gamma = 1.41$$

Substituting the values in the formula,

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

or $$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad \text{or} \quad \frac{T_2}{273} = \left(\frac{44.8}{4.48}\right)^{1.41-1} = (10)^{0.41}$$

or $$T_2 = 273 \times (10)^{0.41}$$

$\therefore$ $$\log T_2 = \log 273 + 0.41 \log 10 = 2.4362 + 0.41 = 2.8462$$

or $$T_2 = \text{antilog } 2.8462 = 701.8 \text{ K}$$

PROBLEMS FOR PRACTICE

1. 14 grams of N_2 at 290 atm are compressed adiabatically from 8 to 5 litres. Calculate the final temperature and the work done on the gas. Assume $C_P = \frac{7}{2}R$

[Ans. 349.9 K, w = 622.5 J]

2. Calculate the change in energy for 2 moles of H_2 warmed at constant volume from 25°, to 50°C. Given that for the gas near room temperature, C_V is constant and is about 5 cal/deg.

[**Ans.** 250 ergs]

3. Two moles of hydrogen at STP are compressed adiabatically to a volume of 10 litres. Calculate the final pressure and temperature of the gas. Given that γ for hydrogen is 1.41.

[Ans. Final pressure = 8.30 atm, Final temperature = 505 K]

[Hint. $V_1 = 2 \times 22.4 = 44.8$ litre, $V_2 = 10$ litres]

4. For a certain ideal gas, C_P = 8.58 cal mol^{-1}. What will be the final volume and temperature when 2 moles of the gas at 20°C and 15 atm are allowed to expand adiabatically and reversibly to 5 atm pressure? Also calculate the work done in the above process.

[Ans. V = 7.44 litres, t = –45.4°C, w = –3625]

[Hint. First calculate T_2, then find out $w = \frac{nRT(T_2 - T_1)}{1 - \gamma}$

$T_1 = 293$ K $T_2 = 227.6$ K

$\gamma = \frac{8.58}{6.58} = 1.30$, $n = 2$, $R = 8.314$ JK^{-1} mol^{-1}]

5. A quantity of air (γ = 1.4) at 300 K is compressed adiabatically to one third of its volume. Find the change in its temperature.

[Ans. 465.5 K]

9.3.2 Comparison of Isothermal and Adiabatic Expansion of a Real Gas

For a ***reversible adiabatic process,*** pressure and volume are related as

$$PV^{\gamma} = \text{constant}$$

While for a ***reversible isothermal process,*** the relationship is simply given by Boyle's law, viz.

$$PV = \text{constant}$$

Since C_P is always greater than C_V,

the ratio $\frac{C_P}{C_V} = \gamma$ is greater than unity.

Hence, the increase of volume for a given decrease of pressure will be less in an adiabatical expansion than in an isothermal expansion. Therefore, the plot of pressure against volume, i.e. pressure-volume curve will be steeper for an adiabatic process than for an isothermal process, starting at the same point, as shown in Fig. 9.20.

Also, since the area under the pressure volume curve gives the work of expansion, from Fig. 9.20 it may be observed that for the same increase of volume, the work done in an adiabatic process is less than in an isothermal process.

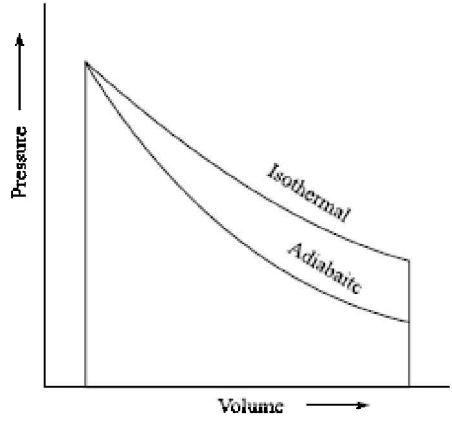


Fig. 9.20 *Isothermal and adiabatic curves*

9.3.3 Calculation of w, q, ΔU and ΔH in Isothermal Reversible Expansion of a Real Gas

1. Expression for w

$$dw = -P_{ext}\, dV$$

For the reversible expansion

$$P_{ext} = P_{int} - dP \simeq P_{int}$$

where P_{int} is the pressure (internal pressure) of the gas.

Hence,

$$dw = -P_{int}\, dV \qquad \ldots(9.76)$$

As the gas is real, P_{int} can be obtained from van der Waals equation, i.e.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

we get

$$P_{int} = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \qquad \ldots(9.77)$$

Putting this value in Eq. (9.76), we get

$$-dw = \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) dV$$

$$-w = \int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) dV$$

$$= nRT\,[\ln (V - nb)]_{V_1}^{V_2} - an^2\left[-\frac{1}{V}\right]_{V_1}^{V_2}$$

or
$$-w = nRT \ln \frac{V_2 - nb}{V_1 - nb} + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \qquad \ldots(9.78)$$

2. Expression for ΔU According to the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial U}{\partial V}\right)_T - P \qquad \ldots(9.79)$$

For a real gas, according to van der Waal's equation,

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \qquad \ldots(9.80)$$

Differentiating w.r.t. T at constant volume, we get

$\therefore$
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb} \qquad \ldots(9.81)$$

Substituting the values from Equations (9.80) and (9.81) in Eq. (9.79) we get

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V - nb} - \left[\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right] = \frac{an^2}{V^2} \qquad \ldots(9.82)$$

For dU, we can write

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (\because U \text{ is a function of } T \text{ and } V) \ldots(9.83)$$

For the isothermal process, $dT = 0$

$\therefore$
$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV = \frac{an^2}{V^2} dV \qquad \text{[Substituting the value from Eq. (9.82)]}$$

Hence, for a finite process,

$$\Delta U = \int_{V_1}^{V_2} \frac{an^2}{V^2} dV$$

or
$$\Delta U = -an^2\left(\frac{1}{V^2} - \frac{1}{V^1}\right) \qquad \ldots(9.84)$$

3. Expression for *q* According to the first law of thermodynamics

$$q = \Delta U - w$$

Substituting the values of w and ΔU from Eqs (9.78) and (9.84) we get

$$q = -an^2\left(\frac{1}{V^2} - \frac{1}{V^1}\right) + nRT \ln\frac{V_2 - nb}{V_1 - nb} + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

or $$q = nRT \ln\frac{V_2 - nb}{V_1 - nb} \qquad \ldots(9.85)$$

4. Expression of ΔH We have

$$\Delta H = \Delta(U + P\Delta V)$$
$$= \Delta U + \Delta(PV)$$

Substituting the value of ΔU and P from Eqs (9.84) and (9.77), we get

$$\Delta H = -an^2\left(\frac{1}{V^2} - \frac{1}{V_1}\right) + \Delta\left[\left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right)\right]$$

$$= -an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT\left(\frac{V_2}{V_2 - nb} - \frac{V_1}{V_1 nb}\right) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= -2an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT\left[\frac{V_2 - nb + nb}{V_2 - nb} - \frac{V_1 - nb + nb}{V_1 - nb}\right]$$

$$= -2an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT\left[\left(1 + \frac{nb}{V_2 - nb}\right) - \left(1 + \frac{nb}{V_1 - nb}\right)\right]$$

$$\Delta H = -2an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + n^2 bRT\left[\left(\frac{1}{V_2 - nb} + \frac{1}{V_1 - nb}\right)\right] \qquad \ldots(9.86)$$

q, w, ΔE and ΔH in adiabatic reversible expansion of a real gas

(a) Value for q

For the adiabatic process, as already explained

$$q = 0$$

(b) Expressions for w and ΔU By the first law of thermodynamics,

$$\Delta U = q + w$$

As $q = 0$, therefore, $$\Delta U = w$$

The expression for ΔU and hence for w can be obtained as follows:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Putting $(\partial U/\partial T)_V = nC_V$ (for n moles) and

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}, \text{ we get}$$

$$dU = nC_V dT + \frac{an^2}{V^2} dV \qquad \ldots(9.87)$$

Hence, for a finite process

$$\Delta U = \int_{T_1}^{T_2} nC_V dT + \int_{V_1}^{V_2} \frac{an^2}{V^2} dV$$

Taking C_V to be independent of temperature, we have

$$\Delta U = nC_V (T_2 - T_1) + an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \quad \ldots(9.88$$

This expression can be used for calculation of ΔU if T_1, T_2, V_1 and V_2 are known. However, if T_2 is not given, it is first calculated as follows.

$$dU = dw = -PdV$$

or $$dU = -PdV \quad \ldots(9.89)$$

For a real gas,

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad \ldots(9.89a)$$

and $$dU = nC_V\, dT + \frac{an^2}{V^2} dV$$

[Refer Eq. (9.87). above.]

Substituting these values in Eq. (9.89), we get

$$nC_V\, dT + \frac{an^2}{V^2} dV = -\frac{nRT}{V - nb} dV + \frac{an^2}{V^2} dV$$

or $$nC_V dT = -\frac{nRT}{V - nb} dV$$

or $$C_V dT = \frac{-RT}{V - nb} dV$$

It can be written as

$$C_V \frac{dT}{T} = -R \frac{dV}{V - nb}$$

Intergrating between suitable limits, we get

$$\int_{T_1}^{T_2} C_V \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V - nb}$$

or $$C_V [\ln T]_{T}^{T_2} = -R [\ln (V - nb)]_{V_1}^{V_2}$$

or $$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2 - nb}{V_1 - nb}$$

or $$\ln \left(\frac{T_2}{T_1} \right)^{C_V} = \ln \left(\frac{V_1 - nb}{V_2 - nb} \right)^{R}$$

or $$\left(\frac{T_2}{T_1} \right)^{C_V} = \left(\frac{V_1 - nb}{V_2 - nb} \right)^{R}$$

or $$\frac{T_2}{T_1} = \left(\frac{V_1 - nb}{V_2 - nb} \right)^{R/C_V}$$

or $$T_2 = T_1 \left(\frac{V_1 - nb}{V_2 - nb} \right)^{R/C_V}$$

Knowing V_1, V_2 and T_1, T_2 (temperature after expansion) can be calculated. This may be substituted in Eq. (9.88) to get ΔU and hence w.

7. Expression for ΔH

$$\Delta H = \Delta (U + PV) = \Delta U + \Delta (PV)$$

$$= \Delta U + \Delta \left[\left(\frac{nRT}{V - nb} - \frac{an^2}{V^2} \right) V \right] \qquad \text{(After substituting for } P \text{ Eq. 9.89a)}$$

$$= \Delta U + nR \left(\frac{V_2 T_2}{V_2 - nb} - \frac{V_1 T_1}{V_1 - nb} \right) - an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

Substituting the value of ΔU from Eq. (9.88), we get

$$\Delta H = n C_V (T_2 - T_1) - 2an^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right) + nR \left(\frac{V_2 T_2}{V_2 - nb} - \frac{V_1 T_1}{V_1 - nb} \right) \quad \ldots (9.90)$$

SOLVED PROBLEMS

Example 12 *State the variables which are kept constant in the following processes: (a) Isothermal (b) Isobaric (c) Isocaloric*

Solution:(a) Temperature (b) Pressure (c) Volume

Example 13 *What are the conditions under which q and w become state functions? Discuss briefly.*

Solution:

(a) At constant volume, there is no work of expansion, hence w=0. By the first law of

thermodynamics, $\Delta U = q_V$, As ΔU is a state function, q_V is also a state function.

(b) At constant external pressure, $w = -P\Delta V$. Hence, w becomes a state function.

(c) $\Delta U = q_P + w$. As ΔU is state function w under constant pressure is also a state function. Therefore, q_P is also a state function.

Example 14 *What are standard state conditions? Which form of carbon is assigned a value of zero for molar enthalpy in the standard state and why?*

Solution: A substance is considered to be in standard state if it is at a temperature of 298.15 K and a pressure of one atmosphere Graphite is assigned a value of zero for enthalpy in the standard state because it is the stable form.

Example 15 *Under what conditions may an extensive property become intensive property? Give an example.*

Solution: An extensive property might become intensive when unit amount of the substance is specified. For example, mass is extensive, but mass per unit volume (i.e. density) is intensive. Similarly, heat capacity is extensive but specific heat (which is heat capacity per unit mass) is intensive.

Example 16 *Which of the following expressions represent work done and under what conditions?*

(a) $P\Delta V$ (b) $\Delta(PV)$ (c) $P_{ext}\int_{V_1}^{V_2} dV$

Solution:

(a) $P\Delta V$ denotes work done against constant external pressure, P when the volume changes from V_1 to V_2 such that $\Delta V = V_2 - V_1$

(b) It does not stand for work done.

(c) It represents the work done when there is reversible expansion of the gas from the volume V_1 to V_2 against external pressure p_{ext}.

SUMMARY

1. *Objectives* of *thermodynamics:* To predict the feasibility of a process, to estimate the yield of products and to deduce important relations in physical chemistry.
2. Part of the universe chosen for thermodynamic consideration is called the *system*, the remaining portion of the universe is called *surroundings*.
3. A system which can exchange both matter and energy with the surroundings is called-an *open* system, that which can exchange only energy is a *closed* system and that which can exchange neither matter nor energy is called an *insulated* system.
4. If a system is uniform throughout, it is called *homogenous*, if not, it is called *heterogeneous*
5. States of a system are composition, pressure, volume and temperature.
6. Properties that depend upon the quantity of matter are called *extensive properties*, for example, mass, volume, energy, etc. Properties that depend upon the nature of the substance and are independent of the quantity of the substance are called *intensive properties*, for example, temperature, viscosity, refractive index, etc.
7. A process which is carried out in a manner that the temperature remains constant throughout is called an *isothermal process*. "When no heat can flow from the system to the surroundings or vice-versa in a process, it is called an *adiabatic process*.
8. A *reversible process* is one which is carried out infinitesimally slowly so that all changes

occurring in the direct process can be exactly reversed and the system remains almost in a state of equilibrium throughout.

9. A process which does not meet the above requirements is called *irreversible process*.
10. Energy associated with a substance is called *internal energy*. Change in internal energy, ΔU is negative if energy is evolved and positive if energy is absorbed.
11. *Heat* is a mode of energy exchange between the system and the surroundings as a result of the difference of temperature between them.
12. *Zeroth law of thermodynamics* states: "When two bodies have equality of temperature with a third body, then they, in turn, have equality of temperature with each other.
13. *First law of thermodynamics* can be stated in a number of ways. Two of the statements are given below:
    (a) Energy can neither be created nor destroyed although it may be converted from one form to the other.
    (b) Total energy of an isolated system remains constant although it may undergo transformation from one form to another.
14. Internal energy is a state function but work and heat are not.
15. The energy change accompanying a process is independent of the path followed and depends only upon the initial and final states.
16. The thermodynamic quantity $U + PV$ is called heat content or enthalpy.
17. Heat capacity of a system is defined as the amount of heat required to raise the temperature of the system through 1°C.
18. When a real gas at a certain pressure expands adiabatically through a porous plug or a fine hole into a region of low pressure, it is accompanied by cooling (except for H_2 and He which get warmed up). This phenomenon is known as Joule – Thomson effect
19. The temperature (at a particular pressure) at which the gas neither cools down nor heats up upon adiabatic expansion is called inversion temperature

KEY RELATIONS

1. $w = P_{ext} \times \Delta V$ (Work of expansion against constant pressure)
2. $\Delta U = q + w$ (First law of thermodynamics)
3. $q_p = \Delta U + P\Delta V$ Also $\Delta H = \Delta U + P\Delta V$
4. $\Delta H = \Delta U + \Delta nRT$
5. Heat capacity $C = \dfrac{q}{\Delta T}$
6. $C_P = \left(\dfrac{\partial H}{\partial T}\right)_P$
7. $C_P - C_V = R$
8. $\gamma = \dfrac{C_P}{C_V}$
9. $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$ Joule's law

10. Joule-Thomson coefficient $\mu = \left(\frac{\partial T}{\partial P}\right)_H$

11. $w = -2.303\, nRT \log \frac{V_2}{V_1} = -2.303\, nRT \log \frac{P_1}{P_2}$

12. For adiabatic process (reversible or irreversible),

$$\Delta U = C_V(T_2 - T_1) \quad \text{and} \quad \Delta H = C_P(T_2 - T_1)$$

$$TV^{\gamma - 1} = \text{constant}, \; TP^{(1-\gamma)/\gamma} = \text{constant and } PV^{\gamma} = \text{constant}$$

$$w = -\frac{nR(T_2 - T_1)}{1 - \gamma} = -\frac{P_2V_2 - P_1V_1}{1 - \gamma}$$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. The first law of thermodynamics is the law of
   (a) enthalpy
   (b) free energy
   (c) conservation of energy
   (d) none of these
2. The mathematical form of the first law of thermodynamics is
   (a) $dq = dU = dw$
   (b) $dq = dU - dw$
   (c) $dU = dq + dw$
   (d) none of these
3. Standard state refers to
   (a) one atmosphere pressure and 25°C temperature
   (b) one atmosphere pressure and 100°C temperature
   (c) one atmosphere pressure and 0°C temperature
   (d) none of these
4. A process during which there is no heat change is called
   (a) an adiabatic process
   (b) reversible process
   (c) irreversible process
   (d) none of these
5. A process in which a system comes to its initial position after a series of operations is called
   (a) reversible
   (b) cyclic
   (c) adiabatic

(d) non of these

6. A process which proceeds infinitesimally slowly is called
   (a) irreversible
   (b) reversible
   (c) isothermal
   (d) adiabatic
7. The heat content of a system is called
   (a) internal energy
   (b) enthalpy
   (c) free energy
   (d) entropy
8. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ q_p is equal to
   (a) $q_V - 2RT$
   (b) $q_V + 2RT$
   (c) $q_V + RT$
   (d) $q_V - RT$
9. The least random state of a water system is
   (a) ice
   (b) liquid water
   (c) steam
   (d) equal randomness in all
10. Identify the intensive quantities from the following:
    (a) Enthalpy
    (b) Temperature
    (c) Volume
    (d) Refractive index.

Answers

1. (c)
2. (c)
3. (a)
4. (a)
5. (b)
6. (b)
7. (b)
8. (a)
9. (a)
10. (a),(d)

SHORT-ANSWER QUESTIONS

1. What do you understand by the state of a system? What are state variables? Why should it be sufficient to specify the values of a few variables to define the state of a system instead of specifying the values of all the variables?
2. Distinguish between
   (a) State function and path function
   (b) Dependent and independent variables.
   (c) Isothermal and adiabatic process
3. What are extensive and intensive properties? Give three examples of each of them.
4. Briefly explain the terms *enthalpy* and *enthalpy change*. Is it intensive or extensive property?
5. What do you understand by inversion temperature?
6. Derive the expression for molar heat capacities $C_V$and C_P in terms of internal energy change and enthalpy change and hence show that $C_P - C_V = R$ for 1 mole of an ideal gas.
7. Derive expression for Joule – Thomson coefficient and inversion temperature in terms of van der Waals constants.
8. Point out the main difference between
   (a) Open, closed and isolated systems
   (b) Reversible and irreversible processes
9. Derive the expression for work done when a gas expands from volume V_1 to V_2 against external pressure P.
10. What is the relationship between heat and mechanical work? Define Joule's mechanical equivalent of heat. What is its value?
11. What generalization do you draw about the relationship between the atomicity of the gases and the ratio (γ) of their specific heats?
12. Define thermodynamics? What are its main objectives?
13. State the first law of thermodynamics in two different ways. Derive its mathematical formulation.
14. State and explain Joule's law about the variation of internal energy of an ideal gas with volume.
15. Write a short note or Joule – Thomson effect.
16. Explain that the work done during reversible expansion is the maximum work for a given increase of volume and minimum to compress the gas for a given decreases of volume.
17. Give in brief the objectives and limitations of thermodynamics.
18. Prove that the heat capacity at constant volume (C_V) for an ideal gas having translational kinetic energy only is constant and equal to 3 cal mol^{-1} and is independent of temperature.
19. Define zeroth law of thermodynamics. What is its most important application?
20. Prove that C_P for an ideal gas is constant and nearly equal to 5 cal $degree^{-1}$ mol^{-1}.

GENERAL QUESTIONS

1. State and explain Joule's law
2. State the first law of thermodynamics in at least three different ways. Derive the mathematical expression for it. Explain the fact that internal energy is a state function but heat and work are not.
3. State and explain the following terms with suitable examples:
   (a) Open, closed and isolated systems

(b) Thermodynamics Reversible and Irreversible processes

(c) Extensive and Intensive properties

(d) State function and path function

4. Derive expressions for w, q, ΔU and ΔH when an ideal gas undergoes

   (a) isothermal reversible expansion, and

   (b) isothermal irreversible expansion.

5. Derive that for reversible adiabatic expansion of an ideal gas:

   (a) PV^{γ} = constant

   (b) Work done, $w = C_V(T_2 - T_1)$

6. What do you understand by heat of reaction at constant volume and that at constant pressure? Derive the relationship between them. Under what conditions are the two equal?

7. Explain the terms:

   (a) 'Enthalpy' and 'Enthalpy change'

   (b) Heat capacity. Derive the expression for heat capacity at constant volume and that at constant pressure. Derive the relationship between them.

8. Briefly explain the terms *internal energy*, *work* and *heat*. Derive the expression for the work of expansion. Explain that work done by a system in a reversible process is the maximum work for a given increase of volume and for a given decreases of volume, it is the minimum work to reverse the process.

9. Prove that for a monatomic gas (having translational kinetic energy only), $C_V = \frac{3}{2} R$

10. Prove thermodynamically that Joule – Thomson coefficient for an ideal gas is zero. Also deduce the expression for Joule – Thomson coefficient for real gases in terms of van der Waals constant 'a' and 'b'.

11. Derive the expressions for w, ΔU, q and ΔH for isothermal reversible expansion of a real gas.

12. What is Joule – Thomson effect? Justify that during this process, enthalpy of the system remains constant. Also explain what you understand by Joule – Thomson coefficient and inversion temperature. Derive that Joule – Thomson coefficient is given by

$$\mu = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

13. Derive expressions for ΔU and ΔH for adiabatic reversible expression of a real gas.

14. Derive the following expression for the reversible adiabatic expansion of a real gas.

$$T_2 = T_1\left(\frac{V_1 - nb}{V_2 - nb}\right)^{R/C_P}$$

15. How can the reversible isothermal expansion of an ideal gas be brought about? Derive an expression for the work of expansion of such a process.

16. (a) Distinguish between reversible isothermal expansion and reversible adiabatic expansion

    (b) Show that for adiabatic expansion of an ideal gas,

$$PV^{\gamma} = \text{constant}$$

17. Derive the expression for the work done in an adiabatic expansion. Will the expression be different for adiabatic expression along a reversible and an irreversible path?

18. Define *standard enthalpy of formation'*. Taking a suitable example, prove that the standard

entahalpy of a compound is equal to its standard enthalpy of formation.

19. What are the values/expression for q, w, ΔU and ΔH for

    (a) irreversible isothermal free expansion of an ideal gas?

    (b) irreversible isothermal intermediate expansion of an ideal gas?
    Out of reversible and irreversible expansion which one will absorb less heat and why?

20. What are the values/expressions, for q, w, ΔU and ΔH for

    (a) irreversible adiabatic free expansion of an ideal gas?

    (b) irreversible adiabatic intermediate expansion of an ideal gas?

21. The work done in a reversible isothermal expansion of an ideal gas is greater than the work done in reversible adiabatic expansion. Explain

22. Compare reversible isothermal expansion with reversible adiabatic expansion of an ideal gas.

23. How is the final temperature of irreversible adiabatic expansion of an ideal gas calculated?

24. How can maximum amount of the work during isothermal expansion of a gas be obtained?

25. Derive an expression for the maximum work obtainable from the isothermal expansion of n moles of a perfect gas.

26. Derive relationship between heat of reaction at constant pressure and that at constant volume.

27. Show that maximum work is produced in a reversible isothermal expansion of a gas.



Thermochemistry 10

LEARNING OBJECTIVES

- Understand enthalpy and enthalpy change
- Follow the latest sign conventions for q, ΔU and w
- Differentiate between exothermic and endothermic reactions
- Define a thermochemical equation
- Identify factors influencing heat of reaction
- Understand heat of combustion and calorific value of foods and fuels
- Define standard state
- Follow enthalpy of formation and standard enthalpy of formation
- Define enthalpy of neutralization, enthalpy of solution, enthalpy of hydration, enthalpy of fusion, enthalpy of vaporisation, enthalpy of sublimation and lattice enthalpy
- Define and understand Hess's law of constant heat summation
- Understand bond enthalpy and its applications
- Understand the variation of heat of reaction with temperature (Kirchoff's equation)

10.1 INTRODUCTION

The branch of chemistry which deals with heat changes accompanying chemical reactions is called thermochemistry

A chemical reaction involves rearrangement of atoms, i.e. some bonds within the reactant molecules are broken while some new bonds in molecules of the products are formed. Energy is consumed in the dissociation of bonds while energy is evolved when the bonds are formed.

If the total energy evolved is greater than the total energy consumed, the net result is the ***release of energy.*** On the other hand, if the energy consumed is greater than the energy evolved, the net result is the ***absorption of energy.***

All chemical reactions are usually accompanied by energy changes. These energy changes appear in the form of heat, light, work, electricity, etc. These energy changes are of great practical utility, both for domestic and industrial purposes. A few reactions along with the form in which the accompanying energy changes appear and the use to which they are put are listed below:

1. Burning of coal in air produces ***heat.*** That is why it is used as a fuel.

$$C(s) + O_2(g) \longrightarrow CO_2(g) + \text{heat}$$

2. ***Digestion and metabolism of carbohydrates*** in biological systems produce ***heat*** which maintains the body temperature.
3. ***Burning of candle (wax) in air produces heat and light.*** It is, therefore, used as a source of light. Wax is a hydrocarbon.
4. ***Reaction that takes place in a galvanic cell*** produces electrical energy which may be used to

run an electric motor or to ring a bell, etc.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Units of Heat and Work The heat changes are measured in calories, kilocalories, joules or kilojoules.

1 calorie = 4.184 J 1 kcal = 4.184 kJ

The SI unit of heat is joule or kilojoule. Work is measured in ergs or joules. The SI unit of work is joule.

$$1 \text{ Joule} = 10^7 \text{ ergs}$$

The SI unit of energy (or work) is joule (J) named after the physicist James Joule. The joule is a fairly small quantity of energy. It is the amount of kinetic energy possessed by a 2 kg mass moving at a speed of 1 m/s.

$$E = \frac{1}{2} m v^2 = \frac{1}{2} (2\,\text{kg})(1\,m/s)^2$$
$$= 1\ \text{kg}\ m^2/s^2 = 1\ \text{J}$$

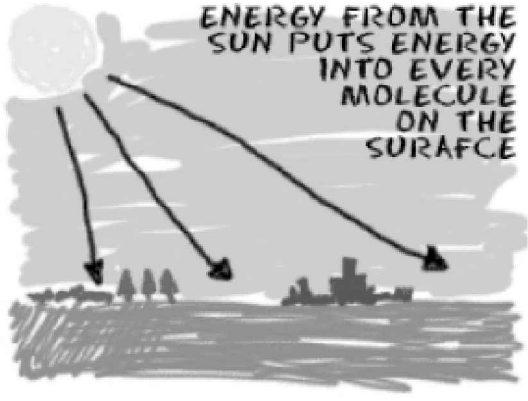


Fig. 10.1 *Energy from the sun*

10.1.1 Enthalpy and Enthalpy Change

When a process is carried out at constant pressure and temperature, there is a change in volume, if the volume increases, some mechanical work is done by the system so that the internal energy decreases. Similarly, if the volume decreases, some mechanical work is done on the system so that the internal energy increases. In all such processes occurring at constant temperature when pressure remains constant, the total energy of a system is given by a thermodynamic quantity called ***heat content*** or ***enthalpy*** of the system and not by internal energy. It is denoted by H and is defined mathematically by the equation

$$H = U + PV \qquad (10.1)$$

where U is the internal energy, and P and V are the pressure and volume of the system respectively. ***The enthalpy of a system may be defined as the sum of the internal energy and the product of pressure and volume of the system.*** The ***physical significance of enthalpy*** may be put as under:

The enthalpy of a substance is the amount of energy stored within the substance, i.e. available for conversion into heat.

Like internal energy, the heat content or enthalpy of a substance is also a state function, i.e.

depends only on the state of the system and is independent of the manner by which the state has been attained.

1. Enthalpy Change Like internal energy, the absolute value of enthalpy of a substance cannot be determined. However, the change in the enthalpy when a system undergoes a change can be determined experimentally accurately and that serves our purpose.

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*IUPAC recommends the use of notation U in place of E for internal energy

A relation between enthalpy change and internal energy change exists as follows:

$$\Delta H = \Delta U + P\Delta V \quad \ldots(10.2)$$

where $\Delta U = U_2 - U_1$ represents the change in internal energy

and $\Delta V = V_2 - V_1$ represents the change in volume of the system

Thus, ***enthalpy change of a system may be defined as the sum of internal energy change and the pressure-volume work done.***

If q_P is the heat absorbed at constant pressure then $q_p = \Delta H$ ...(10.3)

Thus, enthalpy change is the heat absorbed or evolved at constant pressure.

Enthalpy change is a very useful quantity. Knowledge of this quantity is needed when we want to plan the heating or cooling required to carry out an industrial chemical reaction at constant temperature. It is also needed to compute temperature dependence of equilibrium constant.

2. Standard Enthalpy Change Enthalpy change of a reaction when all the reactants and the products are in their standard states, i.e., at 298 K and under a pressure of one atmosphere is known as the standard enthalpy change. It is usually represented by $\Delta H°$.

As a chemical reaction involves breaking of bonds of the reactants and the formation of new bonds in the products, some net energy change (called the enthalpy of reaction) takes place.

$$\text{Enthalpy change of a reaction} = \begin{bmatrix}\text{Energy consumed to}\\ \text{break the bonds of}\\ \text{the reactants}\end{bmatrix} - \begin{bmatrix}\text{Energy relased}\\ \text{in the formation}\\ \text{of the bonds in the}\\ \text{products}\end{bmatrix}$$

If energy consumed > energy released, the net result is the absorption of energy and the reaction is ***endothermic.***

If energy released > energy consumed, the net result is the evolution of energy and the reaction is ***exothermic.***

10.2 LATEST SIGN CONVENTIONS FOR Q OR ΔH, ΔU AND W

1. When heat is absorbed by the system, q is positive.
2. When heat is given out by the system, q is negative.
3. When energy is absorbed by the system, ΔU is positive.
4. When energy is given out by the system, ΔU is negative.
5. When work is done on the system, w is positive.
6. When work is done by the system, w is negative.

10.2.1 Exothermic and Endothermic Reactions

Exothermic reactions are those reactions which are accompanied by the evolution of heat.

The quantity of heat produced is shown along with the products with a 'plus' sign. A few examples of exothermic reactions are given below:

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 393.5 \text{ kJ}$$

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g) + 248.8 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O + 890.4 \text{ kJ}$$

Endothermic reactions are those reactions which are accompanied by absorption of heat. Heat absorbed can be written with the products with a 'minus' sing. A few examples of endothermic reactions are given below:

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) - 180.7 \text{ kJ}$$

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) - 131.4 \text{ kJ}$$

$$C(s) + 2S(s) \longrightarrow CS_2(l) - 92.0 \text{ kJ}$$

The enthalpy change (ΔH) accompanying a reaction is given by

$$\Delta H = \text{Heat content of products} - \text{Heat content of reactants}$$
$$= H_P - H_R$$

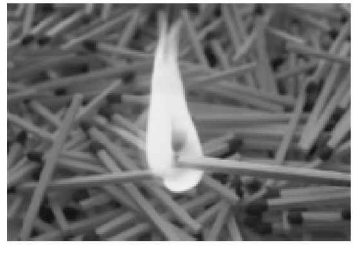


Fig. 10.2 *Burning of wood is an exothermic reaction.*

A reaction is exothermic if the total heat content of the reactants is more than that of the products. i.e., $H_R > H_P$. Thus, ΔH will be negative for an exothermic process.

Thus, the exothermic reactions given above may be written in terms of ΔH as

$$C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H = -393.5 \text{ kJ}$$

$$H_2(g) + = \frac{1}{2} O_2(g)\, O(l) \longrightarrow H_2O(1), \Delta H = -285.8 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(1), \Delta H = -890.4 \text{ kJ}$$

A reaction is endothermic if the total heat content of reactants is less than that of the products, i.e.

$$H_R < H_P$$

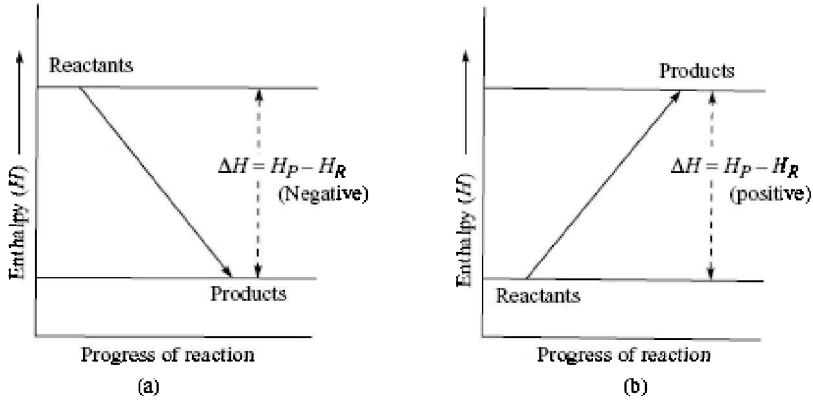


Fig. 10.3 *(a) Exothermic reaction (b) Endothermic reaction.*

Thus, ΔH will be positive for an endothermic reaction.

Endothermic reactions given above may be written in terms of ΔH as

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)\ \Delta H = +180.7\ kJ$$

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g),\ \Delta H = +131.4\ kJ$$

$$C(s) + 2S(s) \longrightarrow CS_2(l)\ \Delta H = +92.0\ kJ$$

Exothermic and endothermic reactions may be represented graphically as shown in Figs. 10.3(a) and (b).

10.2.2 Thermochemical Equation

A balanced chemical equation not only indicating the quantities of the different reactants and products but also indicating the amount of heat evolved or absorbed is called a ***thermochemical equation.***

Fractional coefficients are allowed in writing a thermochemical equation. For example, the formation of water is written as

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l),\ \Delta H = -285.8\ kJ$$

Thus, 285.8 kJ of heat is produced when 1 mole of hydrogen reacts with 0.5 mole of oxygen. If the quantities of reactants are doubled, the heat produced will also be doubled. For example, in the above case, we may write

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)\ \Delta H = -571.6\ kJ$$

SOME IMPORTANT POINTS ABOUT THERMOCHEMICAL EQUATIONS

1. Unless otherwise mentioned, ΔH values are for the standard state of the substances (i.e., 298 K and 1 atm pressure)
2. The physical state (s, *l*, *g*, etc.) of the different substances must be mentioned as the heat evolved or absorbed depends upon the physical state of the substances.
3. If the coefficients of the substances are multiplied or divided by some number, the value of ΔH is also multiplied or divided by the same number.
4. If the reaction is reversed, the sign of ΔH changes but the magnitude remains the same.

10.3 HEAT OF REACTION (OR ENTHALPY OF REACTION)

The amount of heat evolved or absorbed in a chemical reaction when the number of moles of the reactants as represented by the chemical equation have completely reacted, is called the heat of reaction.

Let us consider the following two examples:

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ \Delta H = -393.5\ kJ$$

$$C(s) + 2S(s) \longrightarrow CS_2(l)\ \Delta H = +92.0\ kJ$$

The first equation indicates that when 1 mole of solid carbon (i.e. 12 g) combines completely with 1 mole of oxygen gas (i.e. 32 g), 393.5 kJ of heat are produced. Similarly, the second equation tells that when 1 mole of solid carbon (i.e. 12 g) reacts completely with 2 moles of sulphur (64 g), 92 kJ of heat are absorbed.

Heat of reaction, ΔH = Heat content of products − Heat content of reactants

or ΔH = (Sum of enthalpies of products) − (Sum of enthalpies of reactants)

If the reaction is reversed, the sign of ΔH is also reversed.

10.3.1 Factors Influencing Heat of Reaction

The heat of a reaction depends upon a number of factors as explained below:

1. Quantities of the Reactants Involved If the quantities of the reactants are changed, the heat of reaction changes proportionally.

2. Physical State of the Reactants and Products Since latent heat is involved in the change of state, the physical state of the reactants and products affects the heat of reaction. For example, when hydrogen and oxygen gases combine to form liquid water, the heat of reaction is different from the value when they combine to form water vapours.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l),\ \Delta H = -285.8\ kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g),\ \Delta H = -248.8\ kJ$$

It is, therefore, essential to write the symbols *s*, *l*, *g* or *aq*. to indicate whether a particular substance is solid, liquid, gaseous or an aqueous solution.

3. Allotropic Modifications Heat of reaction changes if a different allotropic form is involved in the reaction. For example,

$$C_{(diamond)} + O_2(g) \rightarrow CO_2(g),\ \Delta H = -395.4\ kJ$$

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g),\ \Delta H = -393.5\ kJ$$

4. Concentration of Solutions If the solutions are involved in a reaction, their concentrations affect the heat of reaction.

5. Temperature The heat of reaction depends upon the temperature at which the reactants and products are taken. Generally, the heat of reaction increases with temperature.

6. Conditions of Constant Pressure or Constant Volume This concerns whether the reaction takes place at constant pressure or at constant volume. If q_p. and q_v represent the heats of reaction at constant pressure and volume respectively then the following equation is applicable:

$$q_p = q_v + \Delta n_g RT$$

where $\Delta n_g = n_p - n_r$

n_p and n_r represent the number of moles of gaseous reactants and the products respectively, R and T have the usual meanings.

Example 1 *One mole of naphthalene was subjected to combustion at constant volume to give $CO_2(g)$ and H_2O (l) at 25°C. The heat evolved was determined to be 5100 kJ. Calculate the enthalpy of combustion at constant pressure. Given that R = 8.314 JK^{-1} mol^{-1}.*

Solution: The thermochemical reaction for the combustion of naphthalene may be written as

$$C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)$$

No. of moles of the reactants in gaseous state, $n_1 = 12$

No. of moles of the products in gaseous state, $n_2 = 10$

$$\Delta n_g = n_2 - n_1 = 10 - 12 = -2$$

Applying the relation between heat of reaction at constant volume and constant pressure,

$$q_p = q_v + \Delta n_g RT$$

Substituting the values in the above equation,

$$q_p = -5100 \text{ kJ} + (-2 \text{ mol}) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$
$$= -5100 \text{ kJ} - 4.96 \text{ kJ} = \mathbf{-5104.96 \text{ kJ}}$$

10.3.2 Heat (or Enthalpy) of Combustion

The heat of combustion of a substance is defined as the heat change (usually the heat evolved when 1 mole of substance is completely burnt or oxidised in oxygen. For example,

$$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -393.5 \text{ kJ}$$

When one mole of carbon (12 g) burns completely in oxygen, 393.5 kJ of heat is evolved.

Thus, heat of combustion of carbon is 393.5 kJ, the significance of the words ***burns completely*** must be clearly understood. For example, carbon may be oxidised to carbon monoxide (CO) or carbon dioxide (CO_2). The heats evolved in the two cases are different, viz.

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g), \Delta H = -110.5 \text{ kJ}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H = -393.5 \text{ kJ}$$

Complete oxidation means oxidation to CO_2 and not to CO. Hence, the heat of combustion of carbon is 393.5 kJ mol^{-1}.

10.3.3 Measuring the Enthalpy of Combustion

We use an accurate calorimeter for measuring the enthalpy of combustion. This calorimeter is called ***Bomb calorimeter*** (Figs. 10.4 and 10.5), the inner part (bomb, Fig. 10.4) is made of strong steel coated inside with some non-oxidisable material. A weighed amount of the substance is taken in the cup *C*. A platinum wire *W* is connected between the rods *R* and *G*. This initiates the reaction when heated electrically. Oxygen is introduced through the inlet tube *T* until a pressure of about 20 atmospheres is attained inside. The bomb is placed inside water in a double-jacketed calorimeter (Fig. 10.5). The substance is ignited by passing electric current through the wire *W*. Once the ignition is initiated, it continues till the whole of the substance is completely burnt with the help of oxygen present. The rise in the temperature of water is noted using a Beckmann thermometer graduated to $\frac{1}{100}$ of a degree.

Also, the heat capacity of the calorimeter is obtained by burning a known mass of a substance of known enthalpy of combustion. Usually, benzoic acid of high purity is taken for this purpose. It has enthalpy of combustion equal to –3226.7 kJ mol^{-1}. Calculations are done based on the principle that total heat lost is equal to total heat gained.

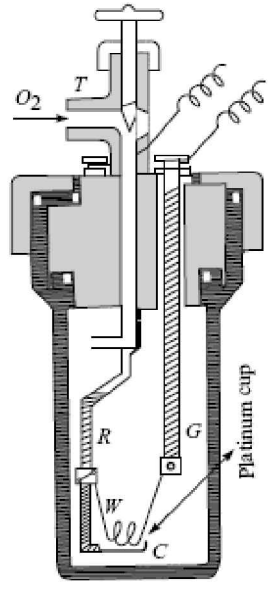


Fig. 10.4 *The bomb*

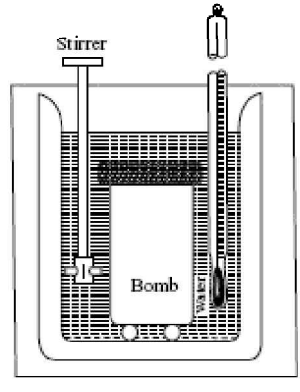


Fig. 10.5 *Bomb calorimeter*

10.3.4 Calorific Values of Foods and Fuels

For the working of the human body, we eat carbohydrates, proteins, fats, etc., in the form of food. The carbohydrates are first decomposed in our body by the enzymes to form glucose which is then oxidised by the oxygen that we inhale to produce energy as given by the following equation.

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2 + 6H_2O(g) + 2900\ kJ$$

This oxidation reaction is usually called ***combustion of food.***

Different foods have different heats of combustion. These are usually expressed in terms of their calorific values.

The calorific value of a fuel or food is the amount of heat in calories or joules produced from the complete combustion of one gram of the fuel or the food.

Thus, according to the above reaction, 1 mole of glucose, i.e. 180 g of glucose, produces 2900 kJ of heat.

Hence, the calorific value of glucose $= \frac{2900}{180} = 16.1 \text{ kJ g}^{-1}$

Calorific values of some foods and fuels are given in Tables 10.1 and 10.2.

Table 10.1 *Calorific values of foods per gram*

Food	Calorific value kJ /gram	Food	Calorific value kJ /gram
Ghee	37.65	Fish	5.2
Butter	30.50	Meat	12.0
Cheese	14.56	Egg (yolk)	5.4
Milk (buffalo's)	4.90	Egg (white)	14.0
Milk (cow's)	2.20	Sugar	16.0
Curd	2.51	Rice	16.7
Soyabean	18.07	Potatoes	4.0

Table 10.2 *Calorific values of some common fuels or in kJ per kg*

Fuel	Calorific value kJ/kg
Wood	16,000
Charcoal	29,000
Natural gas	46,000
Kerosene	38,000

An average-bodied young man needs 10,000 kJ of energy per day for normal functioning.

Applying Chemistry to Life

There is an obsession among people, particularly among women, to lose weight and look slim. Health-conscious consumers of foods make it a point to read food labels and to make dietary choices. People are willing to pay higher prices for packaged foods that both ¡te good and are low in fats and calories.

Caloric content of food is experimentally determined using the techniques of thermochemistry. A weighed sample of food is burnt in a bomb calorimeter and the heat generated by combustion is determined by noting the increase in temperature. The heat generated per gram gives the energy content (calorific value) of the food.



Fig. 10.6 *Calorie consciousness*

Example 2 *A cylinder of Indane gas contains 11.2 kg of butane. An average family needs 25,000 kJ energy per day for cooking. How long will the cylinder of gas last assuming 100% combustion?*

If the efficiency of combustion is 85%, how long will the cylinder last? Heat of combustion of butane is = 2658 kJ mol^{-1}

Solution: Molecular mass of butane is 58 g mol^{-1}. Thus, 58 g of butane on complete combustion produces 2658 kJ

$$\therefore \text{ 11200 g of butane on complete combustion produces} = \frac{2658 \times 11200}{58} \text{ kJ} = 513268.96 \text{ kJ}$$

$$\text{The cylinder will last } \frac{513268.96}{25000} = 20.5 \text{ days}$$

If the efficiency of combustions is only 85%, the cylinder will last 0.85 × 20.5 ≈ 17.5 days

10.4 STANDARD STATE

The standard molar enthalpy of every element at 1 atm pressure and 298.15 K in the most stable state is taken as zero. These conditions of 1 atm pressure and 298.15 K are called standard state conditions. It is not possible to determine the absolute value of molar enthalpy, but we can use the above convention to find out the standard molar enthalpy of a substance. The most stable form of hydrogen is gaseous H_2, that of bromine is liquid Br_2 while that of iodine is solid I_2. Their molar standard enthalpies are taken as zero at 1 atmospheric pressure and 298.15 K temperature. In case of elements exhibiting allotropy, we consider the most stable form under the conditions of standard state.

10.4.1 Enthalpy of Formation and Standard Enthalpy of Formation

Heat of Formation (or Enthalpy of Formation) The enthalpy of formation of a substance is defined as the heat change that takes place when 1 mole of the substance is formed from its elements under given conditions of temperature and pressure. It is usually represented by ΔH_f. Standard enthalpy of formation of a substance is defined as a the heat change accompanying the formation of 1 mole of the substance in the standard state from its elements, also taken in the standard state (i.e., 298 K, and 1 atmospheric pressure). It is usually represented by $\Delta H°_f$.

For example, in the reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g), \Delta H_f^\circ = -393.5 \text{ kJ}$$

When 1 mole of $CO_2(g)$ is formed from its elements, viz. C(s) and $O_2(g)$ (all substances being taken in the standard state), 393.5 kJ of heat is produced. Hence, the standard heat of formation of gaseous CO_2 is 393.5 kJ mol^{-1}

Standard enthalpies of formation of some compounds are given in Table 10.3.

Table 10.3 *$\Delta H°_f$ Values forsome common compounds*

Reaction			ΔH_f° (kJ mol^{-1}) for the compound formed
$C(s) + O_2(g)$	$\longrightarrow$	$CO_2(g)$	−393.5
$C(s) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$CO(g)$	−110.5
$H_2(g) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$H_2O(l)$	−285.9
$H_2(g) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$H_2O(g)$	−245.5
$\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g)$	$\longrightarrow$	$HF(g)$	−271.1
$C(s) + 2H_2(g)$	$\longrightarrow$	$CH_4(g)$	−74.8
$2C(s) + 3H_2(g)$	$\longrightarrow$	$C_2H_6(g)$	−89.2
$2C(s) + 2H_2(g)$	$\longrightarrow$	$C_2H_4(g)$	+52.3
$2C(s) + H_2(g)$	$\longrightarrow$	$C_2H_2(g)$	+226.8
$6C(s) + 3H_2(g)$	$\longrightarrow$	$C_6H_6(l)$	+49.0
$8C(s) + 4H_2(g)$	$\longrightarrow$	$C_8H_8(l)$	−224.4
$Si(s) + O_2(g)$	$\longrightarrow$	$SiO_2(s)$	−910.0
$S(s) + O_2(g)$	$\longrightarrow$	$SO_2(g)$	−297.5
$Na(s) + \frac{1}{2}Cl_2(g)$	$\longrightarrow$	$NaCl(s)$	−411.0
$Ca(s) + \frac{1}{2}O_2(g)$	$\longrightarrow$	$CaO(s)$	−635.5
$1/2\ N_2(g) + \frac{3}{2}H_2(g)$	$\longrightarrow$	$NH_3(g)$	−46.0
$N_2(g) + 2H_2(g)$	$\longrightarrow$	$N_2H_4(l)$	+50.6
$C(s) + 2H_2(g) + 1/2\ O(g)$	$\longrightarrow$	$CH_3OH(l)$	−238.9
$2C(s) + 3H_2(g) + 1/2\ O_2(g)$	$\longrightarrow$	$C_2H_5OH(l)$	−277.7
$10C(s) + 4H_2(g)$	$\longrightarrow$	$C_{10}H_8(s)$	+60.2

10.4.2 Importance of Standard Enthalpies of Formation

Knowing the standard enthalpies of formation of the different compounds involved in a chemical reaction, the standard enthalpy change of the given reaction can be obtained using the formula

$$\Delta H^\circ_{\text{reaction}} = \begin{bmatrix}\text{Sum of standard}\\ \text{heats of formation of}\\ \text{products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard}\\ \text{heats of formation of}\\ \text{reactants}\end{bmatrix}$$

i.e., $$\Delta H^\circ_{\text{reaction}} = \Sigma \Delta H^\circ_f(\text{Products}) - \Sigma \Delta H^\circ_f(\text{Reactants})$$

Thus, for a general reaction

$$aA + bB \longrightarrow cC + dD$$
$$\Delta H^\circ_{\text{reaction}} = [c\Delta H^\circ_f(C) + d\Delta H^\circ_f(D)] - [a\Delta H^\circ_f(A) + b\Delta H^\circ_f(B)]$$

Remember ΔH°_f is Taken as Zero for the Elements in a Reaction Suppose we are interested in finding the heat of combustion of methane. The reaction is represented as

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H^\circ_{\text{reaction}} = [\Delta H^\circ_f \text{for } CO_2 + (2 \times \Delta H^\circ_f \text{for } H_2O)] - [\Delta H^\circ_f \text{for } CH_4 + (2 \times \Delta H^\circ_f \text{for } O_2)]$$

Putting the Values of Heats of Formation in the Standard State

$$\Delta H^\circ_{\text{reaction}} = [-393.5 + 2 \times (-285.8)] - [-74.9 + 0] = -965.1 + 74.9 = -890.2 \text{ kJ}$$

Example 3 *Calculate ΔH° for the reaction*

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$, given that ΔH°_f for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are -393.5, -111.3 and -241.8 kJ mol^{-1} respectively.

Solution: ΔH° for the reaction

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ is

$$\Delta H^\circ = [H^\circ_{f(\text{Products})} - H^\circ_{f(\text{Reactants})}]$$
$$= [(-111.3) + (-241.8)] - [(-393.5) + 0]$$
$$= (-111.3 - 241.8) - (-393.5)$$
$$= -353.1 + 393.5$$
$$\Delta H^\circ = +40.4 \text{ kJ}$$

(Enthalpy of every element in standard state is assumed as zero)

Example 4 *Enthalpies of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are -277.0, -393.5 and -285.8 kJ mole^{-1} respectively. Calculate enthalpy change for reaction*

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

Solution : ΔH° for the reaction

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ is

$$\Delta H^\circ = \Delta H^\circ_{f(\text{Products})} - \Delta H^\circ_{f(\text{Reactants})}$$
$$= [2 \times \Delta H^\circ_f(CO_2) + 3\,\Delta H^\circ_f(H_2O)] - [\Delta H^\circ_f(C_2H_5OH) + 3 \times \Delta H^\circ_f(O_2)]$$
$$= [2 \times (-393.5) + 3\,(-285.8)] - [-277 + 0]$$
$$= -787.0 - 857.5 + 277$$
$$= -1644.4 + 277 = \mathbf{-1367.4 \text{ kJ}}$$

Example 5 *Enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ under standard conditions are 394.65 kJ and 285.84 kJper mole. If the standard enthalpy of combustion of acetaldehyde (CH_3CHO) is 1167.62 kJ per mole, find its enthalpy of formation.*

Solution : From the given data,

(a) $C + O_2 \longrightarrow CO_2(g); \Delta H = -394.65$ kJ

(b) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O(l); \Delta H = -285.84$ kJ

(c) $CH_3CHO + \frac{5}{2} O_2 \longrightarrow 2CO_2 + 2H_2O(g); \Delta H = -1167.62$ kJ

Our aim is to find out the ΔH value for the reaction

$$2C + 2H_2 + = \frac{1}{2} O_2 \longrightarrow CH_3CHO$$

Using standard enthalpy values,

ΔH_f° for $CO_2 = -394.65$ kJ

ΔH° for $H_2O = -285.84$ kJ

ΔH_f° for $O_2 = 0$

($\therefore$ Enthalpy of formation of elements is taken as zero).

Let ΔH°_f for CH_3CHO be x kJ.

ΔH value for any reaction = Enthalpies of the products – Enthalpies of the reactants From the equation,

$$CH_3CHO + \frac{5}{2} O_2 \longrightarrow 2CO_2(g). + 2H_2O$$

$$\Delta H = -1167.62 \text{ kJ}$$

$$\therefore \quad -1167.62 = [2 \times \Delta H_f^\circ(CO_2) + 2 \times \Delta H_f^\circ(H_2O)] - [\Delta H_f^\circ(CH_3CHO) + \frac{5}{2} \times \Delta H_f^\circ(O_2)]$$

$$= 2 \times (-394.65) + 2 \times (-285.84) - x + 0$$

$$= -789.30 - 571.68 - x$$

$$-1167.62 = -1360.98 - x$$

or $$x = -193.36 \text{ kJ}$$

Hence, enthalpy of formation of CH_3CHO is **–193.36 kJ**

10.4.3 Heat (or Enthalpy) of Neutralisation

The heat of neutralisation of an acid by a base is defined as the heat change when one gram equivalent of the acid is neutralised by a base, the reaction being carried out in dilute aqueous solution.

The heat of neutralisation of a base by an acid is defined in a similar manner. For example, when one gram equivalent of HCl is neutralised by NaOH or one gram equivalent of NaOH is neutralised by HCl, in dilute and aqueous solution, 57.1 kJ of heat is produced.

$$NaOH + HCl \longrightarrow NaCl + H_2O, \quad \Delta H = -57.1 \text{ kJ}$$

Hence, the heat of neutralisation of HCl with NaOH or NaOH with HCl is 57.1 kJ.

The heat of neutralisation of any strong acid (HCl, HNO_3, $H2SO_4$) with a strong base (NaOH, KOH) or vice versa, is always the same, i.e. 57.1 kJ. This is because the strong acids, strong bases and

the salts that they form are all completely ionised in dilute aqueous solution. Thus, the reaction between a strong acid and a strong base may be written as

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O, \quad \Delta H = -57.1 \text{ kJ}$$

Cancelling out common ions on the two sides, we have

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l), \quad \Delta H = -57.1 \text{ kJ}$$

Thus, ***neutralisation may be regarded as a reaction between the H^+ ions given by the acid with the OH^- ions given by the base.*** Since strong acid and strong bases ionise completely in a dilute aqueous solution, the number of H^+ ions and OH^- ions produced by one gram equivalent of the strong acid and the strong base is always the same. Hence, the heat of neutralisation between a strong acid and a strong base is always the same, i.e. –57.1 kJ.

Compared to a strong acid, a weak acid produces a smaller number of H^+. Hence, heat of neutralisation is smaller.

Example 6 *Calculate the amount of heat evolved when*

(a) 600 cm^3 of 0.1 M hydrochloric acid is mixed with 200 cm^3 of 0.2 M sodium hydroxide solution

(b) 250 cm^3 of 0.2 M sulphuric acid is mixed with 400 cm^3 of 0.5 M potassium hydroxide solution Assuming that the specific heat of water is 4.18 JK^{-1} g^{-1} and ignoring the heat absorbed by the container, thermometer, stirrer, etc., what would be the rise in temperature in each of the above cases?

Solution:

(a) 600 cm^3 of 0.1 M HCl $= \frac{0.1}{1000} \times 600$ moles of HCl = 0.06 mole of HCl = 0.06 mole of H^+ ions

$$200 \text{ cm}^3 \text{ of } 0.2 \text{ M NaOH} = \frac{0.2}{1000} \times 20 \text{ moles of NaOH}$$

$$= 0.04 \text{ mole of NaOH} = 0.04 \text{ mole of } OH^- \text{ ions}$$

Thus, 0.04 mole of H^+ ions will combine with 0.04 mole of OH^- ions to form 0.04 mole of H_2O and 0.02 mole of H^+ ions will remain unreacted.

Heat evolved when 1 mole of H^+ ions combines with 1 mole of OH^- ions = 57.1 kJ

$\therefore$ heat evolved when 0.04 mole of H^+ ions combines with 0.04 mole of OH^- ions.

$$= 57.1 \times 0.04 = 2.284 \text{ kJ}$$

(b) $$250 \text{ cm}^3 \text{ of } 0.2 \text{ M } H_2SO_4 = \frac{0.2}{1000} \times 250 \text{ moles of } H_2SO_4$$

$$= 0.05 \text{ mole of } H_2SO_4 = 0.10 \text{ mole of } H^+ \text{ ions}$$

$$400 \text{ cm}^3 \text{ of } 0.5 \text{ M KOH} = \frac{0.5}{1000} \times 400 \text{ moles of KOH} = 0.2 \text{ mole of KOH}$$

$$= 0.2 \text{ mole of } OH^- \text{ ions}$$

Thus, 0.10 mole of H^+ ions will neutralise 0.10 mole of OH^- ions (out of 0.2 mole of OH^- ions) to form 0.10 mole of H_2O.

Hence, heat evolved = 57.1 × 0.1 = 5.71 kJ

In Case (a), heat produced = 2.284 kJ = 2284 J

Total mass of the solution = 600 + 200 = 800 g

Specific heat = 4.18 Jk^{-1} g^{-1}

$$Q = m \times s \times \Delta t$$

$$\therefore \quad \Delta t = \frac{Q}{m \times s} = \frac{2284}{800 \times 4.18} = 0.68^\circ$$

In Case (b), heat produced = 5710 J

Total mass of the solution = 250 + 400 = 650 g

$$\therefore \quad \Delta t = \frac{Q}{m \times s} = \frac{4568}{650 \times 4.18} = 1.68^\circ$$

Example 7 *Determine the amount of heat released when*

(a) 0.75 mole of nitric acid is neutralised by 0.75 mole of sodium hydroxide

(b) 0.75 mole of hydrochloric acid is neutralised by 0.5 mole of potassium hydroxide

(c) 900 ml of 0.5 M hydrochloric acid solution of is mixed with 500 ml of 0.4 M sodium hydroxide solution; assuming the specific heat of water as 4.18 $JK^{-1}\ g^{-1}$, also calculate the rise in temperature

(d) 200 ml of 0.2 M sulphuric acid is mixed with 300 ml of 0.1 M sodium hydroxide solution. calculate the rise in temperature

Solution:

(a) The reaction is

(0.75 mole) HNO_3 + (0.75 mole) $NaOH \longrightarrow NaNO_3 + H_2O$.

When one mole of HNO_3 is neutralised by 1 mole of NaOH, heat released is 57.1 kJ. Therefore, when 0.75 mole of HNO_3 is neutralised by 0.75 mole of NaOH, heat released will be

$$57.1 \times 0.75 = 42.8 \text{ kJ}$$

(b) Out of 0.75 mole of HCl, 0.5 mole will react with 0.5 mole of KOH and 0.25 mole of HCl will be left unreacted.

$$\text{Heat released} = 57.1 \times 0.5 = 28.5 \text{ kJ}$$

(c) 1000 ml of 1 M HCl = 1 mole

$$\therefore \quad 900 \text{ ml of } 0.5 \text{ M HCl} = \frac{900 \times 0.5}{1000} = 0.45 \text{ mole}$$

Similarly,

$$500 \text{ ml of } 0.4 \text{ M NaOH} = \frac{500 \times 0.4}{1000} = 0.2 \text{ mole}$$

Out of 0.45 mole of HCl, 0.2 mole of HCl reacts with 0.2 mole of NaOH.

$\therefore$ heat evolved = 57.1 × 0.2 = 11.4 kJ

To calculate the rise in temperature, use the reaction

$$\text{Mass} \times \text{sp. heat} \times \text{Rise in temp.} = \text{Heat evolved}$$

Heat evolved is 11.4 kJ or 11400 J. Mass of the mixture is 900 g + 500 g (assuming the densities of the solution as unity) and sp. heat is 4.18 J.

$$\therefore \quad \text{Rise in temp.} = \frac{\text{Heat evolved}}{\text{Mass} \times \text{sp. heat}} = \frac{11.4 \times 1000}{1400 \times 4.18} = 1.95$$

(d) 1 molecule of H_2SO_4 releases two H^+ ions.

$$200 \text{ ml of } 0.2 \text{ M } H_2SO_4 = \frac{2 \times 200 \times 0.2}{1000} \text{ moles of } H^+ = 0.08 \text{ moles of } H^+$$

$$300 \text{ ml of } 0.1 \text{ M NaOH} = 0.03 \text{ mole } OH^-$$

Out of 0.08 mole of H^+, 0.03 mole of H^+ will react with 0.03 mole of OH^-.

$\therefore$ Heat evolved = $57.1 \times 0.03 = 1.1$ kJ

$\therefore$ Rise in temperature $= \dfrac{1.7 \times 1000}{500 \times 4.18} = 0.8^\circ$

10.5 DIFFERENT KINDS OF HEAT (OR ENTHALPY) OF REACTION

1. Heat of Solution (or Enthalpy of Solution) The heat of solution of a substance in a particular solvent is defined as the heat change (i.e. the amount of heat evolved or absorbed) when 1 mole of the substance is dissolved in such a large volume of the solvent that further addition of the solvent does not produce any more heat change.

Thus, the thermochemical equations for the dissolution of KCl and $CuSO_4$ in water may be represented as

$$KCl(s) + aq \longrightarrow KCl(aq),\ \Delta H = +18.6 \text{ kJ}$$
$$CuSO_4(s) + aq \longrightarrow CuSO_4(aq),\ \Delta H = -66.5 \text{ kJ}$$

Thus, the heat of solution of KCl = +18.6 kJ mol^{-1} and heat of solution of $CuSO_4$ = –66.5 kJ mol^{-1}

It is interesting to note that salts like copper sulphate, calcium chloride, etc., when present in the hydrated state (i.e. $CuSO_4 \cdot 5H_2O$, $CaCl_2 \cdot 6H_2O$, etc.) dissolve with the absorption of heat. For example,

$$CuSO_4 \cdot 5H_2O + aq. \longrightarrow CaSO_4(aq),\ \Delta H = +11.7 \text{ kJ}$$

Thus, it can be generalised that the process of dissolution is usually endothermic for

(a) Salts which do not form hydrates like NaCl, KCl, KNO_3, etc.

(b) Hydrated salts like $CuSO_4 \cdot 5H_2O$, $CaCl_2 \cdot 6H_2O$, etc.

2. Heat (or Enthalpy) of Hydration The amount of heat change (i.e., the heat evolved or absorbed) when one mole of the anhydrous salts combines with the required number of moles of water so as to change into the hydrated salt, is called the heat of hydration. For example, the heat of hydration of copper sulphate is –78.2 kJ mol^{-1}. This is represented as follows:

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O(s),\ \Delta H = -78.2 \text{ kJ}$$

In fact, both the cations and anions get hydrated separately to give the hydrated salt.

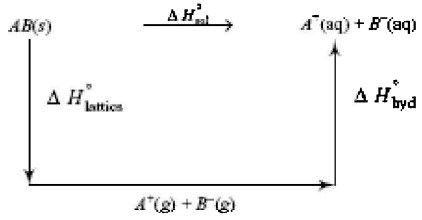
3. Lattice Enthalpy It would be interesting to link enthalpy of solution and enthalpy of hydration with lattice enthalpy.

Lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in the gaseous state. For example, for NaCl, we have

$$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g)\ \Delta H^\circ_{\text{lattice}} = +788 \text{ kJ mol}^{-1}$$

The connection between the lattice enthalpy, enthalpy of solution and enthalpy of hydration can be understood by taking the example of an ionic solid *AB* as under.

where ΔH° stands for standard enthalpy change for different processes under standard conditions of temperature and pressure (278 K and 1 bar) respectively.



Thus, if we know two of three quantities $\Delta H°_{sol}$, $\Delta H°_{lattice}$ and $\Delta H°_{hyd.}$, the third can be calculated. We can also write the following equation, as per Hess's law:

$$\Delta H^\circ_{sol} = \Delta H^\circ_{lattice} + \Delta H^\circ_{hyd.}$$

For most ionic compounds, $\Delta H°_{sol}$ is positive and the dissolution process is endothermic. Therefore, as per Le Chatelier's principle, the solubility increases with the rise of temperature. If the lattice enthalpy is very high, the dissolution may not take place at all. ***We must remember that energy is required to break away the ions from the lattice positions while energy is evolved when hydration of ions takes place.*** In general, we can say

If $\Delta H^\circ_{hyd.} > \Delta H^\circ_{lattice}$, dissolution will take place.

If $\Delta H^\circ_{hyd.} < \Delta H^\circ_{lattice}$, dissolution will not take place.

4. Heat (or Enthalpy) of Fusion Heat of fusion is the heat change that takes place when one mole of a solid substance changes into its liquid state at its melting point Heat of fusion (ΔH_{fus}) of ice (mp = 273 K) is 6.0 kJ mol^{-1}.

It may be represented as follows:

$$\underset{\text{Ice}}{H_2O(s)} \longrightarrow \underset{\text{water}}{H_2O(l)},\ \Delta H = +6.0\ \text{kJ}$$

5. Heat of Vaporisation It is the heat change that takes place when one mole of a liquid changes into its gaseous state at its boiling point.

For example, the heat of vaporisation (ΔH_{vap}) of water into its gaseous state at the boiling point (373 K) is 40.7 kJ. It may be represented as follows:

$$\underset{\text{Ice}}{H_2O(s)} \longrightarrow \underset{\text{water}}{H_2O(l)},\ \Delta H = +6.0\ \text{kJ}$$

6. Heat of Sublimation Heat of sublimation of a substance is the heat change that takes place when 1 mole of a solid changes directly into vapour phase at a given temperature below its melting point.

Sublimation is a process in which a solid on heating changes directly into gaseous state below its melting point. For example, the heat of sublimation of iodine is 62.39 kJ mol^{-1}. It is represented as follows:

$$I_2(s) \longrightarrow I_2(g), \Delta H = +62.39\ \text{kJ}$$

Most solids that sublime readily are molecular solids, e.g., iodine and naphthalene, etc.

10.6 HESS'S LAW OF CONSTANT HEAT SUMMATION

G.H. Hess, a Russian chemist, in 1840, gave a law about the heats of reactions which is stated as

follows:

The total amount of heat evolved or absorbed in a reaction is the same whether the reaction takes place in one step or in a number of steps. In other words, the total amount of heat change in a reaction depends only upon the nature of the initial reactants and the nature of the final products and not upon the path or the manner by which this change is brought about.

An analogy for Hess's law can be made to the floors in a building. Suppose you take the lift from the ground floor to the tenth floor of the building. The net gain in your gravitational potential energy is the same whether you go directly there or move out at each floor on your way up:

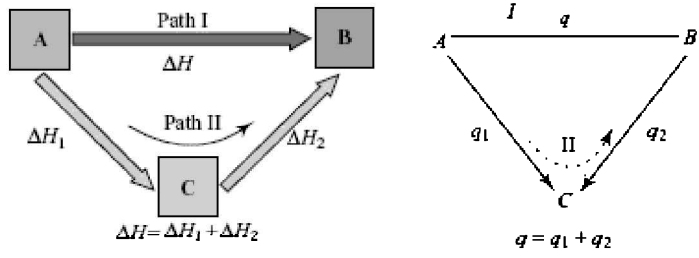


Fig. 10.7 *Illustration of Hess's law*

Hess's law may be illustrated with the help of the following examples:

1. Sulphur (rhombic) burns to form SO_3 to evolve 395.4 kJ of heat.

$$S_R + \frac{3}{2}O_2(g) \longrightarrow SO_3(g),\ \Delta H = -395.4\ \text{kJ}$$

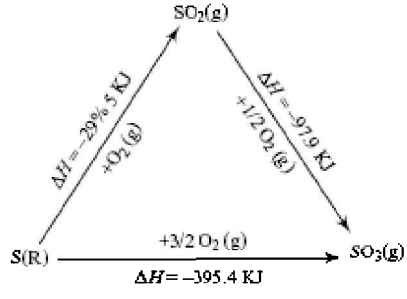




Fig. 10.8 *Germain Henri Hess (1802-50), was born is Switzerland but spent most of his life in Russia. For formulating Hess's law, he is called the father of thermochemistry.*

Sulphur may change to SO_3 in two steps as given below:

$$S_R + O_2(g) \longrightarrow SO_2(g), \quad \Delta H = -297.5 \text{ kJ}$$
$$SO_2(g) + 1/2O_2(g) \longrightarrow SO_3(g), \quad \Delta H = -97.9 \text{ kJ}$$

(See accompanying figure.)

Total heat evolved in two steps is –297.5 + (–97.9) = –395.4 kJ

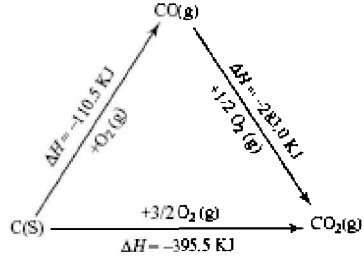
This is the same as for the direct reaction in one step.

2. When carbon (granite) burns to form carbon dioxide directly in one step, 393.5 kJ mol^{-1} of heat is evolved.

$$C(s) + O_2(g) \longrightarrow CO_2(g), \quad \Delta H = -395.5 \text{ kJ}$$

If carbon burns to form carbon monoxide first which then burns to form carbon dioxide, the heats evolved in the two steps are as follows (See accompanying figure):

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g), \quad \Delta H = -111.5 \text{ kJ}$$
$$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g), \quad \Delta H = -282.0 \text{ kJ}$$



Thus, the total heat evolved in two steps comes out to be (–111.5) + (–282.0) = –393.5 kJ which is the same when the reaction takes place directly in one step.

Proof of Hess's Law Consider a general reaction

$$A \longrightarrow D$$

Suppose the heat evolved in this reaction directly is Q joules.

Now suppose the same reaction takes place in three steps as follows:

$$A \xrightarrow{\text{Step 1}} B \xrightarrow{\text{Step 2}} C \xrightarrow{\text{Step 3}} D$$

Suppose the heat evolved in these three steps are q_1, q_2 and q_3 joules respectively (Fig. 10.9).

Thus, the total heat evolved from A to $D = q_1 + q_2 + q_3 = Q'$ joules (say)

According to Hess's law, we must have $Q = Q'$

Suppose Hess's law is not correct. In that case, either $Q' < Q$ or $Q' > Q$. Let us suppose $Q' > Q$. We shall now complete the cycle, i.e. we shall go from A to D through three steps and return to A in one step and we shall see what heat changes take place.

In heat change from A to D, Q joules of heat are evolved. Therefore, in direct process from D to A, Q joules of heat are absorbed. Now if we move from A to D in steps and return to A directly, $Q' - Q$ joules of heat is produced. Thus, by repeating the cyclic process a number of times, a large amount of heat can be created. This is, however, against the law of conservation of energy. Hence, Q' cannot be greater than Q. Similarly, Q' cannot be less than Q. It has to be equal to Q. Thus, Hess's law is proved.

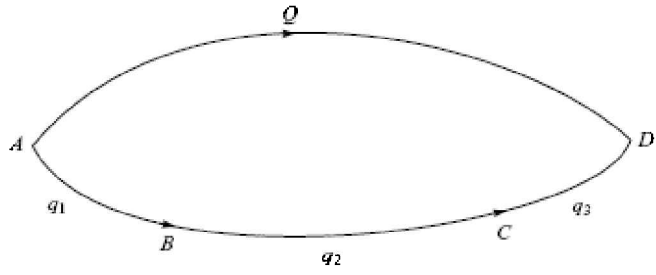


Fig. 10.9 *Theoretical proof of Hess's law*

10.6.1 Applications of Hess's Law

Hess's law is very useful in determining the heats (enthalpies) of many reactions, which cannot otherwise be measured by direct methods. The thermochemical equations are added, subtracted, multiplied or divided just like other algebraic equations. Some important applications of Hess's law are as follows:

1. Determination of Enthalpy of Formation The heats of formation of some compounds cannot be determined directly by experiment. This can be calculated by the application of Hess's law.

Suppose we want to determine the heat of formation of CO.

$$C + 1/2\ O_2 \longrightarrow CO,$$

By direct experiment, it is not possible because in the reaction between carbon and oxygen, we may get a mixture of CO and CO_2. But we require only CO. Therefore, from the experiment it is not possible to determine the heat of formation.

We know experimentally, the heat of combustion of pure carbon and carbon monoxide. It is represented by the following equation:

(a) $C + O_2 \longrightarrow CO_2;\quad \Delta H = -393.5\ kJ$

(b) $CO + 1/2O_2 \longrightarrow CO_2;\quad \Delta H = -283.0\ kJ$

Now applying Hess's law on (a) and (b), we get the required equation for the heat of formation of CO. This can be achieved by subtracting (b) from (a), i.e., by carrying out *(a – b)*.

$$C + 1/2O_2 \longrightarrow CO;\quad \Delta H = -110.5\ kJ$$

Therefore, enthalpy of formation of CO is –110.5 kJ.

2. Determination of Heat (Enthalpy) of Transition Transition of an element from one allotropic form to another is a slow process and requires heating of one allotropic form of the element for a long time at constant temperature. Hence, enthalpies of transition of elements cannot be determined experimentally. They are, however, determined indirectly by means of Hess's law. Thus, Hess's law is useful in determining the enthalpies of transition of the allotropic forms such as rhombic sulphur to monoclinic sulphur, yellow phosphorus to red phosphorus, graphite to diamond, etc.

Suppose we want to determine the enthalpy of transition of sulphur (rhombic) into sulphur (monoclinic). Each variety is combustioned and heats of combustion are found out. This is represented by the following equations:

(a) $S(R) + O_2 \longrightarrow SO_2;\quad \Delta H = -295.1\ kJ$

(b) $S(M) + O_2 \longrightarrow SO_2;\quad \Delta H = -296.4\ kJ$

Subtracting (b) from (a), we get

$$S(R) \longrightarrow S(M);\quad \Delta H = -295.1 - (-296.5) = +1.3\ kJ$$

Thus, transition of one gram atom of rhombic sulphur to monoclinic sulphuric absorbs 1.3 kJ of

heat.

3. Calculation of Enthalpies from Given Data Thermochemical equations can be added, subtracted, multiplied or divided by any numerical factor like algebraic equations. Hess's law is, thus, used for the calculation of enthalpy changes for the reactions for which direct experimental measurements are not available.

Example 8 *Find the heat of formation of SO_2 from the following thermochemical equations:*

(a) $S(s) + \frac{3}{2} O_2(g) \longrightarrow SO_3(g) + x\ kJ$

(b) $SO_2(s) + O_2(g) \longrightarrow SO_3(g) + y\ kJ$

Solution: Our aim is to find out ΔH value for the reaction

$$S + O_2 \longrightarrow SO_2$$

This can be obtained by subtracting (b) from (a), i.e. by carrying out (a – b)

(a) $S(s) + \frac{3}{2} O_2(g) \longrightarrow SO_3(g)$; $\Delta H = -x$ kJ

(b) $SO_2(g) + O_2(g) \longrightarrow SO_3(g)$; $\Delta H = -y$ kJ

$S + O_2 \longrightarrow SO_2(g)$ $\Delta H = -x - (-y) = -x + y = -(x - y)$ kJ

Example 9 *Calculate enthalpy of formation of methane. Given:*

(a) $C(graphite) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5\ kJ$

(b) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$: $\Delta H = -571.8\ kJ$

(c) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -890.3\ kJ$

Solution: We want to find out the value of ΔH for the reaction

$$C(graphite) + H_2(g) \longrightarrow CH_4$$

This can be obtained by the operation (a + b) – c, we get

$$C(graphite) + O_2 + 2H_2 + O_2 \longrightarrow CO_2 + 2H_2O \ldots (a + b)$$

or $$C(graphite) + 2O_2 + 2H_2 \longrightarrow CO_2 + 2H_2O;\ \Delta H = -965.3\ kJ$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O;\ \Delta H = -890.3\ kJ$$

$$C(graphite) + 2H_2 \longrightarrow CH_4 \qquad \Delta H = -75.0\ kJ \ldots (a + b) - c$$

Example 10 *Calculate the heat of formation of carbon disulphide given that the heats of combustion of carbon disulphide, carbon and sulphur are –1109 kJ, –394.6 kJ and –298.7 kJ respectively.*

Solution: The thermochemical equations for the combustion of CS_2, C and S are

(a) $CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$; $\Delta H = -1109$ kJ

(b) $C + O_2 \longrightarrow CO_2$; $\Delta H = -394.6$ kJ

(c) $S + O_2 \longrightarrow SO_2$; $\Delta H = -298.7$ kJ

Our aim is to find out the value of ΔH for the following equation

$$C + 2S \longrightarrow CS_2$$

Multiplying (c) by 2 and adding to (b), we get

$$2S + 2O_2 + C + O_2 \longrightarrow 2SO_2 + CO_2$$

or

(d) $2S + C + 3O_2 \longrightarrow 2SO_2 + CO_2$; $\Delta H = (-298.7) \times 2 + (-394.6) = -992.0$ kJ

Subtracting (a) from (d), we get

$$2S + C + 3O_2 \longrightarrow 2SO_2 + CO_2; \quad \Delta H = -992.0 \text{ kJ}$$
$$\underline{CS + 3O_2 \longrightarrow CO_2 + 2SO_2; \quad \Delta H = -1109 \text{ kJ}}$$
$$2S + C \longrightarrow CS_2; \qquad \Delta H = -992 - (-1109) = +117 \text{ kJ}$$

$\therefore$ heat of formation of $CS_2 = +117$. kJ mol^{-1}

Example 11 *One gram of an organic liquid A (mol. wt = 128) liberates 150 joules of heat on solidification. Calculate the enthalpy of fusion of A.*

Solution: Molecular weight of liquid *A* = 128 g

Heat evolved when 1 gram of liquid *A* solidifies = 150 J

$\therefore$ Heat evolved when 128 grams (1 mole) of liquid *A* solidify = 150 × 128 = 19200 J

$$\text{Liquid } (A) \longrightarrow \text{Solid } (A); \quad \Delta H - 19200 \text{ J}$$

Rearranging this equation, we get

$$\text{Solid } (A) \longrightarrow \text{Liquid } (A); \quad \Delta H = +19200$$

$\therefore$ enthalpy of fusion of *A* = **+19200 joules**

Example 12 *Calculate the heat of hydration of anhydrous copper sulphate ($CuSO_4$) into hydrated copper sulphate ($CuSO_4 \cdot 5H_2O$). Given that the heats of solutions of anhydrous copper sulphate and hydrated copper sulphate are –66.5 and +11.7 kJ mol^{-1} respectively.*

Solution : Data provided is

(a) $CuSO_4(s) + aq. \longrightarrow CuSO_4(aq); \quad \Delta H = -66.5$ kJ

(b) $CuSO_4 \cdot 5H_2O(s) + aq. \longrightarrow CuSO_4(aq.); \quad \Delta H = +11.7$ kJ

Our aim is to find out heat of the following reaction

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s); \Delta H = ?$$

Equation (a) can be written in two steps as

(c) $CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s); \quad \Delta H = q_1$ kJ

(d) $CuSO_4 \cdot 5H_2O(s) + aq. \longrightarrow CuSO_4(aq.); \quad \Delta H = q_2$ kJ

According to Hess's law, $q_1 + q_2 = -66.5$ kJ

Further, equations (b) and (d) are same.

$\therefore$ $q_2 = +11.7$ kJ

Putting this value in Eq. (c) above, we get

$$q_1 + 11.7 = -66.5 \text{ or } q_1 = -66.5 - 11.7 \text{ kJ} = -78.2 \text{ kJ}$$

Thus, Eq. (c) may be written as

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s); \Delta H = \mathbf{-78.2\ kJ}$$

This is what we aimed at. Hence, the required value of the heat of hydration is $\Delta H = -78.2$ kJ

Example 13 *Calculate the heat change accompanying the transformation of C(graphite) to C(diamond). Given that the heats of combustion of graphite and diamond are 393.5 and 395.4 kJ mol^{-1} respectively.*

Solution: Data provided is

(a) $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393.5 \text{ kJ}$

(b) $C_{(\text{diamond})} + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -395.4 \text{ kJ}$

Our aim is to find out ΔH for the following reaction

$$C(\text{graphite}) \longrightarrow C(\text{diamond})$$

Subtracting (b) from (a), we get

$$C(\text{graphite}) - C(\text{diamond}) \longrightarrow 0; \Delta H = -393.5 - (-395.4) = +1.9 \text{ kJ}$$

or $$C(\text{graphite}) \longrightarrow C(\text{diamond}); \Delta H = +1.9 \text{ kJ}$$

Example 14 *Calculate the standard enthalpy of formation of n-butane given that the standard enthalpies of combustion of n-butane (g), C(graphite) and $H_2(g)$ are –2878.5 kJ mol^{-1} 393.5 kJ mol^{-1} and –285.3 kJ mol^{-1} respectively.*

Solution: We aim at the equation

$$4C + 5H_2 \longrightarrow C_4H_{10}; \Delta H = ?$$

The given data can be expressed in the form of the following equations:

(a) $C_4H_{10} + 6\frac{1}{2}O_2 \longrightarrow 4CO_2 + 5H_2O; \quad \Delta H = -2878.5 \text{ kJ}$

(b) $4C + 4O_2 \longrightarrow 4CO_2; \quad \Delta H = 4 \times (-393.5) \text{ kJ}$

(c) $5H_2 + \frac{5}{2}O_2 \longrightarrow 5H_2O; \quad \Delta H = 5 \times (-285.3) \text{ kJ}$

Add (b) and (c) and subtract (a) from the sum.

$$(-1574.0) + (-1426.5) - (-2878.5) = \mathbf{-122.0 \text{ kJ}}$$

Example 15 *Given the following thermochemical equations:*

(a) $S(\text{rhombic}) + O_2(g) \longrightarrow SO_2(g); \quad \Delta H = -297.5 \text{ kJ}$

(b) $S(\text{monoclinic}) + O_2(g) \longrightarrow SO_2(g); \quad \Delta H = -300.0 \text{ kJ}$

Calculate ΔH for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur.

Solution: We aim at:

$$S_{(\text{rhombic})} \longrightarrow S_{(\text{monoclinic})}$$

Equation (a) – Equation (b) gives

$$S_{(\text{rhombic})} - S_{(\text{monoclinic})} \longrightarrow 0$$

$$\Delta H = -297.5 - (-300.0) = 2.5 \text{ kJ}$$

or $$S_{(\text{rhombic})} \longrightarrow S_{(\text{monoclinic})} \quad \Delta H = +2.5 \text{ kJ}$$

Thus, for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur, 2.5 kJ of heat is absorbed.

Example 16 *Calculate the heat of formation of acetic acid if its heat of combustion is 867 kJ mol^{-1}. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are –393.5 kJ mol^{-1} and –285.9 kJ mol^{-1} respectively.*

Solution: The equations given are

(a) $CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O; \quad \Delta H = -867 \text{ kJ}$

(b) $C + O_2 \longrightarrow CO_2; \quad \Delta H = -393.5 \text{ kJ}$

(c) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O; \quad \Delta H = -205.9 \text{ kJ}$

Our aim is to find out ΔH value for the reaction

$$2C + 2H_2 + O_2 \longrightarrow CH_3COOH$$

To obtain this equation, multiply equations (b) and (c) by 2 and add. We get the equation

$$2C + 2O_2 + 2H_2 + O_2 \longrightarrow 2CO_2 + 2H_2O$$

or

(d) $2C + 2H_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O; \quad \Delta H = -1358.8 \text{ kJ}$

Subtracting (a) from (d), we get

$$2C + 2H_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O; \quad \Delta H = -1358.8 \text{ kJ}$$
$$\underline{CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O; \quad \Delta H = -867 \text{ kJ}}$$
$$2C + 2H_2 + O_2 \longrightarrow CH_3COOH \qquad \Delta H = -491.8 \text{ kJ}$$

$\therefore$ Heat of formation of acetic acid = **–491.8 kJ**

Example 17 *Calculate enthalpy of formation of anhydrous Al_2Cl_6 from the following data:*

(a) $2Al(s) + 6HCl(aq.) \longrightarrow Al_2Cl_6(aq.) + 3H_2$; ΔH = 1004.4 kJ

(b) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$; ΔH = 754.74 kJ

(c) $HCl(g) + aq \longrightarrow HCl(aq)$; ΔH = –73.24 kJ

(d) $Al_2Cl_6(s) + aq \longrightarrow Al_2Cl_6(aq)$; ΔH = –642.69 kJ

Solution: Thermochemical equation for the formation of anhydrous Al_2Cl_6 is

$$2Al + 3Cl_2 \longrightarrow Al_2Cl_6(s)$$

To obtain ΔH value for this equation from the given data, we perform

$$[a + (3 \times b) + (6 \times c)] - d$$

Rearranging the given equations, we get

$$2Al(s) + 6HCl(aq) + 3H_2(g) + Cl_2(g) \longrightarrow Al_2Cl_6(aq) + 3H_2(g) + 6HCl(g)$$
$$+ 6HCl(g) + aq. - Al_2Cl_6(s) - aq. \qquad + 6HCl(aq) - Al_2Cl_6(aq)$$
$$2Al(s) + 3Cl_2(g) \longrightarrow Al_2Cl_6(s),$$
$$\Delta H = 1004.4 + 3 \times 754.74 + 6 \times (73.24) - (-642.69) = \mathbf{3471.87 \text{ kJ}}$$

Example 18 *Given thermochemical equations:*

(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; ΔH = –92.40 kJ

(b) $2H_2(g) + O_2(g) \longrightarrow 2H_2O$; ΔH = – 483.79 kJ

Find ΔH_f for $NH_3(g)$ and ΔH_f for $H_2O(g)$

Solution : Heat of formation (ΔH_f) is for one mole

$\therefore$ ΔH_f for $NH_3 = \frac{-92.4}{2}, -46.2$ kJ

$\therefore$ ΔH_f for $H_2O = \frac{-483.79}{2} = -241.895$ kJ

Example 19 *The enthalpy of combustion of ethylene (C_2H_4) is –1410 kJ. What will be calorific value of ethylene per gram?*

Solution : The thermochemical equation for the combustion of C_2H_4 is

$$\underset{28 \text{ grams}}{C_2H_4} + O_2 \longrightarrow 2CO_2 + 2H_2O; \quad \Delta H = -1410 \text{ kJ}$$

It is evident from the above equation that 28 grams of C_2H_4 give heat = –1410 kJ

$\therefore$ 1 gram of C_2H_4 will give heat, $= \frac{-1410}{28} = -50.36$ kJ

$\therefore$ calorific value of ethylene = **–50.36 kJ**

Example 20 *Calculate the heat of formation of KCl from the following data:*

(a) $KOH(aq) + HCl(aq) \longrightarrow KCl(aq) + H_2O(l)$: $\Delta H = -57.3$ *kJ*

(b) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$: $\Delta H = -286.2$ *kJ*

(c) $K(s) + \frac{1}{2} O_2(g) + \frac{1}{2} H_2(g) + aq \longrightarrow KOH\,(aq)$ $\Delta H = -487.4$ *kJ*

(d) $KCl(s) + aq \longrightarrow KCl_{(aq)}$ $\Delta H = +18.4$ *kJ*

(e) $KCl(s) + aq \longrightarrow KCl_{(aq)}$ $\Delta H = +18.4$ *kJ*

Solution : Our aim is to find out ΔH for the following reaction:

(f) $K(s) + \frac{1}{2} Cl_2(g) \longrightarrow KCl(s), \quad \Delta H = ?$

In order to get this thermochemical equation, we follow the following two steps:

Step 1 Adding (c) and (d) and subtracting (e) from the sum we have

(g)

$$K(s) + \frac{1}{2} Cl_2(g) + H_2(g) + \frac{1}{2} O_2(g) \longrightarrow KCl(s) + HCl(aq) + KOH(aq) - KCl(aq)$$

$$\Delta H = -487.4 + (-164.4) - (18.4) = \mathbf{-670.2\ kJ}$$

Step 2 To cancel out the terms of this equation which do not appear in the required equation (g) and (a) to (g) and subtract (b) from their sum. This gives

$$K(s) + \frac{1}{2} Cl_2(g) \longrightarrow KCl(s); \Delta H = -670.2 + 57.3 - (-286.2) = \mathbf{-441.3\ kJ}$$

Example 21 *Calculate the heat of formation of carbon monoxide (CO) from the following data:*

(a) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393$ *kJ*

(b) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$: $\Delta H = -282$ *kJ*

Solution: Our aim is to find out ΔH for the following reaction.

(a) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta H = ?$

Subtracting (b) from (a), we get

$$C(s) + \frac{1}{2}O_2(g) - CO(g) \longrightarrow 0; \quad \Delta H = -393.3 - (-282.8) = -110.5 \text{ kJ}$$

or $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta H = -110.5$ kJ

$\therefore$ Heat of formation of CO, $\Delta H_f = 110.5$ kJ

Example 22 *The heat of combustion of ethyl alcohol (C_2H_5OH) is 1380.7 kJ mol^{-1}. If the heats of formation of CO_2 and H_2O are 394.5 and 286.6 kJ mol^{-1} respectively, calculate the heat of formation of ethyl alcohol.*

Solution: Data provided is

(a) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O; \quad \Delta H = -1380.7$ kJ

(b) $C + O_2 \longrightarrow CO_2; \quad \Delta H = -394.5$ kJ

(c) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O; \quad \Delta H = -286.6$ kJ

(d) Our aim is to determine ΔH for the following reaction

$$2C + 3H_2 + \frac{1}{2}O_2 \longrightarrow C_2H_5OH$$

In order to get this thermochemical equation, multiply (b) by 2 and (c) by 3 and subtract (a) from their sum, i.e. operating 2 × (b) + 3 × (c) – (a), we get

$$2C + 3H_2 + \frac{1}{2}O_2 \longrightarrow C_2H_5OH \quad \Delta H = 2(-394.5) + 3(-286.6) - (-1380.7) = -268.1 \text{ kJ}$$

Thus, the heat of formation of ethyl alcohol $\Delta = \Delta H_f = -268.1$ kJ mol^{-1}

Example 23 *Calculate enthalpy formation of $N_2O_5(g)$:*

$$N_2(g) + \frac{5}{2}O_2(g) \longrightarrow N_2O_5(g)$$

The following information is given:

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g); \Delta H^\circ = +180$ kJ

(b) $4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g); \Delta H^\circ = -120.6$kJ

(c) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g); \Delta H = -114.0$ kJ

Solution : Perform the operation (a) + $\frac{1}{2}$ (c) to get the desired equation as

$$N_2(g) + \frac{5}{2} = O_2(g) \longrightarrow N_2O_5(g)$$

Applying Hess's law, perform the same operation on enthalpies to obtain the enthalpy of formation of $N_2O_5(g)$.

$$\Delta H_f = \left[180 - \frac{1}{2}(120.6) - 114.0\right] \text{kJ}$$
$$= \mathbf{5.7\ kJ}$$

Example 24 *Heats of solution (ΔH) for $BaCl_2\,2H_2O$ and $BaCl_2$ are 8.8 and –20.6 kJ respectively. Calculate the heat of hydration of $BaCl_2$ to $BaCl_2\,2H_2O$.*

Solution : We are given

$$BaCl_2 \cdot 2H_2O(s) + aq \longrightarrow BaCl_2\,(aq); \quad \Delta H = 8.8\ \text{kJ} \qquad \ldots(i)$$
$$BaCl_2(s) + aq \longrightarrow BaCl_2\,(aq); \quad \Delta H = -20.6\ \text{kJ} \qquad \ldots(ii)$$

We aim at

$$BaCl_2(s) + 2H_2O \longrightarrow BaCl_2 \cdot 2H_2O(s); \quad \Delta H = ? \qquad \ldots(iii)$$

Equation (ii) may be written in two steps as

$$BaCl_2(s) + 2H_2O \longrightarrow BaCl_2 \cdot 2H_2O(s); \quad \Delta H = \Delta H_1\ (\text{say}) \qquad \ldots(iv)$$
$$BaCl_2 \cdot 2H_2O(s) + aq \longrightarrow BaCl_2(aq.); \quad \Delta H = \Delta H_2\ (\text{say}) \qquad \ldots(v)$$

Then according to Hess's law,

$$\Delta H_1 + \Delta H_2 = -20.6\ \text{kJ}$$

But $\Delta H_2 = 8.8\ \text{kJ}$ [$\because$ Eq. (i) – Eq. (v)]

$\therefore$ $\Delta H_1 = -20.6 - 8.8 = -29.4\ \text{kJ}$

But Eq. (iii) = Eq. (iv)

Hence, the heat of hydration of $BaCl_2$ = **–29.4 kJ**

PROBLEMS FOR PRACTICE

1. Calculate the standard enthalpy of formation of SO_3 at 298 K using the following reactions and enthalpies:

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g); \quad \Delta H^\circ = -2775\ \text{kJ mol}^{-1}$$
$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g), \quad \Delta H^\circ = -198\ \text{kJ mol}^{-1}$$

[Ans. –445.9 kJ mol^{-1}]

2. Calculate the enthalpy of formation of acetic acid if the enthalpy of combustion to $CO_2(g)$ and $H_2O(l)$ is –867.0 kJ mol^{-1} and enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are respectively –393.5 and –285.9 kJ mol^{-1}.

[Ans. –491.8 kJ mol^{-1}]

3. Ethylene on combustion gives carbon dioxide and water. Its enthalpy of combustion is 1410.0 kJ mol^{-1}. If the enthalpy of formation of CO_2 and H_2O are 393.3 kJ and 286.2 kJ respectively. Calculate the enthalpy of formation of ethylene.

[Ans. +51.0 kJ mol^{-1}]

4. Calculate the enthalpy of formation of acetic acid from the following data:

(a) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.7$ kJ

(b) $H2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -285.8$ kJ

(c) $CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ $\Delta H = -873.2$ kJ

[Ans. -485.8 kJ mol^{-1}]

5. From the following thermochemical equations, calculate the standard enthalpy of formation of HCl(g):

   (a) $H_2(g) \longrightarrow 2H(g)$ $\Delta H = +436.0$ kJ mol^{-1}

   (b) $Cl_2(g) \longrightarrow 2Cl(g)$ $\Delta H = +242.7$ kJ mol^{-1}

   (c) $HCl(g) \longrightarrow H(g) + Cl(g)$ $\Delta H = +431.8$ kJ mol^{-1}

   [Ans. -92.45 kJ mol^{-1}]

6. Calculate the enthalpy of formation of sucrose ($C_{12}H_{22}O_{11}$) from the following data:

   (a) $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O$; $\Delta H = -5200.7$ kJ mol^{-1}

   (b) $C + O_2 \longrightarrow CO_2$; $\Delta H = -394.5$ kJ mol^{-1}

   (c) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$; $\Delta H = -285.8$ kJ mol^{-1}

   [Ans. -2677.1 kJ mol^{-1}]

7. Calculate the enthalpy of formation of *n*-butane from the following data:

   (a) $2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)$ $\Delta H = -5757.2$ kJ mol^{-1}

   (b) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -405.4$ kJ mol^{-1}

   (c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$, $\Delta H = -572.4$ kJ mol^{-1}

   On what law are your calculations based?

   [Ans. -114 kJ mol^{-1}]

8. Calculate the enthalpy of formation of carbon disulphide given that the enthalpy of combustion of carbon disulphide is 110.2 kJ mol^{-1} and those of sulphur and carbon are 297.4 kJ and 394.5 kJ/g atom respectively.

   [Ans. -879.1 kJ mol^{-1}]

9. Calculate the enthalpy of formation of benzene, given that enthalpies of combustion of benzene, carbon and hydrogen are -3281.5 kJ, -394.9 kJ and -286.1 kJ/mol, respectively

10. Calculate the enthalpy of formation of anhydrous Al_2Cl_6 from the following data:

    (a) $2Al(s) + 6HCl(aq.) \longrightarrow Al_2Cl_6(aq) + 3H_2(g) + 1004.2$ kJ mol^{-1}

    (b) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) + 184.1$ kJ mol^{-1}

    (c) $HCl(g) + aq \longrightarrow HCl(aq) + 73.2$ kJ mol^{-1}

    (d) $2Al_2Cl_6(s) + aq \rightarrow Al_2Cl_6(aq) + 643.1$ kJ mol^{-1} [Ans. -1352.6 kJ mol^{-1}]

10.7 BOND ENTHALPY OR BOND ENERGY

The bond energy of a particular bond is defied as the average amount of energy released when one mole of bonds are formed from isolated gaseous atoms or the amount of energy required when 1 mole of bonds are broken so as to get the separated gaseous atoms.

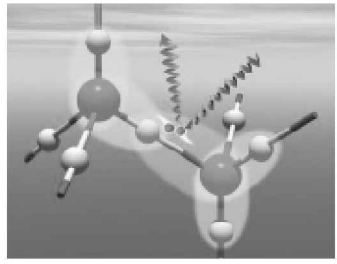


Fig. 10.10 *Energy is absorbed as a chemical bond is broken*

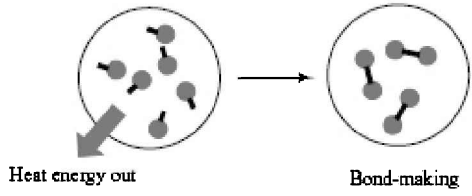


Fig. 10.11 *Energy is evolved in the formation*

For diatomic molecules (like H_2, HCl, etc.), the bond energy is equal to the dissociation energy of the molecules but for a polyatomic ***molecule*** like CH_4, the bond dissociation energies of the four C–H bonds are different. Hence, an average value is taken. Bond energies of some common bonds are given in Table 10.4

Table 10.4 *Bond energies of some common bonds*

Bond	Bond energies (kJ mol^{-1})	Bond	Bond energies kJ mol^{-1}
H–H	436	C–H	414
H–F	565	O–H	463
H–Cl	431	N–H	389
H–Br	364	C–C	347
H–I	297	C=C	619
F–F	155	C≡C	812
Cl–Cl	242	C–Cl	326
Br–Br	190	C–O	335
I–I	149	C=O	707
O–O	138	C–N	293
O=O	494	C=N	616
N≡N	941	C≡N	879

Heat of reaction can be calculated from bond energy data. The following formula can be used directly in these calculations:

$$\Delta H_{\text{reaction}} = \Sigma \text{ Bond energies of reactants} - \Sigma \text{ Bond energies of products}$$

Remember that this relationship is approximate and is valid when all substances (reactants and products) in the reaction are in gaseous state.

10.7.1 Applications of Bond-Dissociation Energies

1. Determination of Enthalpies of Reactions This may be illustrated by taking the example of hydrogenation of ethane to ethane.

$$CH_2 = CH_2(g) + H_2(g) \longrightarrow CH_3 - CH_3(g)$$

In this reaction, four C–H bonds remain intact. A double bond in ethane is broken and H-H bond is broken. On the product side, one C–C bond and two C–H bonds are formed. Thus,

$$\Delta H = -\Delta H_{C-C} - 2\Delta H_{C-H} + \Delta H_{C=C} + \Delta H_{H-H}$$

Substituting the values of bond energies from the table, we have

$$\Delta H = -(347 + 828) + (619 + 436) = -1175 + 1055 = -120 \text{ kJ}$$

2. Determination of Enthalpies of Formation of Compounds Consider the formation of acetone from C, H and O.

$$3\,C(g) + 6\,H(g) + O(g) \longrightarrow H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-H$$

This involves the breaking of three H–H, and half O–O bonds and sublimation of 3C(s) to give six atoms of H(g), one atom of O(g) and three atoms of C(g) respectively (enthalpy of sublimation of C is 720 kJ).

It also involves the formation of two C–C bonds, six C–H bonds and one C=O bond. Thus the enthalpy of formation is given by

$$\Delta H_f = [3(\Delta H_{H-H}) + \frac{1}{2}(\Delta H_{O-O}) + 3(\Delta H_{C(s) \rightarrow C(g)})] - [2(\Delta H_{C-C}) + 6(\Delta H_{C-H}) + \Delta H_{C=O}]$$

Substituting the values, we have

$$\begin{aligned}\Delta H_f &= [3 \times 436 + \frac{1}{2} \times 138 + 3 \times 720] - [2 \times 347 + 6 \times 414 + 707] \\ &= [1308 + 69 + 2160] - [694 + 2484 + 707] \\ &= 3537 - 3885 = \mathbf{-348\ kJ}\end{aligned}$$

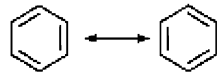
3. Determination of Resonance Energy If a compound exhibits resonance, there is a considerable difference between the experimental and calculated values of enthalpies of formation of the compound. The difference gives the values of resonance energy. Consider the dissociation of benzene.

$$C_6H_6(g) \longrightarrow 6C(g) + 6H(g)$$

Assuming that the benzene molecule consists of three C–C and three C=C and six C–H bonds, the dissociation energy is calculated as

$$\begin{aligned}\Delta H_d &= 3(\Delta H_{C-C}) + 3(\Delta H_{C=C}) + 6(\Delta H_{C-H}) \\ &= (3 \times 347) + (3 \times 619) + (6 \times 414) = 1041 + 1857 + 2484 = \mathbf{5382\ kJ\ mol^{-1}}\end{aligned}$$

Experimental value is known to be 5535 kJ mol^{-1}. This means the compound is more stable than the Kekule structure by an amount 5535 – 5382 = 153 kJ mol^{-1}. This is the value of resonance energy. Resonance energy comes into play because of the resonating structures.



Example 25 *Calculate the bond energy of C–H bond, given the heats of combustion of methane (CH_4), graphite and hydrogen are 891 kJ, 394 kJ and 286 kJ respectively while the heat of sublimation of graphite is 717 kJ and the heat of dissociation of hydrogen molecule is 436 kJ.*

Solution: The data given is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g); \quad \Delta H = -891 \text{ kJ} \qquad \ldots(i)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -394 \text{ kJ} \qquad \ldots(ii)$$

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g); \quad \Delta H = -286 \text{ kJ} \qquad \ldots(iii)$$

$$C(s) \longrightarrow C(g); \quad \Delta H = +717 \text{ kJ} \qquad \ldots(iv)$$

$$H_2(g) \longrightarrow 2H(g); \quad \Delta H = +436 \text{ kJ} \qquad \ldots(v)$$

We want ΔH for the following reaction

$$\frac{1}{2}[CH_4(g)] \longrightarrow C(g) + 4H(g); \quad \Delta H = ? \qquad \ldots(vi)$$

The problem is solved in two steps.

First, we calculate ΔH for $CH_4(g) \longrightarrow C(g) + 4H(g)$ and then divide the result by 4

Operating Eq. (i) + Eq. (iv) + 2 × Eq. (v), we get

$$CH_4(g) + 2O_2(g) + C(s) + 2H_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + C(g) + 2H(g) \qquad \ldots(vii)$$

To cancel out the terms not needed, now operate Eq. (vii) – 2 × Eq. (iii) – Eq. (ii)

$$CH_4(g) \longrightarrow C(g) + 4H(g);$$

$$\Delta H = -891 + 717 + 2 \times 436 - 2 \times (-286) - (-394) = +1664 \text{ kJ}.$$

This is the energy required for the dissociation of 4 moles of C–H bonds.

Bond-dissociation energy for C–H bond $= \frac{1664}{4}$ kJ $= \mathbf{416 \text{ kJ mol}^{-1}}$

Example 26 *Calculate the enthalpy change for the reaction*

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Given that the bond energies of H–H, Br-Br and H–Br are 435, 192 and H – Br and 364 kJ mol^{-1} respectively.

Solution : First method ***By calculating the total energy absorbed and released***

Energy absorbed in the dissociation of 1 mole of H–H bonds = 435 kJ

Energy absorbed in the dissociation of 1 mole of Br–Br bonds = 192 kJ

Total energy absorbed = 435 + 192 = 627 kJ

Energy released in the formation of 1 mole of H–Br bonds = 364 kJ

∴ Energy released in the formation of 2 moles of H–Br bonds 2 × 364 = 728 kJ

Energy released is greater than energy absorbed. Hence, net result is the release of energy.

Energy released = 728 kJ – 627 kJ = 101 kJ

Thus, for the given reaction

$$\Delta H = -101 \text{ kJ}$$

Second Method **Using the formula directly**

$$\Delta H_{reaction} = \Sigma \text{ Bond energies of reactants} - \Sigma \text{ Bond energies of products}$$
$$= [\text{Bond energy (H–H)} + \text{Bond energy (Br–Br)} - [2 \times \text{Bond energy (H–Br)}]$$
$$= 435 + 192 - (2 \times 364) = 627 - 128 = \mathbf{-101\ kJ}$$

Hess's law can also be applied to solve the problem.

PROBLEMS FOR PRACTICE

1. Calculate the enthalpy of hydrogenation of $C_2H_2(g)$ to $C_2H_4(g)$.

   Given bond energies C–H = 414.0 kJ mol^{-1}, C ≡ C = 827.6 kJ mol^{-1}, C=C = 606.0 kJ mol^{-1}, H–H = 430.5 kJ mol^{-1}

   [Ans. –175.9 kJ mol^{-1}]

2. Propane has the structure $H_3C–CH_2–CH_3$. Calculate the change in enthalpy for the following reaction:

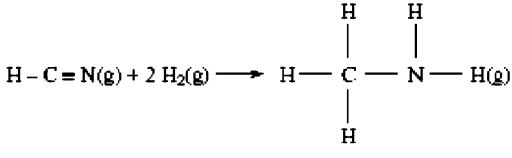
   $$C_3H_8(g) + 5O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(g)$$

   Given that average bond enthalpies are

C–C	C–H	C=O	O=O	O–H
347	414	741	498	464 kJ mol^{-1}

   [Ans. –1662 kJ mol^{-1}]

3. ΔH for the reaction



   is –150 kJ. Calculate the bond energy of C≡N bond. [Given bond energies of C–H = 414 kJ mol^{-1}, H–H = 435 kJ mol^{-1}; C–N = 293 kJ mol^{-1}, N–H = 396 kJ mol^{-1}]

   [Ans. 893 kJ mol^{-1}]

4. Calculate the C–C bond energy from the following data:

   (a) $2C_{(graphite)} + 3H_2(g) \longrightarrow C_2H_6(g)$, $\Delta H = -84.67$ kJ

   $$C_{(graphite)} \longrightarrow C(g); \quad \Delta H = 716.7 \text{ kJ}$$

   (b) $H_2(g) \longrightarrow 2H(g)$, $\Delta H = 435.9$ kJ

   Assume the C–H bond energy as 416 kJ.

   [Ans. –964 kJ mol^{-1}]

5. Calculate the enthalpy change for the following reaction:

   $$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

   Given that the bond dissociation energies of H–H, Cl–Cl and H–Cl are 437 kJ, 244 kJ and 433 kJ mol^{-1} respectively.

   [Ans. –185 kJ]

6. Calculate $\Delta H°$ for the reaction

   $$CH_2 = CH_2 + 3O_2 \longrightarrow 2CO_2 + H_2O$$

Given that the average bond energies of the different bonds are

Bond	C–H	O=O	C=O	O=H	C=C
Bond energy (kJ mol^{-1})	414	499	724	460	619

[Ans. –964 kJ mol^{-1}]

SOLVED EXAMPLES

Example 27 *From the thermochemical equation*

$$C_6H_6(l) + 7\frac{1}{2}O_2(g) \longrightarrow 3H_2O(l) + 6CO_2(g) \quad \Delta H = -3264.64 \text{ kJ mol}^{-1}$$

calculate the energy evolved when 39 g of C_6H_6 is burnt in an open container.

Solution: 1 mole of benzene = 78 g

When 78 g of C_6H_6 burn, heat evolved = 3264.64 kJ

$\therefore$ when 39 g of C_6H_6 burn, heat evolved $= \dfrac{3264.64}{78} \times 39 =$ **1632.32 kJ**

Example 28 *The heat evolved in the combustion of glucose is shown in the following equation. $C_6H_{12}O_6 + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g)$ $\Delta H = -2840$ kJ*

What is the energy requirement for production of 0.36 g of glucose by the reverse reaction?

Solution: *Data provided is*

$$C_6H_{12}O_6 + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g); \quad \Delta H = -2840 \text{ kJ}$$

Writing the reaction in reverse direction

$$6CO_2(g) + 6H_2O(g) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g); \quad \Delta H = +2840 \text{ kJ}$$

For production of 1 mole of $C_6H_{12}O_6$ (180 g), heat required (absorbed) = 2840 kJ

$\therefore$ For production of 0.36 g of glucose, heat absorbed

$$= \frac{2840}{180} \times 0.36 = \mathbf{5.68\ kJ}$$

Example 29 *If a man takes a diet which gives him energy equal to 9500 kJ per day and he expends energy in all forms to a total of 12000 kJ per day, what is the change in internal energy per day? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 1 kg? Ignore water loss.*

Solution: Loss of energy per day = 12000 – 9500 = 2500 kJ

For a loss of 1632 kJ of energy, sucrose ($C_{12}H_{22}O_{11}$) lost = 100 g (given)

$\therefore$ for a loss of 2500 kJ of energy, sucrose lost $= \dfrac{100}{1632} \times 2500$ g

$= 153.2$ g

Thus, loss of 153.2 g in weight takes place in 1 day.

Time taken to lose 1 kg or 1000 g glucose $= \dfrac{1}{153.2} \times 1000 = 6.5$ days

Example 30 *The thermochemical equation for solid and liquid rocket fuels are given below:*

$$2Al(s) + 1\frac{1}{2}\,O_2(g) \longrightarrow Al_2O_3(g); \quad \Delta H = -1667.8\ kJ$$

$$H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -285.9\ kJ$$

(a) If equal masses of aluminum and hydrogen are used, which is a better rocket fuel?

(b) Determine ΔH for the reaction:

$$Al_2O_3(s) \longrightarrow 2Al(s) + 1\frac{1}{2}\,O_2(g)$$

Solution: 2 moles of Al = 54 g

54 g of Al on combustion give heat = 1667.8 kJ

$\therefore$ 1 g of Al on combustion give heat $= \dfrac{1667.8}{54} = 30.9$ kJ

1 mole of $H_2 = 2$ g

2 g of H_2 on combustion give = 285.9 kJ of heat

$\therefore$ 1 g of H_2 on combustion will give $= \dfrac{285.9}{2} = 142.95$ kJ of heat

Thus, H_2 is a better rocket fuel.

(b) Writing the reverse of the first reaction, we have

$$Al_2O_3(s) \longrightarrow 2Al(s) + 1\frac{1}{2}\,O_2(g) \quad \Delta H = +1667.8\ kJ$$

Thus, for the reaction given in part (b) of the problem,

ΔH = **+1667.8 kJ**

Example 31 *The heat evolved in the combustion of methane is given by the following equation:*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \quad \Delta H = -890.3\ kJ$$

(a) How many grams of methane would be required to produce 445.15 kJ of heat on combustion?

(b) How many grams of carbon dioxide would be formed when 445.15 kJ heat are evolved?

(c) What volume of oxygen at STP would be used in the combustion process (a) or (b)?

Solution:

(a) From the given equation, heat produced from 1 mole of CH_4, i.e. 16 g of CH_4 = 890.3 kJ
Heat produced from 8 g of CH_4 = 445.15 kJ

(b) From the given equation,
When 890.3 kJ of heat are evolved, CO_2 formed = 44 g
$\therefore$ When 445.15 kJ of heat are evolved, CO_2 formed = 22 g

(c) O_2 used in the production of 890.3 kJ of heat = 44.8 litres at STP
Hence, O_2 used in the production of 445.15 kJ of heat = **22.4 litres at STP**

10.8 VARIATION OF HEAT OF REACTION WITH TEMPERATURE—KIRCHHOFF'S EQUATION

Heat evolved or absorbed depends upon the temperature at which the reaction is carried out. The

relationship showing the variation of the heat of reaction with temperature was given by Kirchhoff in 1856.

The change in the heat of reaction at constant pressure for every degree change of temperature is equal to the change in the heat capacity at constant pressure, accompanying the reaction.

It can be derived as under:

Consider the general equation

$$A \longrightarrow B$$

As shown in Fig. 10.12, from A at temperature T_1, we can reach B at temperature T_2 by two different paths:

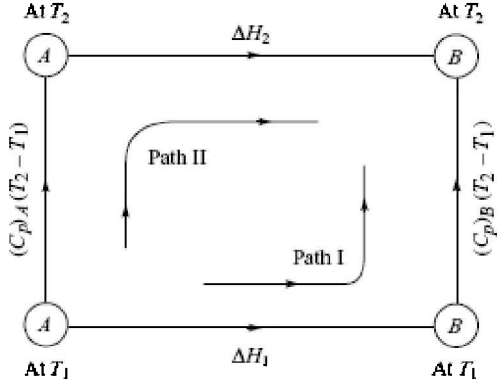


Fig. 10.12 *Changing A to T_1 to B at T_2 by two different paths*



Fig. 10.13 *Gustav Robert Kirchhoff was a German physicist who contributed to the fundamental understanding of black-body radiation and thermochemistry.*

Path I We perform the reaction at temperature T_1 to obtain B at the same temperature and then heat this up to the temperature T_2 then

Heat evolved in the first stage = ΔH_1

Heat absorbed in the second stage = $(C_P)_B\ (T_2 \rightarrow T_1)$

where $(C_P)_B$ is the average molar heat capacity of the products.

$\therefore$ Net heat evolved = $\Delta H_1 - (C_P)_n\ (T_2 \rightarrow T_1)$

Path II We first heat up the reactants to the temperature T_2 and then perform the reaction to give the products at the same temperature. Then if $(C_P)_A$ is the average molar heat capacity of the reactants A.

Heat *absorbed* in the first stage = $(C_P)_A\ (T_2 \rightarrow T_1)$

Heat *evolved* in the second stage = ΔH_2

$\therefore$ Net heat evolved = $\Delta H_2 \rightarrow (C_P)_A\,(T_2 \rightarrow T_1)$

Since the initial and the final states are the same in both the above cases, therefore, by law of conversation of energy, we must have

Net heat evolved by path I = Net heat evolved by path II

i.e. $$\Delta H_1 - (C_P)_B\,(T_2 - T_1) = \Delta H_2 - (C_P)_A\,(T_2 - T_1)$$

or $$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

When the Reaction is Carried Out at Constant Volume We have the thermodynamic relation

$$\Delta H = \Delta U + P\Delta V$$

Under conditions of constant volume, $\Delta V = 0$

$\therefore$ $$\Delta H = \Delta U$$

Hence, equation derived above takes the form $\dfrac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V$

where $\Delta C_V = (C_V)_B - (C_V)_A$ is the change in the heat capacity at constant volume accompanying the reaction, $(C_V)_A$ and $(C_V)_B$ are the mean molar heat capacities at constant volume of the reactants and the products respectively, ΔE_1 and ΔE_2 are the internal energy changes (i.e. heats of reaction at constant volume) when the reaction is carried out at temperatures T_1 and T_2 respectively. Thus, Kirchhoff's equation may also be expressed as follows:

The change in the heat of reaction at constant volume for every degree change of temperature is equal to the change in the heat capacity at constant volume, accompanying the reaction.

Example 32 *Calculate the heat of formation of HCl at 348 K from the following data:*

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl; \quad \Delta H = -92300\ J$$

The mean heat capacities over this temperature range are

$$H_2(g); \quad C_P = 28.53\ JK^{-1}\,mol^{-1}$$
$$Cl_2(g); \quad C_P = 32.26\ JK^{-1}\,mol^{-1}$$
$$HCl(g); \quad C_P = 28.49\ JK^{-1}\,mol^{-1}$$

Solution:

The reaction under consideration is $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$

For this reaction,

$$\Delta C_P = (C_P)_{HCl} - \frac{1}{2}(C_P)_{H_2} - \frac{1}{2}(C_P)_{Cl_2}$$

$$= 28.49 - \frac{1}{2}(28.53) - \frac{1}{2}(32.26)$$

$$= 1.91\ JK^{-1}mol^{-1}$$

We are given that

$\Delta H_1 = -92300\ J\ T_1 = 298\ K\ \Delta H_2 = ?$

According to Kirchhoff's equation,

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

or
$$\Delta H_2 = \Delta H_1 + \Delta C_P(T_2 - T_1)$$
$$= -92300 + (-1.91)(348 - 298) = -92300 - 95.5$$
$$= -92395.5 \text{ J}$$

PROBLEMS FOR PRACTICE

1. Calculate the heat of formation of H_2O (liquid) at 383 K, if ΔH for the reaction

$$H_2(g) + \frac{1}{2} + O_2(g) \longrightarrow H_2O(l)$$

At 298 K, ΔH is –298.06 kJ. The average value of heat capacities between the two temperatures for H_2 (g), O_2(g) and H_2O(l) are 27.61, 29.50 and 75.31 JK^{-1} mol^{-1} respectively.

[Ans. –283.92 kJ]

2. If the standard heat of formation of HCl gas at 25°C is –22.66 kcal mol^{-1}, calculate the value at 60°C. C_P for H_2(g) – 6.82 cal mol^{-1} deg^{-1}.

3. The heat of solution of ammonia at 25°C was found to be –11.04 kcal. Calculate the heat of solution at 348 K. Given that the mean heat capacities of N_2, H_2 and NH_3 are 6.80, 6.77 and 8.86 cal/degree/mol. respectively.

[*Hint.* $\frac{1}{2}N_2 + \frac{3}{2}H_2 \longrightarrow NH_3$

$$\Delta C_P = (C_P)\,NH_3 - \frac{1}{2}C_P(N_2) - \frac{3}{2}(C_P)_{H2}$$
$$T_1 = 25 + 273 = 298 \text{ K}$$
$$T_2 = 348 \text{ K}]$$

4. The molar heat capacities at constant pressure of H_2(g), Cl_2(g) and HCl(g) are respectively 29.3, 34.7 and 28.9 JK^{-1}. Ifthe heat of formation of HCl(g) at constant pressure at 293 K is –91.2 kJ, what will be its heat of formation at 313 K?

[Ans. –91.27 kJ]

5. Consider the reaction

$$H_2O(g) \longrightarrow H_2 + \frac{1}{2}O_2;\ \Delta H° = +57780 \text{ cal at } 18°C$$

What would be $\Delta H°$ value at 25°C? The C_P values are $C_P(H_2O)$ = 8.02, $C_P(H_2)$ = 6.89 and $C_P(O_2)$ = 7.96 cal deg^{-1} mol^{-1}

[Ans. 57796.45 kcal]

SOLVED PROBLEMS

Example 33 *What is the thermodynamic basis of Hess's law?*

Solution : Enthalpy is a state function. That means enthalpy change during a reaction does not depend upon the reaction path in which the change is brought about. It depends only upon the nature of the reactants and the final products.

Example 34 *In the case of polyatomic molecules, why is the energy of a particular type of bond, the average value?*

Solution : Bond energy for the dissociation of a particular bond is not the same in different molecules. It is not the same even in the same molecules like CH_4. Bond energies of four C–H bonds are not equal because after the dissociation of every C–H bond, the electronic environments change. Hence, the average value is taken.

SUMMARY

1. *Thermochemistry* is the branch of chemistry which deals with heat changes accompanying chemical reactions.
2. *Enthalpy* of a system may be defined as the sum of internal energy and the product of pressure and volume of the system. Enthalpy may also be defined as the energy stored within the substance, i.e. available for conversion into heat.
3. *Enthalpy change* of a system may be defined as the sum of internal energy change and the pressure-volume work done. In other words, enthalpy change is the heat evolved or absorbed at constant pressure.
4. If heat is evolved in a reaction, it is *exothermic.* If heat is absorbed in a reaction, it is an *endothermic* reaction.
5. A balanced equation indicating the amount of heat evolved or absorbed is called *thermochemical* equation.
6. The amount of heat evolved or absorbed in a chemical reaction when the number of moles of the reactants as represented by the chemical equation have completely reacted, is called the *heat of reaction.*
7. *The heat of combustion* of a substance is defined as the heat change when one mole of a substance is completely burnt or oxidised.
8. The *calorific value* of a fuel or food is the amount of heat in calories or joules produced from the complete combustion of one gram of the fuel or the food.
9. The conditions of 1 atm presume and 298.15 K are called *standard state.*
10. The *standard enthalpy of formation* of a substance is defined as the heat change that takes place when one mole of the substance is formed from its elements in the standard state, i.e. 298 K and 1 atm pressure.
11. *Heat of neutralisation* of an acid by a base is defined as the heat change when one gram equivalent of the acid is neutralised by a base, the reaction being carried out in dilute solution.
12. *Hess's law:* The total amount of heat evolved or absorbed in a reaction is the same whether the reaction takes place in one step or in a number of steps.
13. The *bond energy* of a particular bond is defined as the average amount of energy released when one mole of bonds are formed from isolated gaseous atoms or the amount of energy required when 1 mole of bonds are broken so as to get separate gaseous atoms.
14. *Kirchhoff's law:* The change in the heat of reaction at constant pressure for every degree change of temperature is equal to the change in the heat capacity at constant pressure accompanying the reaction.

KEY RELATIONS

1. Enthalpy change of a reaction $= \begin{bmatrix}\text{Energy consumed to}\\ \text{break the bonds of}\\ \text{the reactants}\end{bmatrix} - \begin{bmatrix}\text{Energy relased in}\\ \text{the formation of bonds}\\ \text{in the products}\end{bmatrix}$

2. $q_P = q_V + \Delta n_g RT$
3. $\Delta H°_{\text{reaction}} = \Sigma \Delta H°_f$ (Products) – $\Sigma \Delta H°_f$ (Reactants)
4. $\Delta H_{\text{reaction}}$ = Σ Bond energies of reactants – Σ Bond energies of products
5. $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$ (Kirchhoff's equation) at constant pressure

   $\frac{\Delta E_2 - \Delta E_1}{T_2 - T1} = \Delta C_V$ at constant volume

EXERCISES

Based on Different University Papers
Multiple-Choice Questions

1. Endothermic reaction is one in which
   (a) heat is converted into electricity
   (b) heat is absorbed
   (c) heat is given out
   (d) heat is converted into mechanical work
2. Thermochemistry is the study of
   (a) heat changes accompanying chemical reactions
   (b) net entropy change in a reaction
   (c) net free energy change in a chemical reaction
   (d) none of these
3. A reaction whose heat of reaction shows the bond energy of HCl is
   (a) $HCl(g) \longrightarrow H(g) + Cl(g)$
   (b) $2HCl(g) \longrightarrow Hl(g) + Cll(g)$
   (c) $HCl(g) \longrightarrow \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g)$
   (d) $HCl(g) \longrightarrow H^+(g) \longrightarrow Cl^-(g)$
4. The equations showing the effect of temperature change on the heat of reaction is known as
   (a) Arrhenius equation
   (b) Kirchhoff's equation
   (c) Ostwald's equation
   (d) none of these
5. The heat of neutralisation is maximum for the reaction
   (a) NaOH and HCl
   (b) NaOH and CH_3COOH
   (c) HCl and NH_4OH
   (d) NH_4OH and CH_3COOH
6. "The resultant heat change in a chemical reaction is the same whether it takes place in one or several stages." This statement is called

(a) Le-Chatelier's principle

(b) Hess's law

(c) Lavoisier-Laplace law

(d) Joule-Thomson effect

7. Standard heat of formation of an element is

   (a) infinite

   (b) zero

   (c) 100 kJ

   (d) 200 kJ

8. The apparatus used for measuring heat of reaction at constant volume is called

   (a) calorimeter

   (b) colourimeter

   (c) pyrometer

   (d) pyknometer

9. The enthalpies of elements in their standard states are taken as zero. Thus, the enthalpy of formation of a compound

   (a) will always be positive

   (b) will always be negative

   (c) may be positive or negative

   (d) will always be zero

10. The heat of neutralisation of HCl and NaOH is 13.7 kcal and that of NaOH and CH_3COOH is 13.2 kcal. Heat of ionisation of CH_3COOH is

    (a) 13.3 kcal

    (b) 13.7 kcal

    (c) 0.5 kcal

    (d) none of these

Answers

1. (b)
2. (a)
3. (a)
4. (b)
5. (a)
6. (b)
7. (b)
8. (a)
9. (d)
10. (c)

SHORT-ANSWER QUESTIONS

1. Define thermochemistry. Give two examples of reaction that are accompanied by evolution of heat.
2. Define enthalpy and enthalpy change.
3. What are the latest sign conventions for ΔH, ΔU and W?
4. Differentiate between exothermic and endothermic reactions giving one example of each.
5. What is meant by thermochemical equation? Explain with an example.
6. Briefly describe two factors that influence the rate of a reaction.
7. Discuss calorific value of a food and a fuel. What is the energy requirement of an average-bodied man for normal functioning?
8. Explain the following:
   (a) Heat of solution
   (b) Heat of fusion
9. Give the proof of Hess's law of constant heat summation.
10. What is meant by bond energy? How do we determine the heat of a reaction from bond energy data of the reactants and products?
11. State and explain Kirchhoff's law.

GENERAL QUESTIONS

1. Define *bond energy*. How is bond energy of a bond calculated for a polyatomic molecule? How is it used to calculate the enthalpy change of a reaction?
2. Define standard enthalpy of reaction, standard enthalpy of formation and enthalpy of combustion. What is Hess's law? What is the thermodynamic basis of Hess's law?
3. Briefly explain the term *enthalpy of neutralization*. Comment on their values if both are strong or one of them is weak or both are weak.
4. Derive thermodynamically Kirchhoff's equation giving the variation of heat of reaction with temperature.
5. Derive thermodynamically Kirchhoff's equation

   or

   Show that the temperature dependence of heat of reaction is given by the relation

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$$

   Name the equation.
6. Define *bond energy* for a diatomic molecule and for a polyatomic molecule. How does bond-energy data help calculate the enthalpy change of a reaction?
7. Calculate ΔH_f for methane, i.e. ΔH for the reaction

$$C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g) \text{ from the following data:}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890.3 \text{ kJ}$$

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -285.9 \text{ kJ}$$

$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

   [Ans. -75.56 kJ mol^{-1}]

8. What is meant by the term *bond energy?* How would you determine the following from bond energies:

   (a) Enthalpy of formation of compounds

   (b) Resonance energy

9. Define the terms: $\Delta H_{comb.}$, $\Delta H_{neut.}$, $\Delta H_{solu.}$, and ΔH_f

10. Calculate ΔH for the reaction $CH_2 = CH_2(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$ at 25°C, given the following bond energies.

Bond	C – H	O = O	C = O	O – H	C = C
Bond energy (kJ mol^{-1})	416.2	493.7	711.3	464.4	615.0

[Ans. –941.9 kJ]



Themodynamics-II

11

LEARNING OBJECTIVES

- Understand the need for second law
- State second law of thermodynamics in different ways
- Understand Carnot cycle and Carnot theorem
- Appreciate the concept of entropy
- Apprise yourself about entropy changes in reversible and irreversible processes
- Compute entropy change for an ideal gas under different conditions
- Derive entropy change using Boltzmann probability equation
- Know the physical significance of entropy
- Calculate entropy change on mixing of ideal gases
- Understand Helmholtz free energy and Gibbs free energy
- Derive the expression for variation of Gibbs free energy with temperature and pressure
- Know the criteria for feasibility of a process
- Derive Maxwell relations
- Derive Gibbs-Helmholtz equation and understand its applications

11.1 INTRODUCTION

11.1.1 Need for the Second Law of Thermodynamics

A major limitation of the first law of thermodynamics is that it is silent about the feasibility of a process. For example, it dose not tell us whether water can run uphill itself, whether a gas diffuses from a region of low pressure, whether heat can flow from a cold body to a hot body, etc. Of course, it tells, that there is an exact equivalence between various forms of energy and that heat gained is equal to heat lost. But that does not serve the whole purpose. The second law of thermodynamics answers the questions that remain unanswered by the first law.

The second law helps us to know the direction in which energy can be transferred. It also helps us to predict, through the concept of entropy, whether a given reaction can take place spontaneously. It also helps us to know the equilibrium conditions.

The first law states that when heat is converted into work, the work performed is equivalent to heat absorbed. However, this is not precisely correct. It has been seen from day-to-day experience that heat absorbed cannot be completely converted into work without leaving some change in the system or surroundings.

In order to sort out these issues, the second law of thermodynamics was proposed. It has a number of statements. Different statements of the second law of thermodynamics provide

answers to various questions.

11.1.2 Different Statements of the Second Law of Thermodynamics

1. All spontaneous processes like the flow of heat from hot end to cold end, diffusion of gas from high pressure to low pressure or flow of water down a hill, etc., are thermodynamically irreversible.

   Spontaneous process means a process which can take place without the help of any external agency. All natural processes, some of which are mentioned above, are spontaneous processes. Further, the first law states that when heat is converted into work, the work obtained is equal to heat absorbed. However, it has been seen from experience that the heat absorbed cannot be completely converted into work without leaving some change in the system or the surroundings. Hence, the second law is also stated as follows:

   The complete conversion of heat into work is impossible without leaving some effects elsewhere.

2. It is impossible to construct a machine, functioning in cycles, which can convert heat completely into the equivalent amount of work without producing changes elsewhere.
3. Without the use of external agency, heat cannot by itself pass from a colder to a hotter body.

1. Spontaneous or Irreversible Processes Processes taking place in nature are ***spontaneous*** and ***irreversible.*** Some example of such processes are given below:

(a) On mixing two solutions of different concentrations, the diffusion of the solute takes place from more concentrated solution to less concentrated solution till the concentration throughout becomes the same. It is a spontaneous reaction. Once this has happened, it is not possible spontaneously to make one part more concentrated than the other.

(b) A gas expands spontaneously from a region of higher pressure to lower pressure or vacuum.

(c) Heat flows from a hot body to a cold body spontaneously. For the transfer of heat from a cold body to a hot body, we need to supply energy from outside.

(d) Electricity flows from a higher potential to a lower potential spontaneously. The direction of flow can be reversed only by applying an external field in the opposite direction.

Thus, all natural processes proceed spontaneously and are thermodynamically irreversible in character.

We can obtain work from spontaneous processes but as they occur irreversibly, the work obtained is much less than we can expect from reversible processes. Spontaneous processes proceed at definite and measureable speeds while thermodynamically reversible processes occur infinitesimally slow.

2. Cyclic Process When a system returns to its original position after a series of changes, it is said to have completed a cycle. Such a process is called cyclic process. As the internal energy is a state function, the change of internal energy is zero.

$$\Delta U = 0 \qquad \ldots(11.1)$$

According to the first law of thermodynamics,

$$\Delta U = q + w \qquad \ldots(11.2)$$

From Eqs. (11.1) and (11.2),

$$q + w = 0$$

or $$q = -w$$

Although, it is not possible to have strictly reversible cycle processes, the concept is highly useful in deriving certain relationships as for Carnot cycle, which we shall see in a later section.

11.1.3 Efficiency of a Machme

The fraction of heat absorbed by machine that can transform into work is called the ***efficiency*** of a machine. Thus, if Q is the heat absorbed and W is the work done then the efficiency of a machine is given by.

$$\eta = \frac{W}{Q}$$

The machine used for conversion of heat into work is called ***heat engine:*** In order to bring about this conversion, the engine absorbs heat from a heat reservoir at a higher temperature, called the *source,* converts a part of it into work and returns the remainder to the heat reservoir at a lower temperature, called the ***sink.***

11.2 CARNOT CYCLE

A Carnot cycle is a process in which the system returns to its original sate after a number of successive changes. A process conducted in this manner is called a cyclic process. The Carnot cycle consists of four different operations which can be shown on a pressure-volume diagram as shown in Fig. 11.1.

A Carnot engine consists of a cylinder containing 1 mole of an ideal gas as the working substance and fitted with weightless, fractionless piston so that all the operations in the cycle are carried out reversibly. For this reason it is also called a reversible heat engine. The cylinder is supposed to be insulated on all sides except at the bottom so that heat can flow to and from the system only through the bottom. Further, it is supposed that there are two heat reservoirs, one at higher temperature T_2 (called the source) and the other at the lower temperature T_1 (called the sink). If some operation is carried out by placing the cylinder in the source or the sink, it can exchange heat and hence the temperature remains constant so that the process is isothermal. On the other hand, if the cylinder is placed on an insulating material, no heat exchange can take place between the system and the surroundings and hence, the process is adiabatic.

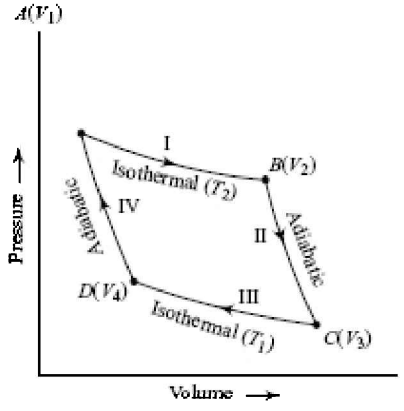


Fig. 11.1 *Carnot cycle*

Four different operations are carried out as shown in Fig. 11.2 and are described below:

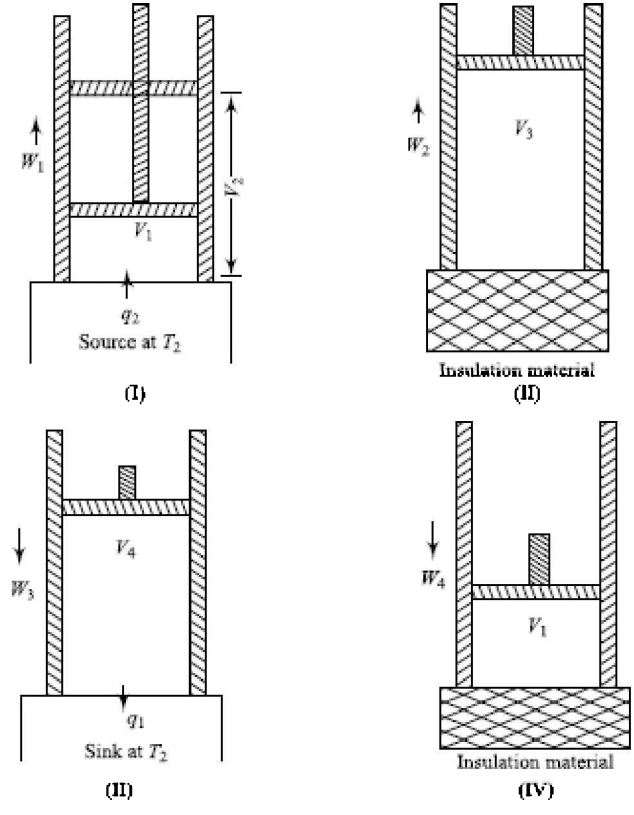


Fig. 11.2 *Different operations of Carnot cycle*

1. Isothermal Expansion The cylinder containing 1 mole of an ideal gas, occupying a volume V_1, is placed in contact with the source (i.e. heat reservoir at the temperature T_2). The gas absorbs heat q_2 from the source and expands isothermally and reversibly till its volume has increased to V_2. Since the gas is ideal, the work done by one mole of an ideal gas w_1 will be given by

$$-w_1 = RT_2 \ln \frac{V_2}{V_1} \qquad (11.3)$$

Further, for an ideal gas, the work done is equal to heat absorbed, q_2 so that

$$-w_1 = q_2 = RT_2 \ln \frac{V_2}{V_1} \qquad ...(11.4)$$

Hence, w_1 work done by the system has been taken as negative and q_2 as positive as per latest SI conventions.

2. Adiabatic Expansion The cylinder is now removed from the source and placed in a perfectly insulating material so that the gas now expands adiabatically and reversibly. Work done in the expansion is continued till the temperature has fallen to T_1 which is the temperature of the sink. Suppose the corresponding volume becomes V_3. The path is shown by the adiabatic curve BC in Fig. 11.1. The work done is w_2 which is given by,

$$-w_2 = C_V(T_1 - T_2)$$

or

$$w_2 = -C_V(T_2 - T_1) \qquad ...(11.5)$$

where C_V is heat capacity of the ideal gas. Here again, w_2 is negative by sign conversions.

3. Isothermal Compression The cylinder is now removed from the insulating material and placed in contact with the sink (i.e. the heat reservoir at the lower temperature T_1). The gas is compressed isothermally and reversibly till the volume decreases from V_3 to V_4. The process represented is taken as positive by new conventions and will be given by —

$$w_3 = RT_1 \ln \frac{V_4}{V_3} \qquad ...(11.6)$$

During the operation, an amount of heat q_1, exactly equal to w_3, will be returned to the sink at T_1. According to sign conventions, q_1 will be negative and w_3 will be positive.

$$-q_1 = w_3 = RT_1 \ln \frac{V_4}{V_3} \qquad ...(11.7)$$

4. Adiabatic Compression The cylinder is now removed from the sink and placed again on the insulating material. The gas is then compressed adiabatically and reversibly along DA till the initial state A is regained. The temperature of the gas rises from T_1 and T_2. The work done on the system is positive and is given by

$$w = C_V(T_2 - T_1) \qquad ...(11.8)$$

Consequent to these four operations, the system has returned to its original state so that a reversible cycle has been completed. The net work *(w)* done by the system will be given by,

$$w = (-w_1) + (-w_2) + (w_3) + (w_4) \qquad \ldots(11.9a)$$

$$= RT_2 \ln \frac{V_2}{V_1} - C_V(T_2 - T_1) + RT_1 \ln \frac{V_4}{V_3} + C_V(T_2 - T_1)$$

$$= RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3} \qquad \ldots(11.9b)$$

V_1 and V_4 lie on one adiabatic curve and V_3 and V_2 lie on another. Applying volume–temperature relationships, we have

$$\left(\frac{V_4}{V_1}\right)^{\gamma-1} = \frac{T_2}{T_1} \qquad \ldots(11.10)$$

and

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \qquad \ldots(11.11)$$

Comparing Eqs (11.10) and (11.11), we get

$$\left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$$

or

$$\frac{V_4}{V_1} = \frac{V_3}{V_2}$$

or

$$\frac{V_4}{V_3} = \frac{V_1}{V_2} \qquad \ldots(11.12)$$

Substituting this value in Eq. (11.9b), we get

$$w = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_1}{V_2}$$

$$= RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_2}{V_1}$$

$$- R(T_2 \quad T_1) \ln \frac{V_2}{V_1} \qquad \ldots(11.13)$$



Fig. 11.3 *Nicolas Leonard sadi Carnot (1796-1832) was a French military engineer and physicist, often described as "father of thermodynamics".*

Dividing Eq. (11.14) by (11.13), we get

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} \qquad \ldots(11.14)$$

This gives the efficiency of the Carnot cycle or engine. From Eq. (11.14), it is clear that the efficiency of the reversible heat engine depends only upon the temperature of the source and the sink and is independent of the nature of the working substance.

The quantity $\frac{T_2 - T_1}{T_2}$, which represents efficiency is always less than unity. The efficiency of a heat engine is thus always less than unity.

11.2.1 Carnot Theorem

The result that follows from the Carnot cycle is called the Carnot theorem.

The Carnot theorem may be stated as under:

The efficiency of a reversible heat engine depends only upon the temperatures of the source and the sink and is independent of the nature of the working substance. In other words, all reversible heat engines working between the same temperature have the same efficiency.

Combining equations (11.4), (11.7) and (11.9b) in the previous section, we get

$$w = q_2 - q_1$$

i.e. net work done by the system is equal to net heat absorbed by the system. Putting the volume of *w* in Eq. (11.4) above, we have

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

Hence, the efficiency of a heat engine may be given by any one of the following expressions.

$$\eta = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

Obviously, the efficiency of the engine can be increased by widening the difference in the temperature of the source and sink.

Example 1 *Calculate the maximum efficiency of a steam engine operating between 110° and 25°C. What would be the efficiency of the engine if the boiler temperature is raised to 140°C, the temperature of the sink remaining the same?*

Solution: *First Case* Given that

$$T_2 = 110°C = (110 + 273)\,K = 383\,K$$
$$T_1 = 25°C = (25 + 273)\,K = 298\,K$$
$$\eta = \frac{T_2 - T_1}{T_2} = \frac{383 - 298}{383} = 0.222 = 22.2\%$$

Second Case Given that

$$T_2 = 140°C = (140 + 273)\,K = 413\,K$$
$$T_1 = 25°C = (25 + 273)\,K = 298\,K$$
$$\eta = \frac{T_2 - T_1}{T_2} = \frac{413 - 298}{413} = 0.278 = 27.8\%$$

Example 2 *Compare the thermodynamic efficiencies to be expected:*

(a) When an engine is allowed to operate between 1000 K and 300 K

(b) When an engine is allowed to operate between 1000 K and 600 K and then waste heat is passed on to another engine which operates between 600 K and 300 K

Solution: *Case (a)*

$$\eta = \frac{1000 - 300}{10000} = 0.70 = 70\%$$

Case (b)

(i) $\eta = \dfrac{1000 - 600}{1000} = 0.40 = 40\%$

(ii) $\eta = \dfrac{600 - 600}{600} = 0.50 = 50\%$ of the rejected 60% of (i) = 30%

$\therefore$ Total $\eta = (40 + 30)\% = 70\%$

Example 3 *Calculate the amount of heat supplied to Carnot's cycle working between 368 K and 288 K if the maximum work obtained is 895 joules.*

Solution: It is given that-

$$T_1 = 368\,K \quad T_2 = 288\,K \quad w = 895 \text{ Joules}$$

Substituting these values in the formula,

$$\eta = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

we have, $$\frac{895}{q_2} = \frac{368 - 288}{368} \quad \text{or} \quad q_2 = \frac{895 \times 368}{80} = \mathbf{4117\ Joules}$$

11.3 THERMODYNAMIC SCALE OF TEMPERATURE

An ideal gas or a perfect gas ceases to exist at a temperature of −273.15°C. This temperature is called ***zero degree absolute.*** The scale developed on this basis is called ***perfect gas temperature scale.*** It is found to be independent of the ideal gas taken.

Lord Kelvin was the first to develop a scale of temperature that was independent of the nature of the gas. This was based on the efficiency of a reversible gas engine. This scale of temperature is called ***thermodynamic scale of temperature*** or ***Kelvin scale of temperature.*** It is found to be similar to the ideal gas temperature scale. Thermodynamic scale of temperature is developed as under.

Assume two heat reservoirs, one acting as a source and the other acting as a sink. Imagine a reversible heat engine operating between them. We further assume that the temperature of the source on the new scale is proportional to the quantity of heat absorbed from it and the temperature of the sink is proportional to the heat lost to it.

Let the

Heat absorbed from the source = Q_2 Heat lost to the sink = Q_1

Temperature of source on thermodynamic scale = θ_2

Temperature of sink on thermodynamic scale = θ_1

According to the above assumptions

$$\frac{Q_2}{Q_1} = \frac{\theta_2}{\theta_1}$$

Taking reciprocal of both sides and subtracting the result from 1, we get

$$1 - \frac{Q_1}{Q_2} = 1 - \frac{\theta_1}{\theta_2} \quad \text{OR} \quad \frac{Q_2 - Q_1}{Q_2} = \frac{\theta_2 - \theta_1}{\theta_2}$$

Putting $\theta_1 = 0$, i.e. zero of the new scale,

$$\frac{Q_2 - Q_1}{Q_2} = 1$$

This signifies that zero on the Kelvin scale is the temperature of the sink for a reversible heat engine whose efficiency is 1, i.e. complete conversion of heat into work. But this is possible only at absolute zero on the perfect gas scale of temperature. We conclude from here that gas scale and Kelvin scale are similar, provided the gas taken is ideal (perfect).

Thermodynamic scale of temperature derived from the second law of thermodynamics is more fundamental than that derived from ideal gas because we can use any fluid in the former.

11.4 CONCEPT OF ENTROPY

For a reversible Carnot cycle working between temperatures T_2 and T_1

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad \ldots(11.15)$$

where q_2 is heat absorbed isothermally and reversibly at the temperature T_2 and q_1 is heat lost iso-thermally and reversibly at the temperature T_1.

The above equation can be written as

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

or
$$\frac{q_2}{T_2} = \frac{q_1}{T_1} \qquad \ldots(11.16)$$

or
$$\frac{q}{T} = \text{constant.}$$

Thus, heat absorbed or lost isothermally and reversibly divided by the temperature at which heat is absorbed or lost is a constant quantity for a particular system. In Eq. (11.16), q_2 is heat absorbed at temperature T_2 and q_1 is heat lost at temperature T_1. If q_1 were the heat absorbed at the temperature T_1, Eq. (11.16) would be rewritten as

$$\frac{q_2}{T_2} = \frac{-q_1}{T_1} \quad \text{or} \quad \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

i.e.
$$\sum \frac{q}{T} = 0 \qquad \ldots(11.17)$$

Consider any reversible cycle *ABA*. It may be regarded as being made up of a number of Carnot cycles drawn across the diagram as shown in Fig. 11.4. Starting from *A* and going through all the cycles successively from *A* to *B*, it can be shown that all paths inside the closed curve *ABA* cancel each other leaving only the zig-zag outer path. The zigzag path is almost the same as the path *ABA* of the reversible cycle. By making each Carnot cycle smaller and increasing their number, it can be made to match *ABA* more closely. The reversible cycle can be regarded as being constituted of an infinite number of Carnot cycles. For each of these cycles, we have

$$\sum \frac{q}{T} = 0$$

Hence, for an infinite number of Carnot cycles,

$$\sum \frac{\delta q}{T} = 0 \qquad \ldots(11.18)$$

where δq is a very small quantity of the heat absorbed at the temperature T during the small isothermal change of the reversible process.

The above term may be divided into two parts, one for the paths *A* to *B* and the other for the back path *B* to *A*.

Thus,

$$\sum \frac{\delta q}{T} = \sum_{A \to B} \frac{\delta q}{T} + \sum_{B \to A} \frac{\delta q}{T} = 0$$

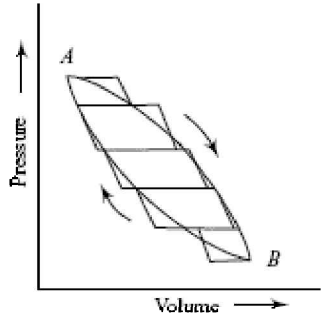


Fig. 11.4 *Carnot cycles drawn across the reversible cycle*

It may be written it as follows:

$$\sum_{A \to B} \frac{\delta q}{T} = -\sum_{B \to A} \frac{\delta q}{T}$$

or

$$\left(\frac{q}{T}\right)_{A \to B} = -\left(\frac{q}{T}\right)_{B \to A} \qquad \ldots(11.19)$$

This means that the total value of the quantity $\frac{q}{T}$ for the path A to B is equal to the total value of quantity $\frac{q}{T}$ for the reverse path B to A.

Thus, ***quantity $\frac{q}{T}$ is a state function, i.e. its value depends only upon the initial state (A) and final state (B) and is independent of the path.*** Obviously, $\frac{q}{T}$ is the change in the value of a quantity or a function having some definite value at A and B depending upon the values of pressure, volume and temperature. This quantity or the function is called ***entropy*** and is usually represented by the symbol s. Thus, if S_A is the value of the entropy at A and S_B is the value at B then we have

$$\frac{q}{T} = S_B - S_A = \Delta S \qquad \ldots(11.20)$$

where, ΔS represents the total change in entropy in going from the state A to the final state B.

Hence, entropy is a state function, the change in the value of which from the initial state to the final state is equal to the quantity $\frac{q}{T}$, i.e. the total heat absorbed reversibly and isothermally in going from the initial state to the final state divided by the absolute temperature at which the heat is absorbed. From Eq. (11.20), the **entropy change** ***may be defined as the quantity of heat absorbed isothermally and reversibly divided by the absolute temperature*** *(T)* ***at which the heat is absorbed.***

Since the derivation of the above result is based upon Carnot cycle in which the heat is absorbed reversibly, therefore the expression (11.20) for the entropy change is valid only when the heat is absorbed reversibly. Thus, it is better to use the symbol q_{rev} in place of q. The expression (11.20) may, therefore, be written as

$$\Delta S = \frac{q_{rev}}{T} \qquad \ldots(11.21)$$

Further, as entropy is a state function, a small change in its value can be represented by **dS.** Hence, we may write.

$$dS = \frac{q_{rev}}{T}$$

Units of Entropy Entropy change is expressed by dividing a heat term by absolute temperature. Therefore, it is expressed in terms of joules per degree Kelvin (JK^{-1}). This is called as entropy unit e.u.

Let us try to understand how we have arrived at the relation $\Delta S = q_{rev}/T$

Whenever heat is added to the system, it increases molecular motion causing increased randomness (entropy) of the system; thus, the heat q has a randomising effect on the system. But we cannot equate DS and q because the distribution of heat also depends upon the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Therefore, heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. Thus, entropy change is directly proportional to the heat added but inversely proportional to the temperature at which it is added. Combining these two effects, we have

$$\Delta S = \frac{q_{rev}}{T}$$

Example 4 *Predict in which of the following processes entropy increases or decreases:*

(a) A liquid crystallises into a solid.

(b) Temperature of crystalline solid is raised from 0 K to 115 K.

(c) The following reactions are carried out:

(i) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(ii) $H_2(g) \rightarrow 2H(g)$

Solution:

(a) Molecules are in more organised state in the frozen (crystalline) state. Hence, entropy decreases.

(b) On raising the temperature, the constituent particles at lattice positions start oscillating. Thus, the entropy increases.

(c) (i) On the reactant side, we have only the solid state while on the product side, we have two substances in the vapour phase also. Vapour state provides greater entropy. Hence, the entropy increases.

(ii) One particle (of H_2 molecule) dissociates to give two particles (of hydrogen atoms). Therefore, entropy increases.

11.4.1 Entropy Change in a Reversible Process

If q_{rev} is the heat absorbed by the system reversibly then the heat lost by the surroundings will also be q_{rev}.

If the process takes place isothermally at the absolute temperature **T** then

1. Entropy change of system is given by

$$\Delta S_{system} = \frac{q_{rev}}{T} \qquad \ldots(11.22)$$

2. Entropy change of the surroundings is given by

$$\Delta S_{surroundings} = \frac{-q_{rev}}{T} \qquad \ldots(11.23)$$

Thus, the total entropy change for the combined system and the surroundings will be

$$\Delta S_{system} + \Delta S_{surroundings} = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \qquad \ldots(11.24)$$

We may conclude that in a reversible process, the net entropy change for the combined system and the surroundings is zero.

11.4.2 Entropy Change in an Irreversible Process

Suppose that the total heat by the surroundings is q_{irrev}. This heat is absorbed by the system but the entropy change of the system does not depend upon the heat actually absorbed but it depends upon the heat absorbed reversibly, i.e. on the quantity q_{rev}. Thus, if the heat is absorbed isothermally by the system at the absolute temperature T, the entropy change of the system is given by

$$\Delta S_{system} - \frac{q_{rev}}{T} \qquad \ldots(11.25)$$

Further, suppose that the loss of heat (q_{irrev}) by the surroundings takes place infinitesimally slowly (because the surroundings are much bigger in size and magnitude compared to the system) i.e. reversibly and isothermally at the temperature T. Then the entropy change of the surroundings is given by

$$\Delta S_{surroundings} = -\frac{q_{irrev}}{T} \qquad \ldots(11.26)$$

The total entropy change for the combined system and the surroundings will, become

$$\Delta S_{system} + \Delta S_{surroundings} = \frac{q_{rev}}{T} - \frac{q_{irrev}}{T} \qquad \ldots(11.27a)$$

We know that the work done in a reversible process is the maximum work, i.e.

$$w_{rev} > w_{irrev} \qquad \ldots(11.27b)$$

Further, as the internal energy (U) is the state function, the value of ΔU is the same whether

the process is carried out reversibly or irreversibly. Therefore,

$$\Delta U = q_{rev} - w_{rev} = q_{irrev} - w_{irrev} \quad \ldots(11.28)$$

Combining results (11.27b) and (11.28), we come to the conclusion

$$q_{rev} > q_{irrev} \quad \text{or} \quad \frac{q_{rev}}{T} > \frac{q_{irrev}}{T}$$

$$\frac{q_{rev}}{T} - \frac{q_{irrev}}{T} > 0 \quad (11.28a)$$

From (11.27b) and (11.28a) we have,

$$\Delta S_{system} + \Delta S_{surroundings} > 0 \quad (11.29)$$

Thus, it may be concluded that in an irreversible process, the ***entropy change for the combined system and the surroundings is greater than zero, i.e. an irreversible process is accompanied by net increase of entropy.***

Since all spontaneous processes are thermodynamically irreversible it may be stated that

All spontaneous processes are accompanied by a net increase of entropy.

11.4.3 Clausius Inequality

For an irreversible process, we may write

$$\Delta S_{system} + \Delta S_{surroundings} > 0$$

or

$$\Delta S_{system} > -\Delta S_{surroundings} \quad \ldots(11.30)$$

It q_{irrev} is the heat change in surroundings at the temperature T then

$$\Delta S_{surroundings} = -\frac{q_{irrev}}{T} \quad \ldots(11.31)$$

Substituting this value in (11.30) above, we get,

$$\Delta S_{system} > \frac{q_{irrev}}{T} \quad \ldots(11.32)$$

If the change in entropy is small, Eq. (11.3i) can be written as,

$$dS_{system} > \frac{q_{irrev}}{T} \quad \ldots(11.33)$$

Expressions (11.3i) and (11.33) are known as Clausius inequality. Clausius assumed that the universe could be taken as an isolated system in which all naturally occurring processes are irreversible.

Entropy of the Universe is Increasing All the processes occurring in nature are thermodynami-cally irreversible and these are accompanied by increase of entropy. Hence, it may be concluded that *the entropy of the universe is continuously increasing.*

Thus, the main ideas of the first and the second law of thermodynamics may be summed up as follows:

The energy of the universe is constant whereas the entropy of the universe is continuously

increasing and tends to a maximum value.

11.5 ENTROPY CHANGE FOR AN IDEAL GAS UNDER DIFFERENT CONDITIONS

Consider one mole of an ideal gas enclosed in a cylinder fitted with a fractionless piston. If a small amount of heat δq_{rev} is supplied to the system reversibly and isothermally at the temperature T then the entropy change accompanying the process is given by

$$\delta S = \frac{\delta q_{rev}}{T} \qquad \ldots(11.34)$$

According to the first law of thermodynamics, for an infinitesimal process,

$$\delta q = dE + \delta W \qquad \ldots(11.35)$$

If the process is carried out reversibly, Eq. (11.35) may be written as

$$\delta q_{rev} = dE + \delta W \qquad \ldots(11.36)$$

Also, if the work is restricted to the work of expansion,

$$\delta W = PdV \qquad \ldots(11.37)$$

where, δV is the small increase in volume and P is the pressure of system. Putting the value of dw from Eq. (11.37) in Eq. (11.36), we get

$$\delta q_{rev} = dE + PdV \qquad \ldots(11.38)$$

Substituting, this value in Eq. (11.34) we get,

$$dS = \frac{dE + PdV}{T}$$

or it may be written as,

$$TdS = dE + PdV \qquad \ldots(11.39)$$

For 1 mole of an ideal gas, we know that

$$C_V = \frac{dE}{dT}$$

i.e. $$dE = C_V dT \qquad \ldots(11.40)$$

where C_V is the molar heat capacity at constant volume and

$$PV = RT$$

i.e. $$P = \frac{RT}{V} \qquad \ldots(11.41)$$

where V is the volume of the system at the temperature T and pressure P, and R is the gas

constant. Substituting the values of dE and P from Eq. (11.40) and (11.41) in Eq. (11.39), we get.

$$TdS = C_V dT + \frac{RT}{V} dV$$

or
$$dS = C_V \frac{dT}{T} + R \frac{dV}{V} \qquad \ldots(11.42)$$

If the volume changes from V_1 to V_2 when the temperature changes from T_1 to T_2 then the entropy change accompanying the complete process is given by the equation

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} R \frac{dV}{V} \qquad \ldots(11.43)$$

Assuming that C_V remains constant in the temperature range T_1 to T_2, Eq. (11.43) may be put as

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \qquad \ldots(11.44)$$

With the help of this equation, we can calculate the entropy change of 1 mole of an ideal gas accompanying a process when temperature changes from T_1 to T_2 and the volume changes from V_1 to V_2.

Further for 1 mole of an ideal gas, we may write

$$P_1V_1 = RT_1 \text{ for the initial state} \qquad \ldots(11.45)$$

and
$$P_2V_2 = RT_2 \text{ for the final state} \qquad \ldots(11.46)$$

Dividing Eq. (11.46) by Eq. (11.45), we have

$$\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1}$$

or
$$\frac{V_2}{V_1} = \frac{T_2P_1}{T_1P_2} \qquad \ldots(11.47)$$

Substituting this value in Eq. (11.44), we get

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{T_2P_1}{T_1P_2} \qquad \ldots(11.48)$$

Also, we have the relation,

$$C_P - C_V = R \quad \text{or} \quad C_V = C_P - R$$

Putting this value in Eq. (11.48), we get

$$\Delta S = (C_P - R) \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2}$$

$$= C_P \ln \frac{T_2}{T_1} - R \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

or
$$\Delta S = C_P \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \quad \ldots(11.49)$$

This equation gives the entropy change of 1 mole of an ideal gas during a process when temperature changes from T_1 to T_2 and pressure changes from P_1 to P_2.

1. If temperature is kept constant ***(isothermal process),***

$$T_1 = T_2$$

Equations (11.44) and (11.49) are reduced to

$$\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2} \quad \ldots(11.50)$$

2. If pressure is kept constant ***(isobaric process)***

$$P_1 = P_2$$

Equation (11.49) is reduced to

$$\Delta S = C_P \ln \frac{T_2}{T_1} \quad \ldots(11.51)$$

3. If volume is kept constant ***(isochoric process)***

$$V_1 = V_2$$

Equation (11.44) converts to

$$\Delta S = C_V \ln \frac{T_2}{T_1} \quad \ldots(11.52)$$

Another Derivation for Change in Entropy The equation $\Delta S = R \ln \frac{V_2}{V_1}$ Eq. (11.50) for isothermal process can also be obtained using the Boltzmann equation

$$S = k \ln W \quad \ldots(11.53)$$

where k is the Boltzmann constant and W is the number of energetically equivalent different ways the molecules in a system can be arranged. We shall explain it with the help of the process shown in Fig. 11.5.

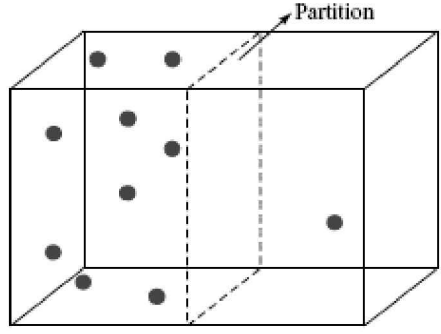


Fig. 11.5 *Rapidly moving gas molecules which were restricted to a portion of the container spread out spontaneously to fill the whole container when the partition is removed.*

Before the removal of the partition, each molecule had a particular location somewhere in the left of the container. We imagine that each side of the container is divided into a number of cells (with equal smaller volumes). In the simplest case, when we have just one molecule in the box, the number of possible locations of the molecule is equal to the number of cells, X. If the system contains two molecules, the number of possible arrangements W will become X^2. Every time we increase the number of molecules by one, the number of arrangements increases by a factor equal to the number of the cell. Thus, for N molecules in the container, the number of arrangements in the system will be given by the relation

$$W = X^N \qquad \ldots(11.53a)$$

Change in entropy ΔS of a system may be written as

$$\Delta S_{sys} = S_{final} - S_{initial} \qquad \ldots(11.53b)$$

Using Eq. (11.53b) above, we may write

$$\Delta S_{sys} = k \ln W_{final} - k \ln W_{initial} = k \ln \frac{W_{final}}{W_{initial}} \qquad \ldots(11.54)$$

Combining this result with Eq. (11.53a), we have

$$\Delta S_{sys} = k \ln \frac{(X_{final})^N}{(X_{initial})^N} = k \ln \left[\frac{X_{final}}{X_{initial}}\right]^N = k N \ln \frac{X_{final}}{X_{initial}} \qquad \ldots(11.55)$$

X is the number of cells, with volume of each cell taken as v. Total volume of the system is given by

$$V = Xv \quad \text{or} \quad X = \frac{V}{v} \qquad \ldots(11.56)$$

Combining Eqs (11.55) and (11.56), we have
We have

$$\Delta S_{sys} = kN \ln \frac{V_{final}/2}{V_{initial}/2} = kN \ln \frac{V_{final}}{V_{initial}} \quad \ldots(11.57)$$

We have the relation

$$k = \frac{R}{N_A} \quad \ldots(11.58)$$

When we have *one mole* of the gas $N_A = N$, Eq. (11.58) reduces to

$$k = \frac{R}{N} \quad \ldots(11.59)$$

From (11.57) and (11.59),

$$\Delta S_{sys} = R \ln \frac{V_{final}}{V_{initial}} \quad \ldots(11.60)$$

If V_1 is the initial volume and V_2 is the final volume, we have

$$\Delta S_{sys} = R \ln \frac{V_2}{V_1} \quad \ldots(11.61)$$

We get the same equation, i.e. Eq. (11.50) which was derived by using the relation $\delta S = \delta q_{rev}/T$

Entropy Change During Phase Change

A phase change involves one of the following:

1. Melting of solid into liquid and freezing of liquid into solid
2. Boiling of liquid into vapour and condensation of vapour into liquid

1. Entropy of Melting

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

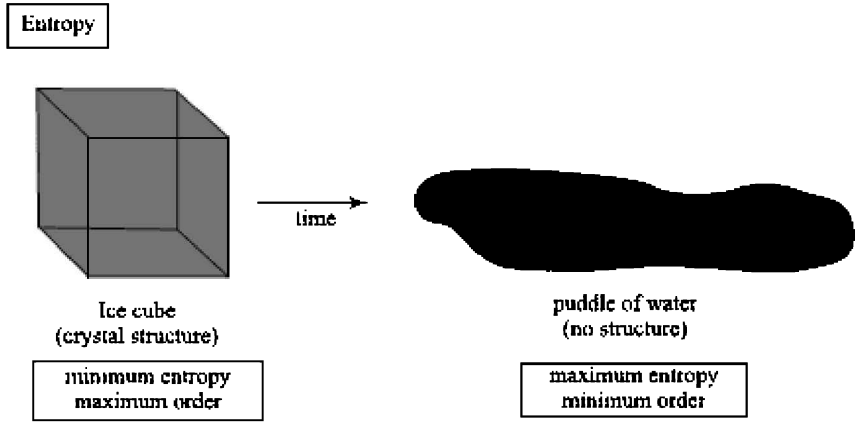


Fig. 11.6 *Increase in entropyin the melting of ice to water*

where, ΔH_m is the latent heat of melting and T_m is the melting temperature.

2. Entropy of Vaporisation

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

where ΔH_V is the latent heat of vaporisation and T_b is the boiling temperature.

Processes like melting and evaporation involve absorption of heat which is taken as positive by sign convention; therefore ΔS for these processes is positive, i.e., these processes are accompanied by ***increase of entropy.*** On the other hand, the reverse processes like freezing and condensation involve ***evolution of heat*** which is taken as negative. Therefore, for these processes ΔS is ***negative,*** i.e. these processes are accompanied by ***decrease of entropy***

Example 5 *Calculate the entropy change for the fusion of 1 mole of a solid which melts at 300 K. The latent heat of fusion is 2.51 kJ mot*^{1}.

Solution: Given that

$$\Delta H_m = 2510 \text{ J mol}^{-1}$$
$$T_m = 300 \text{ K}$$

$$\therefore \quad \Delta S = \frac{\Delta H_m}{T_m} = \frac{2510}{300} = 8.37 \text{ JK}^{-1}\text{mol}^{-1}$$

Example 6 *Calculate the entropy change for the isothermal reversible expansion of 5 moles of an ideal gas from a volume of 100 litres at 300 K.*

Solution: We have the following expression for ΔS in terms of temperature and volume:

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \text{ for 1 mole of an ideal gas}$$

For isothermal process, $T_1 = T_2$

$\therefore$ $$\Delta S = R \ln \frac{V_2}{V_1} \quad \text{for 1 mole of an ideal gas}$$

and $$\Delta S = nR \ln \frac{V_2}{V_1} \quad \text{for '}n\text{' moles of an ideal gas}$$

or $$\Delta S = 2.303\, nR \log \frac{V_2}{V_1}$$

Given that, $n = 5$ $\quad V_1 = 10$ litres $\quad V_2 = 100$ litres $\quad R = 8.314\ \text{JK}^{-1}\text{mol}^{-1}$

$$\Delta S = 2.303 \times 5 \times 8.314 \times \log \frac{100}{10}$$

$$= \mathbf{95.75\ JK^{-1}mol^{-1}}$$

Example 7 *Calculate the increase in entropy in the evaporation of 1 mole of water at 373 K. Latent heat of vaporisation of water is 2.26 KJ/g (molecular mass of water = 18)*

Solution:

Given that

$$T_1 = 373\ \text{K}$$

$$\Delta H_v = 2260\ \text{J}^{-1}\text{g} = 2260 \times 18\ \text{J mol}^{-1} = 40680\ \text{J mol}^{-1}$$

$$\Delta S = \frac{\Delta H_v}{T_b} = \frac{40680}{373} = 109\ \text{JK}^{-1}\text{mol}^{-1}$$

Example 8 *100 g of ice at 0°C was added to an insulated beaker containing 150 g of water at 100°C. Calculate*

(a) The final temperature of the system (b) The entropy change of the process

Heat of fusion of ice is 80 cal/g and heat capacity of water is 1.0 cal/g degree (ignore the heat capacity of the beaker).

Solution:

(a) Let the final temperature after mixing be t°C.

Heat lost by water = $150 \times (100 - t)$ cal

Heat gained by ice = $100 \times 80 + 100 = (t - 0)$
$= 8000 + 100\,t$ cal

Heat gained = Heat lost

$8000 + 100\,t = 150(100 - t)$ or t=28°C

(b) The process involves the following steps:

(i) 100 g of ice melts at 0°C to give 100 g of liquid water.

(ii) 100 g of liquid water gets heated up from 0°C to 28°C.

(iii) 150 g of water gets cooled from 100°C to 28°C.

When temperature remains constant (i.e. for isothermal process), $\Delta S = \frac{q_{rev}}{T}$.

When temperature varies (but volume and pressure remains constant), $\Delta S = C \ln \frac{T_2}{T_1}$, where C is C_V or C_p.

$$\text{Entropy change in } \textit{Step (i)} = \frac{(100\text{ g}) \times (80\text{ cal/g})}{273} = \frac{8000}{273} = 29.30\text{ cal deg}^{-1}$$

$$\text{Entropy change in } \textit{Step (ii)} = (100\text{ g})(1\text{ cal/g}) \times 2.303 \times \log \frac{28+273}{0+273}$$

$$= 230.3 \log \frac{301}{273}$$

$$= 230.3 \times 0.0424 = 9.765\text{ cal deg}^{-1}$$

$$\text{Entropy change in Step (iii)} = (150\text{ g}) \times (1\text{ cal/g}) \times 2.303 \log \frac{28+273}{100+273}$$

$$= 345.45 \log \frac{301}{373}$$

$$= 345.45 \times (-0.0931) = -32.16\text{ cal deg}^{-1}$$

$\therefore$ net entropy change in the process is given by $= 29.30 + 9.765 - 32.16$

$$= 6.905\text{ cal deg}^{-1}$$

Example 9 *Calculate the temperature at which the reaction,*

$Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2} O_2(g)$ *at 1 atmospheric pressure will be in equilibrium. The values of ΔH and ΔS for the reaction are 30.58 kJ and 66.11 JK^{-1} respectively and these values do not change much with temperature.*

Solution: For a reaction in equilibrium,

$$\Delta S = \frac{\Delta H}{T}$$

Given that,

$$\Delta H = 30.58\text{ kJ} = 30580\text{ J} \quad \text{and} \quad \Delta S = 66.11\text{ JK}^{-1}$$

Substituting the values in above equation we have

$$66.11 = \frac{30580}{T} \quad \text{or} \quad \mathbf{T = 462.6\ K}$$

Example 10 *For the oxidation of iron*

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Entropy change is −549.4 JK^{-1}mol^{-1} at 298 K. In spite of negative entropy change of this reaction, why is the reaction spontaneous?

(ΔH° for this reaction is −164.8 × 10^3 J mol^{-1})

Solution: One decides the spontaneity of a reaction by considering

ΔS_{total} (i.e. $\Delta S_{sys} + \Delta S_{surr}$). For calculating Δs_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta H°$. At temperature T_1, the entropy change of the surroundings is given by

$$\Delta S_{surr} = -\frac{\Delta H°}{T} = \frac{-(-164.8 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}} = 5530 \text{ JK}^{-1} \text{ mol}^{-1}$$

Total entropy change for the reaction is

$$\Delta S_{total} = 5530 \text{ JK}^{-1} \text{ mol}^{-1} + (-549.4 \text{ JK}^{-1} \text{ mol}^{-1}) = 4980.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

Thus, the total change in entropy is positive
That is why the reaction takes place spontaneously.

PROBLEMS FOR PRACTICE

1. For the reaction $H_2O(l) \rightarrow H_2O(g)$

$$\Delta H = 9710 \text{ cal mol}^{-1}, P = 1 \text{ atm}, \Delta S = 26 \text{ cal deg}^{-1}\text{mol}^{-1}$$

find out the temperature at which liquid water and water vapour at 1 atmospheric pressure are in equilibrium.

[Ans. 100.46°C]

2. Calculate the entropy change involved in the conversion of 1 mole of ice at 273 K to water at the same temperature. Latent heat of fusion of ice is 335 joules per gram.

[Ans. 22.1 JK^{-1}]

3. Calculate the entropy change when 1 mole of solid SO_2 melts at –76°C. The latent heat of fusion is 1769 cal mol^{-1}.

[Ans. 8.98 cal $K^{-1}mol^{-1}$]

4. Calculate the entropy change when 2 moles of an ideal gas are allowed to expand from a volume of 1.0 litres to a volume of 10.0 litres at 27°C.

[Ans. 38.29 $JK^{-1}mol^{-1}$]

5. Calculate the change in entropy when 40 g of water at 50°C are mixed with 80 g of water at −20°C

[Ans. 0.12 cal deg^{-1}]

6. For a certain ideal gas, $C_P = \frac{5}{2} R$ joules mol^{-1} Meg^{-1}. Calculate the change in entropy suffered by 3 moles of a gas on being heated from 300 K to 600 K at (a) constant pressure, and (b) constant volume.

[Ans. (a) 43.2 JK^{-1} (b) 25.9 JK^{-1}]

7. One mole of an ideal gas expands from a volume of 5 dm^3 to a volume of 60 dm^3 in an isothermal reversible process at 300 K. Calculate the entropy change during the process. (R = 8.314 JK^{-1} mol^{-1}).

[Ans. 20.67 JK^{-1} mol^{-1}]

8. A heated copper block at 130°C loses 340 J of heat to the surrounding which are at room temperature of 32°C. Calculate

(a) entropy change of copper block

(b) entropy change of the surroundings

(c) total entropy change of the universe due to this process. Assume, that the temperature of the block and the surroundings remain constant.

[Ans. (i) 0.84 JK^{-1} (ii) +1.11 JK^{-1} (iii) +0.27 JK^{-1}]

9. 1 g. of ice at 0°C is added to 10 g of water at boiling point. What will be the final temperature and what is the entropy change accompanying this process? Assume that the heat of fusion of ice is 80 cal/g and the specific heat of water is 1 cal/degree.

[Ans. t = 83.6°C, ΔS = 0.11 cal deg^{-1}]

11.5.2 Physical Significance of Entropy

1. Entropy as a Measure of Disorder of the System Various processes which are accompanied by a net increase of entropy are associated with an increased randomness of distribution. The following examples are cited.

(a) The Melting of a Solid is accompanied by a net increase of entropy. We know that the molecules, atoms or ions in a solid have fixed positions and they become free to move about in the molten state. This is expressed by saying that there is no ***disorder*** among the molecules, atoms or ions in a solid but the disorder sets in when the solid changes into liquid. In other words, we can say that the ***randomness*** has increased.

(b) The Vaporisation of a Liquid is accompanied by a net increase of entropy. The disorder or randomness also increases because the molecules of vapour are more random than the molecules in the liquid.

Thus, ***Entropy is a measure of randomness or disorder of the system.***

This concept may be further understood with the help of the following analogy.

In a college when all classes are being held, all the students are sitting in their respective classrooms seriously and the disorder is minimum. As soon as the bell goes, the students of different classes move out to go to other rooms and disorder sets in. In other words, the disorder or the randomness increases.

(b) Entropy as a Measure of Probability All spontaneous processes lead to increase in entropy and increase in disorder. It means when a process is spontaneous, it is proceeding from a less probable to a more probable state. Thus, there is a close relationship between entropy S and probability W of the state of the system. The relationship between the two was given by Boltzmann as

$$S = k \ln W$$

Here, k is Boltzmann constant (R/N_A).

At absolute zero temperature, a solid is considered to be in the most ordered state. Here, W = 1 and hence S_o = 0. The entropy of the crystalline solids at absolute zero temperature is, therefore, taken as zero.

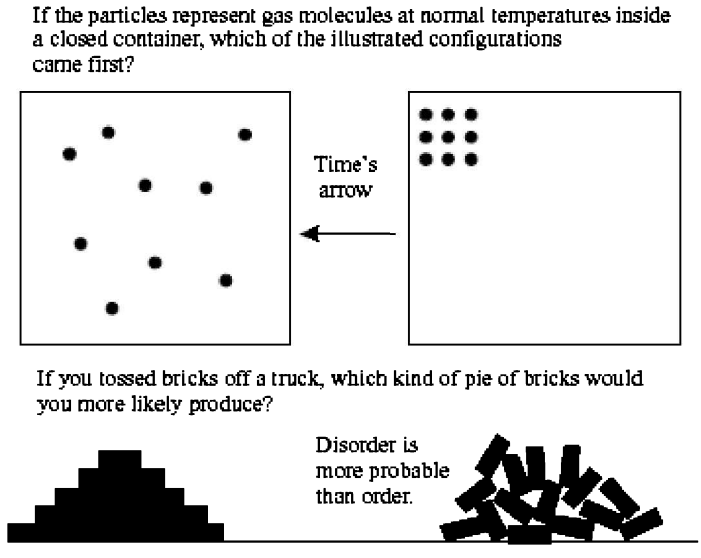


Fig. 11.7 *Illustration of the concept of entropy*

Example 11 *Write the expression for the efficiency of Carnot cycle in terms of work done, heat absorbed and temperatures of source and sink.*

Solution:

$$\eta = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

where, w = Net work done

q_2 = Total heat absorbed

$q_2 - q_1$ = Net heat absorbed ($\therefore w = q_2 - q_1$)

T_2 = Temperature of source

T_1 = Temperature of sinks

Example 12 *Can the efficiency of a heat engine be greater than unity? If not, why?*

Solution: $\eta = \frac{T_2 - T_1}{T_2}$; Efficiency ($\eta$) cannot be greater than unity because temperature of sink (T_1) has to be less than the temperature of the source (T_2)

Example 13 *Which of the following has the higher value of S?*

(a) CO_2 at 15°C, 1 atm or dry ice at 1 atm

(b) A coiled spring or spring relaxed.

(c) 1 g of liquid water at 25°C, or 1 g of water vapour at 25°C.

(d) Silica glass or quartz (crystalline silica)

Solution:

(a) CO_2 at 15°C because gas is more random than solid.

(b) A relaxed spring is more random.

(c) Water vapour has greater randomness than liquid water.

(d) Silica is more random than quartz because in former SiO_4 tetrahedra are random, while in the latter, they are arranged in perfect order.

Example 14 *Write the expression for the entropy change in the following cases:*

(a) Temperature change from T_1 to T_2 and volume changes from V_1 to V_2 for 1 mole of an ideal gas.

(b) Temperature change from T_1 to T_2 and pressure changes from p_1 to p_2 for 1 mole of an ideal gas.

(c) 1 mole of a solid melts at the melting point.

(d) 1 mole of a liquid of a liquid vaporises at the boiling point.

Solution:

(a) $\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

(b) $\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$

(c) $\Delta_{fus} S = \frac{\Delta_{fus} H}{T_f}$

(d) $\Delta_{vap} S = \frac{\Delta_{vap} H}{T_b}$

Example 15 *In the following processes, state whether the entropy of the system increases, decreases or remains constant.*

(a) Vaporisation of a mole of water into steam at its boiling point

(b) Solidification of a mole of liquid at its freezing point.

(c) Isothermal compression of a liquid.

(d) Separation of a mixture into its two constituents.

Solution:

(a) Entropy increases

(b) Entropy decreases

(c) Entropy remains almost constant

(d) Entropy decreases.

Example 16 *Is it possible to construct a reversible heat engine of unit efficiency? Give detailed reason for any answer.*

Solution: $\eta = \frac{T_2 - T_1}{T_2}$ For, η to be equal to unity, T_1 should be 0 K, i.e., temperature of the sink should be zero degree absolute which is not practicable. Hence, it is not possible to construct a reversible heat engine of unit efficiency.

Example 17 *How can the efficiency of a Carnot engine be increased?*

Solution: $\eta = \frac{T_2 - T_1}{T_2}$. Hence, to increase the efficiency of the heat engine, the temperature of the sink (T_1) should be minimum possible for a particular temperature of the source (T_2).

Example 18 *Select the most random system of the following:*

(a) Sugar cubes in the box

(b) Sugar cubes scattered on a table

(c) Sugar dissolved in water

(d) Finely powdered sugar

Solution: Sugar dissolved in water is the most random system because the molecules are free to move about the solution.

Example 19 *What is the basis of the thermodynamic scale of temperature? Why is it more basic than that based on perfect or ideal gas?*

Solution: The thermodynamic scale of temperature, as defined on the basis of the second law of thermodynamics, is more basic than based on the ideal gas. This is because it is independent of the working substance.

Example 20 *Tell which will have greater entropy in each of the following cases. Justify your answer.*

(a) Magnetised iron pieces or nonmagnetised piece of iron.

(b) A mole of gas contained in a vessel of one litre capacity or that contained in a vessel of two-litre capacity.

(c) A mole of $CaCO_3(s)$ or a system containing one mole of each $CaO_{(s)}$ and $CO_2(g)$.

Solution:

(a) Nonmagnetised piece of iron.

(b) A mole of gas contained in a vessel of 2-litre capacity has greater randomness and hence greater entropy.

(c) One mole of CaO + CO_2 will have greater entropy because the gas has greater randomness.

Example 21 *Justify the 'Second law of Thermodynamics' which states that "The net entropy of the universe tends to increase."*

Solution: All spontaneous processes occurring in nature are thermodynamically irreversible and every irreversible process is accompanied by increase in entropy. Hence, entropy of the universe is continuously increasing.

11.6 ENTROPY CHANGE ON MIXING OF IDEAL GASES

Let us suppose at constant temperature, n_1 moles of an ideal gas 1 at the initial pressure $P°_1$ are mixed with n_2 moles of another ideal gas 2 at initial pressure P°. After mixing, let their partial pressures in the mixtures be $\mathbf{P_1}$ and $\mathbf{P_2}$ respectively. We know, at constant temperature, the entropy change of an ideal gas when its pressure changes from initial pressure P_i to final pressure P_f is given by,

$$\Delta S = R \ln \frac{P_i}{P_f} \text{ mol}^{-1}$$

∴. Entropy change of the first gas when the pressure of n_1 moles of the gas changes from $P°_1$ to P_1 is given by

$$\Delta S_1 = n_1 R \ln \frac{P°_1}{P_1} \qquad \ldots(11.62)$$

Similarly, entropy change of the second gas when pressure of n_2 moles of the gas changes from $P°_2$ to P_2 is given by,

$$\Delta S_2 = n_2 R \ln \frac{P°_2}{P_2} \qquad \ldots(11.63)$$

Total entropy change on mixing the two gases will be the sum of the above two changes.

$$\Delta S_{\text{mixing}} = n_1 R \ln \frac{P°_1}{P_1} + n_2 R \ln \frac{P°_2}{P_2} \qquad \ldots(11.64)$$

Let P be the total pressure of the mixture. Then, $P = P_1 + P_2$

Further, let x_1 and x_2 be the mole fractions of gases 1 and 2 in the mixture. By Dalton's law of partial pressures,

$$P_1 = x_1 P \quad \text{and} \quad P_2 = x_2 P$$

Substituting these values in Eq. (11.64), we get,

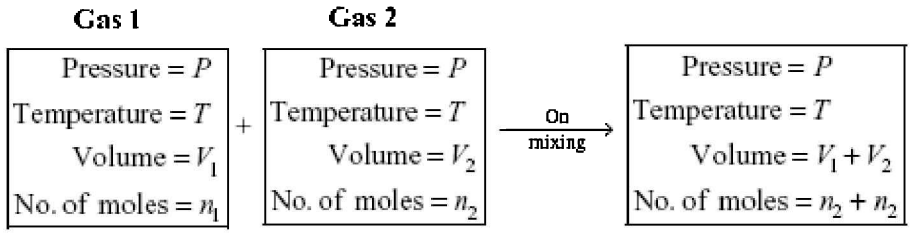
$$\Delta S_{\text{mixing}} = n_1 R \ln \frac{P°_1}{x_1 P} + n_2 R \ln \frac{P°_2}{x_2 P} \qquad \ldots(11.65)$$

Take the simplest case in which each gas is taken at the same initial pressure. Under these conditions, after mixing, the volume of mixture will be the sum of their initial volumes, i.e. $V = V_1 + V_2$. And final pressure of the mixture will be nearly the same as initial pressure of each gas, i.e. $P°_1 = P°_2 = P$ as shown in the diagram below. Equation (11.65) then is simplified to

$$\Delta S_{\text{mixing}} = -n_1 R \ln x_1 - n_2 R \ln x_2$$

or

$$\Delta S_{\text{mixing}} = -R(n_1 \ln x_1 + n_2 \ln x_2) \qquad \ldots(11.66)$$



For a mixture of a number of gases, Eq. (11.66) can be written in the general forms as under:

$$\boxed{\Delta S_{\text{mixing}} = -R\sum n_i \ln x_i} \qquad \ldots(11.67)$$

Entropy change for 1 mole of the mixing is obtained by dividing Eq. (11.66) by $(n_1 + n_2)$

$$\Delta S_{\text{mixing}} = -R\left(\frac{n_1}{n_1+n_2}\ln x_1 + \frac{n_2}{n_1+n_2}\ln x_2\right)$$

or
$$\Delta S_{\text{mixing}} = -R(x_1 \ln x_1 + x_2 \ln x_2) \qquad \ldots(11.68)$$

which can be generalised to the form

$$\boxed{\Delta S_{\text{mixing}} = -R\sum x_i \ln x_i} \qquad \ldots(11.69)$$

Conclusions We make the following conclusions from the above equations

1. ΔS_{mixing} is independent of the temperature.
2. As $x_i < 1$, ΔS_{mixing} will always be positive, i.e. mixing of gases is accompanied by increase in entropy.

Example 22 *Calculate the molar entropy change of mixing 0.2 mole of oxygen and 0.6 mole of nitrogen at 25°C assuming that they are gases.*

Solution: $n_1 = 0.2$ mole, $n_2 = 0.6$ mole

$$\therefore \quad x_1 = \frac{0.2}{0.8} = 0.25,\ x_2 = \frac{0.6}{0.8} = 0.75$$

$$\therefore \quad \begin{aligned}\Delta S_{\text{mixing}} &= -R(x_1 \ln x_1 + x_2 \ln x_2)\\ &= -2.303\, R(x_1 \log x_1 + x_2 \log x_2)\\ &= -2.303 \times 8.314(0.25 \log 0.25 + 0.75 \log 0.75)\\ &= +2.303 \times 8.314 \times 0.2443\ \text{JK}^{-1}\text{mol}^{-1}\\ &= \mathbf{4.678\ JK^{-1}mol^{-1}}\end{aligned}$$

11.7 HELMHOLTZ FREE ENERGY

One more thermodynamic quantity which is used in the study of thermodynamics is called ***work function or Helmholtz free energy.***

This is denoted by A and is defined by the equation,

$$A = U - TS \qquad \ldots(11.70)$$

where U is internal energy of the system, T is temperature and S is entropy.

Since, U, T and S are the functions of the state of the system only and do not depend upon its previous history, therefore, A also must be a state function.

In order to understand the physical significance of the work function, consider an isothermal change taking place at temperature T. Then

$$A_1 = U_1 - TS_1 \quad \text{for initial state}$$

and

$$A_2 = U_2 - TS_2 \quad \text{for final state} \qquad \ldots(11.71)$$

where A_1, U_1 and S_1 are respectively the values of work function, internal energy and entropy of the system in the initial state and A_2, U_2 and S_2 are the corresponding values in the final state.

$\therefore$ Change in the function A accompanying the process is given by,

$$A_2 - A_1 = (U_2 - TS_2) - (U_1 - TS_1)$$

$$= (U_2 - U_1) - T(S_2 - S_1) \qquad \ldots(11.72)$$

or

$$\Delta A = \Delta U - T\Delta S$$

According to the definition of entropy,

$$\Delta S = \frac{q_{rev}}{T} \qquad \ldots(11.73)$$

According to the first law of thermodynamics as applied to an isothermal reversible process, we have

$$\Delta U = q_{rev} - w_{max} \qquad \ldots(11.74)$$

Substituting the values of ΔS and ΔU from equations (11.73) and (11.74) in Eq. (11.72), we get,

$$\Delta A = (q_{rev} - w_{max.}) - T\frac{q_{rev}}{T}$$

or

$$-\Delta A = w_{max} \qquad \ldots(11.75)$$

Thus, for a process occurring at constant temperature, the decrease in the work function A is equal to the maximum work done by the system. It is for this reason that the thermodynamics quantity has been termed work function.

11.8 GIBBS FREE ENERGY (OR GIBBS ENERGY)*

Another thermodynamic quantity is Gibbs free energy. This is usually denoted by G and is defined by the equation,

$$G = H - TS \qquad \ldots(11.76)$$

where, H, T and S are the heat constant, temperature and entropy of the system respectively. Since H, T and S are the functions of state only, therefore, G is also a function of state of the system only. Hence, for the isothermal process occurring at the temperature T, we can write,

$$G_1 = H_1 - TS_1 \quad \text{for the initial state} \qquad \ldots(11.77a)$$

or
$$G_2 = H_2 - TS_2 \quad \text{for the final state} \qquad \ldots(11.77b)$$

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$
$$= (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \qquad (11.78)$$

ΔG = Change in Gibbs free energy of the system

ΔH = Enthalpy change of the system

and ΔS = Entropy change of the system

Units of Gibbs Energy Change ΔG has the units of energy because both ΔH and $T\Delta S$ are energy terms since $T\Delta S = (K)\ (J/K) = J$.

The physical significance of Gibbs free energy may be understood as follows:

At constant temperature (T),

$$\Delta S = \frac{q_{rev}}{T}$$

i.e.
$$T\Delta S = q_{rev} \qquad \ldots(11.79)$$

At constant pressure (P).

$$\Delta H = \Delta U + P\Delta V \qquad \ldots(11.80)$$

*IUPAC recommends the name Gibbs energy for Gibbs free energy.)

Substituting the values of $T\Delta S$ and ΔH from equations (11.79) and (11.80) in Eq. (11.78), we get,

$$\Delta G = (\Delta U + P\Delta V) - q_{rev}$$
$$= (\Delta U - q_{rev}) + P\Delta V \qquad \ldots(11.81)$$

According to the first law of thermodynamics,

$$\Delta U = q_{rev} - w_{max} \text{ (work done by the system carries negative sign)}$$

or
$$\Delta U - q_{rev} = -w_{max}$$

Substituting these values in Eq. (11.81), we get,

$$\Delta G = -w_{max} + P\Delta V$$
$$\Delta G = w_{max} - P\Delta V$$

But, $P\Delta V$ is the *work of expansion* done by the system corresponding to increase in volume ΔV. Hence, $(w_{max} - P\Delta V)$ gives the maximum work other than the work of expansion. This is called maximum useful work available from the process. We conclude that ***for a process occurring at constant temperature and constant pressure, the decrease in Gibbs free energy is equal to the*** *maximum useful work* ***obtainable from the process, i.e. the total work minus the pressure volume work (or work of expansion).***

Variation of Work Function with Temperature and Volume The work function is given by the equation

$$A = U - TS \qquad \ldots(11.82)$$

Complete differentiation of this equation gives

$$dA = dU - TdS - SdT \quad \ldots(11.83)$$

Entropy change is given by,

$$dS = \frac{\delta q_{rev}}{T} \quad \ldots(11.84)$$

From the first law of thermodynamics,

$$\Delta q_{rev} = dU - \delta w \quad \ldots(11.85)$$

and if the work is restricted to the work of expansion only,

$$-\delta w = PdV \quad \ldots(11.86)$$

Putting this value in Eq. (11.85), we get,

$$\delta q_{rev} = dU + PdV \quad \ldots(11.87)$$

Putting this value in Eq. (11.84), we get,

$$dS = \frac{dU + PdV}{T}$$

$$TdS = dU + PdV \quad \ldots(11.88)$$

Putting this value in Equation (11.83), we obtain

$$dA = dU - dU - PdV - SdT$$

$$= -PdV - SdT \quad \ldots(11.89)$$

(a) If temperature is kept constant, $dT = 0$, Eq. (11.89) takes the form

$$(dA)_T = -(PdV)_T \quad \ldots(11.90)$$

or

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \ldots(11.91)$$

(b) If volume is kept constant, $dV = 0$, Equation (11.89) becomes,

$$(dA)_V = -(SdT)_V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \ldots(11.92)$$

Thus, variation of work function with temperature and volume is given by equations (11.91) and (11.92).

11.8.1 Variation of Gibbs Free Energy with Temperature and Pressure

The free energy is given by the equation

$$G = H - TS \quad \ldots(11.93)$$

But $$H = U + PV \quad \ldots(11.94)$$

Substituting this value in Eq. (11.93), we get

$$G = U + PV - TS \quad \ldots(11.95)$$

Complete differentiation of the equation gives,

$$dG = dU + PdV + VdP - TdS - SdT \quad \ldots(11.96)$$

but $$dS = \frac{\delta q_{rev}}{T} = \frac{dU + PdV}{T}$$

or $$TdS = dU + PdV \quad \ldots(11.97)$$

Substituting this value in Eq. (11.97), we get,

$$dG = dU + PdV + VdP - (dU + PdV) - SdT = VdP - SdT$$

i.e. $$dG = VdP - SdT \quad \ldots(11.98)$$

This expression gives the change in free energy with the change in pressure and change in temperature in a reversible process. Equation (11.98) is called ***total differential equation.***

(b) If temperature is kept constant, $dT = 0$, Eq. (11.98) takes the form,

$$(dG)_T = (VdP)_T \quad \ldots(11.99)$$

or $$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \ldots(11.100)$$

(c) If pressure is kept constant, $dP = 0$, Eq. (11.98) becomes,

$$(dG)_P = -(SdT)_P$$

or $$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \ldots(11.101)$$

Thus, variation of free energy with pressure and temperature is given by Eqs (11.100) and (11.101) respectively.

11.8.2 Change in Free Energy for a Process Under Isothermal Condition

The change in free energy for a complete process under isothermal conditions can be obtained as under: For an infinitesimal change, under isothermal conditions, we have the equation

$$(dG)_T = VdP \quad \ldots(11.102)$$

For a complete process, under isothermal conditions, when pressure changes from P_1 to P_2, we have,

$$(\Delta G)_T = \int_{P_1}^{P_2} VdP \quad \ldots(11.103)$$

For 'n' moles of an ideal gas, $PV = nRT$, i.e. $V = \dfrac{nRT}{P}$

Substituting for V in Eq. (11.103), we have

$$(\Delta G)_T = \int_{P_1}^{P_2} \frac{nRT}{P}\, dP$$

$$= nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$= nRT \ln \frac{P_2}{P_1} \qquad \ldots (11.104)$$

For an isothermal process,

$$P_1V_1 = P_2V_2 \quad \text{or} \quad \frac{P_2}{P_1} = \frac{V_1}{V_2}$$

Substituting this value in Eq. (11.104), we get

$$\boxed{(\Delta G)_T = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}} \qquad \ldots (11.105)$$

Example 23 *Calculate the free-energy change which occurs when one mole of an ideal gas expands reversibly and isothermally at 300 K from the initial volume of 5 litres to 50 litres.*

Solution: Given that,

$n = 1$ mole $T = 300$ K $V_1 = 5$ litres $V_2 = 50$ litres

Taking $R = 8.314$ JK^{-1} mol^{-1}

Substituting the values in the expression for $(\Delta G)_T$, we have

$$(\Delta G)_T = 2.303\, nRT \log \frac{V_1}{V_2}$$

$$= 2.303 \times 1 \times 8.314 \times 300 \times \log \frac{50}{500} = \mathbf{-5744.1\ joules}$$

Example 24 *Calculate the free-energy change accompanying the compression of 1 mole of CO_2 at 57°C from 5 atm to 50 atm. Assume that CO_2 behaves like an ideal gas.*

Solution: Given that,

$n = 1$ mole $T = 57 + 273$ K $= 330$ K $P_1 = 5$ atm. $P_2 = 50$ atm.

Taking $R = 1.987$ cal deg^{-1}mol^{-1}, we get,

$$(\Delta G)_T = 2.303 \times nRT \log \frac{P_2}{P_1}$$

$$= 2.303 \times 1 \times 1.987 \times 303 \times \log \frac{50}{5} = \mathbf{1510.1\ cal}$$

PROBLEMS FOR PRACTICE

1. 1 mole of an ideal gas is allowed to expand at 25°C till its pressure falls to one-fifth of its original pressure. Find out the free-energy change accompanying the process.

[Ans. −953.2 cal]

2. Four moles of an ideal gas expand isothermally from 1 litre to 10 litres at 300 K. Calculate the change in free energy of the gas. (R = 8.314 JK^{-1} mol^{-1})

[Ans. −22.98 kJ]

3. During an isothermal reversible compression of one mole of an ideal gas, its volume decreases from 10 litres to 1 litre. The process was carried out at 27°C. Calculate the change in entropy and change in free energy of the gas. (R = 2 cal/degree/mol)

[Ans. ΔS = −4.606 cal deg^{-1}, ΔG = + 1381.8 cal]

4. The pressure of one mole of an ideal gas at 25°C falls from 5.0 bar to 0.2 bar. Evalulate the change in free energy. (R = 8.314 $JK^{-1}mol^{-1}$)

[Ans. 7976.2 J]

11.9 CRITERIA FOR FEASIBILITY OR SPONTANEITY OF A PROCESS

In the earlier sections in this chapter, the following generalisations were derived.

(i) If $\Delta S_{system} + \Delta S_{surroundings} > 0$; the process is irreversible, i.e., it is spontaneous or feasible.

(ii) If $\Delta S_{system} + \Delta S_{surroundings} = 0$; the process is reversible, i.e., the system is in equilibrium.

The above two results may be combined and represented as

$$\Delta S_{system} + \Delta S_{surroundings} \geq 0 \qquad \ldots(11.106)$$

where, the sign ***greater than*** refers to an irreversible process (i.e. spontaneous process) and a sign ***equal to*** for a reversible process.

Equation (11.106) requires the knowledge of change in the entropy of surroundings which is not so convenient to determine. Hence, we would search other criteria which involves change in entropy of the system only, in order to arrive at the criteria for feasibility of a process.

For an infinitesimal change, the above criterion may be written as,

$$dS_{system} + dS_{surroundings} \geq 0 \qquad \ldots(11.107)$$

where the sign > stands for irreversible process (i.e. spontaneous process) and the sign = for the reversible process.

If the surroundings lose heat δq reversibly and isothermally at temperature T (which may be

absorbed by the system reversibly or irreversibly) then

$$dS_{\text{surround}} = \frac{-\delta q_{\text{rev}}}{T} \qquad \ldots(11.108)$$

According to the first law of thermodynamics,

$$\delta q_{\text{rev}} = dU + PdV \qquad \ldots(11.109)$$

Substituting this value in Eq. (11.108), we get

$$dS_{\text{surrounding}} = -\frac{dU + PdV}{T} \qquad \ldots(11.110)$$

Substituting this value in Eq. (11.107), we get

$$dS_{\text{system}} - \frac{dU + PdV}{T} \geq 0$$

or $$TdS - dU - PdV \geq 0$$

or $$TdS \geq dU + PdV \qquad \ldots(11.111)$$

where dS stands for entropy change of the system without the subscript system.

Equation (11.111) is the fundamental equation which leads to a number of criteria for predicting the feasibility of a process. In this equation, the sign '=' stands for the reversible process and the sign '>' for irreversible process. For Eq. (11.111), the various criteria may be deduced as under.

1. In Terms of Entropy Change of the System If the internal energy and the volume of the system is kept constant,

$$dU = 0 \text{ and } dV = 0$$

Then, from Eq. (11.111), we have

$$(TdS)_{U,V} \geq 0$$

or $$(dS)_{U,V} \geq 0 \qquad \ldots(11.112)$$

where the sign '=' is for the reversible process and the sign '>' for irreversible process. The subscripts U and V indicate that these properties remain constant.

2. In Terms of Internal Energy Change of the System If the entropy and volume of the system kept constant,

$$dS = 0,\ dV = 0$$

Equation (11.111) becomes,

$$0 \geq (dU)_{S,V}$$

or $$(dU)_{S,V} \leq 0 \qquad \ldots(11.113)$$

where the sign '=' stands for reversible process and the sign '<' for the irreversible process. This implies that ***if a process under constant entropy and volume is accompanied by a decrease of internal energy, the process is irreversible. If no change of entropy takes place, the process is reversible.***

3. In Terms of Enthalpy Change of the System

$$H = U + PV$$

Complete differentiation of the Equation gives

$$dH = dU + PdV + VdP$$
$$dU + PdV = dH - VdP$$

Putting this value in Eq. (11.111), we get,

$$TdS \geq dH - VdP$$

If entropy and pressure of the system are kept constant,
$dS = 0$ and $dP = 0$, so that

$$0 \geq (dH)_{S,P}$$

or
$$(dH)_{S,P} \leq 0 \qquad \ldots(11.114)$$

where the sign '=' refers to reversible process and the sign '<' refers to the irreversible process.

4. In Terms of If the Change of Work Function of the System

$$A = U - TS$$

Complete differentiation of the equation gives,

$$dA = dU - TdS - SdT$$

or
$$TdS = dU - SdT - dA$$

Putting this value in Eq. (11.111), we get.

$$dU - SdT - dA \geq dU + PdV$$

or
$$-SdT - dA \geq PdV$$

or
$$SdT + dA \leq -PdV$$

If temperature and volume of the system are kept constant $dT = 0$, $dV = 0$, so that we have

$$(dA)_{T,V} \leq 0 \qquad \ldots(11.115)$$

As usual, sign '=' is for the reversible process and sign '<' for irreversible process.

5. In Terms of Free Energy Change of the System

$$G = H - TS$$

Further,
$$H = U + PV$$

$\therefore$
$$G = U + PV - TS$$

Complete differentiation of this equation gives,

$$dG = dU + PdV + VdP - TdS - SdT$$

or
$$dU + PdV = dG - VdP + TdS + SdT$$

Substituting this value in Eq. (11.111), we get

$$TdS \geq dG - VdP + TdS + SdT$$

or
$$0 \geq dG - VdP + SdT$$

or
$$dG - VdP + SdT \leq 0$$

If pressure and temperature of the system is kept constant, $dP = 0$, $dT = 0$, so that we obtain,

$$(dG)_{P,T} \leq 0 \qquad \ldots(11.116)$$

where, as before, the sign '=' refers to the reversible process and the sign'<' refers to the irreversible process.

This criterion in terms of energy change is most important because most of the processes take place at constant temperature and pressure.

(i) If $(dG)_{P, T} < 0$, the process is irreversible, i.e. it is feasible.

(ii) If $(dG)_{P, T} = 0$, the process is reversible, i.e. system is in equilibrium.

(iii) If $(dG)_{P, T} > 0$, the process does not occur, i.e. it is not feasible.

Criterion for the spontaneity of a reaction in terms of ΔG can also be obtained as under:

We know $$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \quad \ldots(11.117)$$

If the system is in thermal equilibrium with surroundings then the temperature of the surroundings is the same as that of the system. Also, increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Hence,

Entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left(\frac{-\Delta H_{sys}}{T}\right) \quad \ldots(11.118)$$

Multiplying the above equation by T throughout,

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys} \quad \ldots(11.119)$$

For spontaneity of a reaction, $\Delta S_{total} > 0$

$\therefore$ $$T\Delta S_{sys} - \Delta H_{sys} > 0 \quad \ldots(11.120)$$

or $$-(\Delta H_{sys} - T\Delta S_{sys}) > 0 \quad \ldots(11.121)$$

Using the equation $\Delta G = \Delta H - T\Delta S$, we can write Eq. (11.121) as

$$-\Delta G > 0 \text{ or } \Delta G < 0$$

or $$\Delta G = \Delta H - T\Delta S < 0$$

ΔG gives us the criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative, the process is spontaneous.

(ii) If ΔG is positive, the process is nonspontaneous.

(iii) If ΔG is zero, the process is in equilibrium.

11.10 MAXWELL RELATIONSHIPS

We can summarise the relations between U, H, A and G along with the parameters such as S, P, T and V as under.

$$dU = TdS - PdV \quad \ldots(11.122)$$

$$dH = TdS + VdP \quad \ldots(11.123)$$

$$dA = -SdT - PdV \quad \ldots(11.124)$$

$$dG = -SdT + VdP \quad \ldots(11.125)$$

At constant volume $dV = 0$. Eq (11.122) will become

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \ldots(11.126)$$

If entropy remains constant, $dS = 0$. Eq. (11.122) reduces to

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad \ldots(11.127)$$

Differentiate Eq. (11.126) w.r.t. V keeping S constant and Eq. (11.127) w.r.t. S keeping V constant. We get

$$\frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \quad \ldots(11.128)$$

and

$$\frac{\partial^2 U}{\partial V \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots(11.129)$$

From equations (11.128) and (11.129), we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots(11.130)$$

Following the same procedure, we can obtain the following expressions from equations (11.123), (11.124) and (11.125).

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \ldots(11.131)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \ldots(11.132)$$

And

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(11.133)$$

Equations (11.130), (11.131), (11.132) and (11.133) are called Maxwell relations. Similarly, we derive another set of relations using equation (11.122) to (11.125).

From (11.122) and (11.123), $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$ $\ldots(11.134)$

From (11.122) and (11.124), $\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T$ $\ldots(11.135)$

From (11.123) and (11.125), $\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$ ...(11.136)

From (11.124) and (11.125), $\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P$ ... (11.137)

Example 25 *Prove that* $\left(\frac{\partial U}{\partial S}\right)_P = T - P\left(\frac{\partial T}{\partial P}\right)_S$

Solution: For a system undergoing expansion

$$dU = TdS - PdV$$

Dividing by dS keeping P constant, we have

$$\left(\frac{\partial U}{\partial S}\right)_P = T - P\left(\frac{\partial V}{\partial S}\right)_P$$

As $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$ [from Eq. (11.131)], we have

$$\left(\frac{\partial U}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

11.11 GIBBS-HELMHOLTZ EQUATION

The Gibbs free energy (G) is given by the equation,

$$G = H - TS$$

For an ***isothermal*** process, we can write,

$G_1 = H_1 - TS_1$ for the initial state ...(11.138)

And $G_2 = H_2 - TS_2$ for the final state ...(11.139)

Subtracting Eq. (11.138) from Eq. (11.139), we get

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$
$$= (H_2 - H_1) - T(S_2 - S_1)$$

or $\Delta G = \Delta H - T\Delta S$ ...(11.140)

where, ΔG is the change in free energy of the system
ΔH is the change in enthalpy of the system.

And ΔS is the entropy change of the system.

Putting $H = U + PV$ in the equation $G = H - TS$ we get

$G = U + PV - TS$ ...(11.141)

Differentiating this equation completely, we get

$$dG = dU + PdV + VdP - TdS - SdT \quad \ldots(11.142)$$

but $$dS = \frac{\delta q_{rev}}{T} = \frac{dU + PdV}{T}$$ (from first law of thermodynamics)

or $$TdS = dU + PdV$$

Substituting this value in Eq. (11.142), we get

$$dG = VdP - SdT$$

If pressure is kept constant, $dP = 0$, so that the above equation reduces to

$$(dG)_P = -(SdT)_P$$

or $$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \ldots(11.143)$$

∴ for the initial state, $$\left(\frac{\partial G_1}{\partial T}\right)_P = -S_1 \quad \ldots(11.144)$$

For the final state, $$\left(\frac{\partial G_2}{\partial T}\right)_P = -S_2 \quad \ldots(11.145)$$

Subtracting Eq. (11.144) from (11.145), we get

$$\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = -S_2 - (-S_1) = -S_2 + S_1 = -(S_2 - S_1) = -\Delta S$$

It may also be written as,

$$\left[\frac{\partial (G_2 - G_1)}{\partial T}\right]_P = -\Delta S$$

$$\left[\frac{\partial (\Delta G)}{\partial T}\right]_P = -\Delta S \quad \ldots(11.146)$$

Substituting this value of $-\Delta S$ in Eq. (11.140), we get

$$\Delta G = \Delta H + T\left[\frac{\partial (\Delta G)}{\partial T}\right]_P \quad \ldots(11.147)$$

This is the most common form of Gibbs-Helmholtz equation. An analogous equation involving the work function A can be obtained using the equation,

$$A = U - TS$$

Proceeding in a similar manner as above, we obtain the following equation

$$\Delta A = \Delta U + T\left[\frac{\partial (\Delta A)}{\partial T}\right]_V \quad \ldots(11.148)$$

1. Gibbs Helmholtz Equation can be Obtained in Another Form as Under Writing the Gibbs-Helmholtz equation in its common form

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

Dividing the above equation by T^2

$$\frac{\Delta G}{T^2} = \frac{\Delta H}{T^2} + \frac{1}{T}\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

or
$$\frac{1}{T}\left[\frac{\partial(\Delta G)}{\partial T}\right]_P - \frac{\Delta G}{T^2} = -\frac{\Delta H}{T^2}$$

or
$$\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$$

2. Applications of Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation has the following applications

(a) Knowing the free energy change at any two different temperatures, the enthalpy change accompanying the process can be calculated.

(b) When a redox reaction (e.g. $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$) is allowed to take place in a single beaker, heat is evolved. It was believed earlier that when the same reaction is allowed to take place in an electrochemical cell, the electrical energy produced was equivalent to the heat evolved. This was explained by Gibbs-Helmholtz by stating that the ***electrical energy produced was equal to the decrease in the free energy (ΔG) accompanying the cell reaction.*** They pointed out that if V is the number of electrons given by one of the electrodes (e.g. for $Zn \rightarrow Zn^{2+} + 2e^-$, $n = 2$) or taken up by the other electrode (e.g. $Cu^{2+} + 2e \rightarrow Cu$, $n = 2$) then the quantity of the electricity produced = ***nF*** faradays, where F = 1 faraday = 96.500 coloumbs. If ***E*** is the emf of the cell then

Electrical energy produced by the cell = ***nFE***

$\therefore$ Decrease in free energy, $-\Delta G = nFE$

Substituting this value in the Gibbs-Helmholtz equation,

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

We have,
$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_P$$

or
$$nFE = -\Delta H + T n F\left(\frac{\partial E}{\partial T}\right)_P$$

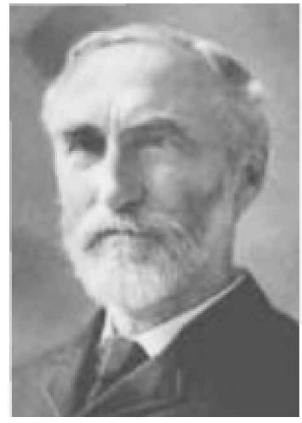


Fig. 11.8 *Josiah Willard Gibbs was an American scientist who made important theoretical contributions to physics, chemistry and mathematics.*



Fig. 11.9 *Hermann von Helmholtz was a German physician and physicist who made significant contribution to varied areas of modern science.*

Thus, knowing the temperature coefficient of the emf of the cell, i.e. $(\partial E/\partial T)_p$, ΔH can be calculated if E is known or vice versa. The electrical energy produced (nFE) is equal to the heat evolved $(-\Delta H)$ only when $(\partial E/\partial T)_p = 0$.

Example 26 *The free-energy change for a reaction at 298 K is found to be 18.0 kJ. Calculate the free energy at 350 K given that the enthalpy change for the reaction is +80 kJ. It is assumed that AH is independent of temperature.*

Solution: Writing Gibbs-Helmholtz equation in the form,

$$\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T} = -\frac{\Delta H}{T^2} \quad \text{or} \quad d\left(\frac{\partial G}{T}\right) = -\frac{\Delta H}{T^2}\,dT$$

Integrating both sides of above equation, we get,

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Given that

$$\Delta G_1 = 18.0\ \text{kJ}, \Delta H = 80.00\ \text{kJ}$$
$$T_1 = 298\ \text{K}, T_2 = 350\ \text{K}$$

Substituting the values, we get,

$$\frac{\Delta G_2}{398} - \frac{18.0}{298} = 80\left(\frac{1}{350} - \frac{1}{298}\right) \quad \text{or} \quad \frac{\Delta G_2}{398} = -0.03988 + 0.060402$$

$$\Delta G_2 = 0.020522 \times 398 \quad \text{or} \quad \Delta G_2 = \mathbf{8.168\ kJ}$$

Example 27 *The free energy change involved in a process is –1235 J at 300 K and –1200 J at 310 K. Calculate the change in enthalpy of the process at 306 K.*

Solution: Using Gibbs-Helmholtz equation,

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

where $\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = \frac{\Delta G_2 - (-1235)}{310 - 300}$

substituting values we have, $\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = \frac{-1200 - (-1235)}{310 - 300} = \frac{35}{10} = 3.5\ \text{JK}^{-1}$

The free-energy change at 305 K can be taken as the average values of free-energy change at 300 K and 310 K.

Thus, $\Delta G_{(\text{at } 305\ \text{K})} = \frac{1}{2}[-1200 + (-1235)] = -1217.5\ \text{J}$

Gibbs-Helmholtz equation can be written as,

$$\Delta H = \Delta G - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

Substituting the values, we get

$$\Delta H = -1217.5 - 305 \times 3.5 = -2285\ \text{J}$$

PROBLEMS FOR PRACTICE

1. Assuming that for a certain reaction ΔH remains constant in the temperature range 427° to 627°C, calculate ΔG for this reaction at 627°C from the following data:
[ΔH = –25 kJ, ΔG (427°C) = –40 kJ]

[Ans. –44.26 kJ]

2. The free-energy change accompanying a given process is –85.8 kJ at 25°C and –82.6 kJ at 35°C. Calculate the enthalpy change of the process at 25°C.

[Ans. –82.56 kJ]

SOLVED EXAMPLES

Example 28 *What is total differential equation? How does Gibbs function vary with pressure at constant temperature and with temperature at constant pressure?*

Solution: Total differential equation is written as

$$dG = VdP - SdT \qquad \ldots(i)$$

When temperature is constant, $dT = 0$
Equation (i) may be written as

$$dG = VdP \quad \text{or} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

When pressure is constant, $dP = 0$
Equation (i) may be written as

$$dG = -SdT \quad \text{or} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Example 29 *Write the expressions for total change in Gibbs function when at constant temperature, the volume changes from V_1 to V_2 or pressure changes from P_1 to P_2.*

Solution:

$$(\Delta G)_T = nRT \ln \frac{P_2}{P_1} \qquad \ldots(i)$$

But

$$\frac{P_2}{P_1} = \frac{V_1}{V_2} \qquad \ldots(ii)$$

From equations (i) and (ii), we have

$$(\Delta G)_T = nRT \ln \frac{V_1}{V_2}$$

Example 30 *What is the difference between Helmholtz function and Gibbs function? Under*

what conditions, does the former become equal to the latter?

Solution: Helmholtz function A is given by the relation

$$A = U - TS$$

where U = Internal energy T = Temperature S = Entropy
Gibbs function $G = H - TS$
ΔA and ΔG are given by the following relations:

$$-\Delta A = W_{\max.} \quad \text{and} \quad -\Delta G = W_{\max.} - P\Delta V$$

Thus, if during the process there is no change in volume $P\Delta V = 0$, we have $-\Delta G = -\Delta A$.

Example 31 *Under what condition is electrical energy produced in a cell reaction equal to the heat evolved in the cell reaction?*

Solution:

$$nFE = -\Delta H + TnF\left(\frac{\partial E}{\partial T}\right)_P$$

Thus, $nFE = -\Delta H$, when $\left(\frac{\partial E}{\partial T}\right)_P = 0$, i.e. when the temperature coefficient of the emf of the cell = zero.

Example 32 *Write expressions for the following:*

(a) Variation for the Helmholtz function with volume at constant temperature

(b) Variation of Helmholtz function with temperature at constant volume

(c) Total change in Helmholtz function at constant temperature when volume changes from V_1 to V_2.

Solution: (a) $\left(\frac{\partial A}{\partial V}\right)_T = -P$ (b) $\left(\frac{\partial A}{\partial T}\right)_V = -S$ (c) $(\Delta A)_T = -nRT \ln \frac{V_2}{V_1}$

Example 33 *Write criteria for spontaneity and equilibrium conditions in terms of S, U, H, A and G.*

Solution: $(dS)_{U,V} \geq 0, \quad (dU)_{S,V} \leq 0, \quad (dH)_{S,P} \leq 0, \quad (dA)_{T,V} \leq 0, \quad (dG)_{P,T} \leq 0.$

Sign '=' refers to reversible process (i.e. equilibrium) and > or < refers to irreversible process (spontaneity).

SUMMARY

1. The second law of thermodynamics helps us know the direction in which energy can be transferred. It also helps us know through the concept of entropy whether a given reaction can take place spontaneously

2. Some statements of the second law of thermodynamics are

(a) The complete conversions of heat into work is impossible without leaving some effects elsewhere

(b) Without the use of external agency, heat cannot, by itself, pass from a colder to a hotter body

3. Processes taking place in nature are spontaneous and irreversible.

4. A cyclic process is a process when the system returns to its original position after a series of changes. One such process is Carnot cycle.

5. Carnot theorem states: The efficiency of a reversible heat engine depends only upon the temperatures of the source and the sink and is independent of the nature of the working substance.

6. The entropy change may be defined as the quantity of heat absorbed isothermally and reversibly divided by the absolute temperature *(T)* at which the heat is absorbed.

7. All spontaneous processes are accompanied by a net increase of entropy. That is why the entropy of the world is increasing while the energy of the universe is constant.

8. Physical significance of entropy is: it is a measure of disorder or randomness of the system

9. Helmholtz free energy (*A*) is a thermodynamic quantity which is used in the study of thermodynamics. Gibbs free energy (*G*) is another thermodynamic quantity.

10. If a process under constant entropy and volume is accompanied by a decrease of internal energy, the process is irreversible. If no change in entropy takes place, the process is reversible.

11. Relations between *U*, *H*, *A*, and *G* along with parameter such as *S*, *P*, *T* and *V* are called Maxwell relations.

KEY RELATIONS

1. Efficiency, $\eta = \dfrac{W}{Q}$ where *W* and *Q* stand for work done and heat supplied

2. $\eta = \dfrac{W}{q_2} = \dfrac{q_2 - q_1}{q_2} = \dfrac{T_2 - T_1}{T_2}$

3. $\Sigma \dfrac{q}{T} = 0$ and $dS = \dfrac{q_{\text{rev}}}{T}$

4. $\dfrac{q_{\text{rev}}}{T} - \dfrac{q_{\text{irr}}}{T} > 0$

5. $\Delta S = C_V \ln \dfrac{T_2}{T_1}, \Delta S_m = \dfrac{\Delta H_m}{T_m}, \Delta S_v = \dfrac{\Delta H_v}{T_v}$

6. $\Delta S_{\text{mixing}} = n_1 R \ln \dfrac{P_1^\circ}{x_1 P} + n_2 R \ln \dfrac{P_2^\circ}{x_2 P}$

7. $\Delta A = \Delta U - T\Delta S$

8. $\Delta G = \Delta H - T\Delta S$

9. $dG = VdP - SdT$ (Total differential equation)

10. $\left(\frac{\partial G}{\partial P}\right)_T = V, \left(\frac{\partial G}{\partial T}\right)_P = -S$

11. $(\Delta G)_T = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$

12.

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \text{ (Gibbs–Helmholtz equation) and } \Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V$$

13. $nFE = -\Delta H + TnF\left(\frac{\partial E}{\partial T}\right)_P$

EXERCISES

Based on Different University Papers
Objective Questions
Multiple-Choice Questions

1. Which of the following is not the criterion for spontaneity of a process?
   (a) $(dG)_{T,P} \geq 0$ (b) $(dA)_{T,V} \leq 0$
   (c) $(dG)_{T,P} \leq 0$ (d) $(dS)_{U,V} \geq 0$

2. Under what conditions is change in work function equal to change in Gibbs free energy, i.e. $\Delta A = \Delta G$
   (a) When there is no change in volume, i.e. $\Delta V = 0$
   (b) When there is no change in enthalpy, i.e. $\Delta H = 0$
   (c) When there is no change in temperature
   (d) When there is no change in pressure

3. For an isothermal process, the total change in work function is given by the expression.
   (a) $-(\Delta A)_T = -nRT \ln \frac{V_1}{V_2}$
   (b) $(\Delta A)_T = -nRT \ln \frac{P_2}{P_1}$
   (c) $(\Delta A)_T = -nRT \ln \frac{V_2}{V_1}$
   (d)

4. Point out the correct relationship:
   (a)
   (b)
   (c)
   (d)

5. The relationship between decrease in Gibbs free energy and electrical energy is

(a) $-\Delta G = nFE_{cell}$

(b) $\Delta G = nRT \ln E_{cell}$

(c) $-\Delta G = -nFE_{cell}$

(d) $\Delta G = -nRT \ln E_{cell}$

6. Gibbs Helmholtz equation is:

(a)

(b)

(c)

(d)

7. Choose the incorrect relationship:

(a)

(b)

(c)

(d)

8. The most preferred criterion for spontaneity of a process is

(a)

(b)

(c)

(d)

9. Point out the incorrect statement:

(a)

(b)

(c)

(d)

Answers

1. (a)
2. (b)
3. (c)
4. (c)
5. (a)
6. (d)
7. (a)
8. (c)
9. (c)

SHORT-ANSWER QUESTIONS

1. Explain that in a reversible process, there is no net entropy change.
2. Show that the efficiency of a reversible Carnot cycle is where T_2 and T_1 temperatures of the source and the sink respectively.
3. Explain how thermodynamic scale of temperature was developed. Why is it considered more basic than the ideal or perfect gas scale of temperature?
4. Show that for an irreversible process, $\Delta S_{sys} + \Delta S_{surroundings} > 0$.
5. Explain the term *Entropy*. Show that it is a state function.
6. What is Carnot cycle? How does it lead to the definition of entropy? Justify that

7. Why was there a need for introduction to second law of thermodynamics? Illustrate with a suitable example.
8. Explain giving reasons—the efficiency of a steam engine can be increased by superheated steam.
9. Calculate the total entropy change (ΔS_{total}) during an irreversible process when heat flows from a body at higher temperature T_2 to a body at lower temperature T_1.

Or

Prove that for an irreversible process when heat flows from a body at higher temperature T_2 to a body at lower temperature T_1,

10. Explain the meaning of each of the following expressions:

11. Derive thermodynamically the relationships

12. Differentiate between Gibbs free energy and Helmholtz free energy. How does decrease in free energy signify the chemical affinity of a reaction? Explain with suitable examples. What do you understand by the terms *free energy* and *work function?* Derive a relationship between the two. Under what conditions does ΔG become equal to ΔA*?*
13. Show that for an irreversible process, $dG_{P,\ T} < 0$.
14. Show that
15. Show that the change in free energy is equal to net work done.
16. Show that
17. Explain the term *free energy*. What information does the free energy of the reaction give about the spontaneity of the reaction to occur?
18. Derive the following thermodynamic expressions:

19. For a system in equilibrium at a given temperature and pressure, the free energy is minimum. Explain.
20. Show that $\Delta A \leq 0$ is the criterion for spontaneity and equilibrium.

21. Explain: the entropy of a system and the surroundings increase in an irreversible process but remain constant in a reversible process.

22. State and explain Carnot's theorem.

23. Explain the terms *free energy* and *maximum work done*. Derive a relationship between the two.

24. Find the change in free energy when the system undergoes reversible change of pressure as well as temperature.

25. Show that $\Delta G \leq 0$ is a criterion for spontaneity and equilibrium.

GENERAL QUESTIONS

1. Derive an expression for entropy change when n_1 mole of an ideal gas 1 are mixed with n_2 moles of an ideal gas 2.

2. Derive that for an ideal gas,

3. Derive an expression to calculate of the entropy change of an ideal gas when the temperature change from T_1 to T_2 and the pressure changes from P_1 to P_2.

4. Derive an expression for the entropy change on mixing of ideal gases. From this expression, what do you conclude about

(a) Effect of temperature on entropy change of mixing.

(b) Decrease or increase of entropy on mixing $_V$

5. Starting from basic principles, show that in isothermal expansion of an ideal gas,

6. Derive an expression for the molar entropy change of mixing of two ideal gases.

7. Derive the required expression to show that entropy change on mixing of ideal gases is independent of temperature.

8. State and explain Carnot's theorem. Explain how on the basis of efficiency of reversible heat engine, the thermodynamic scale of temperature was developed by Lord Kelvin.

9. Derive the required expression to show that mixing of gases is always accompanied by increase in entropy.

10. Explain how entropy changes take place in a reversible process and in an irreversible process. What do you conclude about the entropy change of the universe?

11. Most processes taking place in nature are spontaneous in character and all spontaneous processes are accompanied by a net increase of entropy. If entropy is regarded as the measure of randomness in a system, it would then mean that the universe is heading towards chaos. Is it true? Explain clearly.

12. What are the limitations of the first law of thermodynamics? How have these been overcome by the second law of thermodynamics? Define it in as many ways as you can.

13. Derive that for an ideal gas,

14. On the basis of the reversible Carnot cycle, how was the concept of entropy developed? Define entropy and state its units.

15. What is Clausius inequality? Show that for spontaneous cooling, $dS_{total} > 0$

16. What is Clausius inequality? Explain that in spontaneous expansion as well as spontaneous cooling, dS_{total} is positive.

17. Explain giving reasons that the entropy of the universe tends to increase.

18. Describe Carnot's cycle. Derive an expression for the efficiency a reversible heat engine working between temperatures T_1 and T_2 ($T_2 > T_1$).

19. Derive an expression for the calculation of the entropy change of an ideal gas when the temperature changes from T_1 to T_2 and volume changes from V_1 to V_2.

20. What is Clausius inequality in thermodynamics? Show that for an irreversible adiabatic expansion, $dS_{total} > 0$.

21. Show that

22. Explain the term *Gibbs function.* Deduce that decrease in its value is equal to the maximum net work obtainable from the system. Also, explain how it varies with temperature and pressure?

23. Bring out clearly the criteria for reversibility and irreversibility in terms of S, U, H, A and G. What do you mean by a reversible and an irreversible process?

24. Derive an expression relating the changes in free energy and entropy of a closed thermodynamic system at constant pressure.

25. Derive the *total differential equation* and hence derive the following expression for an isothermal process when the volume changes from V_1 to V_2 or pressure changes from P_1 to P_2.

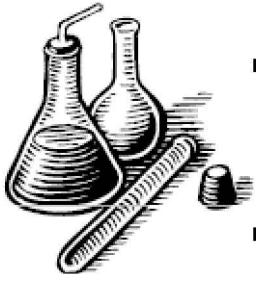
26. What are the applications of Gibbs-Helmholtz equations?

27. Explain the term *Helmholtz function.* How can you deduce that for a process occurring at constant temperature, the decrease in constant temperature A is equal to maximum work done by a system? Also explain how it varies with temperature and volume.

28. Derive Gibbs-Helmholtz equation in terms of free energy and enthalpy change at constant pressure. Bring out its importance.

29. Discuss Gibbs-Helmholtz equation with regard to its application to a galvanic cell.

30. Show that



Themodynamics-III

12

LEARNING OBJECTIVES

- Know the Nernst heat theorem which gives the variation of enthalpy change (ΔH) and free-energy change of a system with decrease of temperature
- To know that the third law of thermodynamics originates from the Nernst heat theorem
- State the third law of thermodynamics in different forms
- Understand the importance of the third law in calculating absolute entropies
- Test the validity of the third law of thermodynamics
- Learn about residual entropy
- Know partial molar properties
- Derive the Gibbs-Duhem equation
- Study the variation of chemical potential with temperature and pressure
- Study the chemical potential in a system of ideal gases
- Derive the Clausius-Clapeyron equation
- Understand the applications of the Clausius-Clapeyron equation
- Understand the terms *fugacity, activity* and *activity coefficient*

12.1 THIRD LAW OF THERMODYNAMICS

While the first and second laws of thermodynamics have provided concepts of heat content and entropy, the third law does not provide us any new concept as such. It only places the limit on the value of entropy in a crystalline solid. However, nothing has been observed or experienced contrary to the statement of the third law. Hence, it has been accepted as a law. The results of the Nernst heat theorem led to a generalisation which has been called the third law of thermodynamics. In other words, the third law of thermodynamics originates from the Nernst heat theorem which is discussed as under:

Nernst Heat Theorem

This theorem gives the variation of enthalpy change *(ΔH)* and free-energy change (ΔG) of a system with decrease of temperature.

According to the Gibbs-Helmholtz equation,

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p \qquad (12.1)$$

From this equation it is evident that at the absolute zero, i.e., when $T = 0$, $\Delta G = \Delta H$. Nernst observed that as the temperature is lowered towards absolute zero the value of $\partial(\Delta G)/\partial T$ decreases and then approaches zero asymptotically. This means that **ΔG *and* ΔH *are not only equal at absolute zero but the values approach each other asymptotically near this temperature.*** This equation is known as the Nernst heat theorem. Mathematically, it may be expressed as,

$$\lim_{T \to 0} \frac{d(\Delta G)}{dT} = \lim_{T \to 0} \frac{d(\Delta H)}{dT} = 0 \qquad (12.2)$$

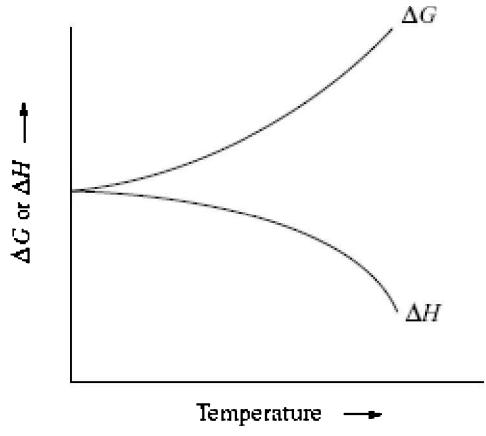


Fig. 12.1 *Nernst heat theorem*

Graphically, the result may be represented by Fig. 12.1.

In Fig. 12.1, ΔG has been shown as greater than ΔH at a temperature away from absolute zero. However, the reverse is also possible because $\partial(\Delta G)/\partial T$ can be both positive or negative.

Further, $$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S \qquad ...(12.3)$$

and $$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_p \text{ (Kirchoff's equation)} \qquad ...(12.4)$$

From equations (12.2), (12.3) and (12.4), we can say, as $T \to 0$.

$$\Delta S = 0 \quad \text{and} \quad \Delta C_p = 0$$

i.e., as the temperature is lowered to absolute zero, the enthalpy change of the reaction and difference in the heat capacities of the products and reactants also tends to be zero.

Since gases do not exist at absolute zero, the heat theorem is not applicable to gases. Similarly, it has been found to be inapplicable to liquids also. The Nernst heat theorem is applicable to solids only.

12.2 STATEMENTS OF THIRD LAW OF THERMODYNAMICS

The third law of thermodynamics is stated thus:

The entropy of all perfectly crystalline solids may be taken as zero at the absolute zero temperature.

The law may also be stated as follows:

Every substance has finite positive entropy but at absolute zero temperature, the entropy may become zero and in fact it does become zero in case of perfectly crystalline solids.

12.2.1 Importance of the Third Law

Calculation of Absolute Entropies It helps in the calculation of the absolute entropies of chemical compounds at any desired temperature as explained below:

The infinitesimal entropy change is given by,

$$dS = \frac{dq}{T} \qquad \ldots(12.5)$$

But $$C_p = \frac{dq}{dT} \text{ so that } dq = C_p dT$$

Substituting this value in Eq. (12.5), we have

$$dS = \frac{C_p dT}{T}$$

Entropy change of a substance when its temperature changes from absolute zero to the temperature *(T)* can be calculated using the equation,

$$\int_{S=S_0}^{S=S} dS = \int_{T=0}^{T=T} C_p \frac{dT}{T}$$

or $$S - S_0 = \int_0^T C_p \frac{dT}{T} \qquad \ldots(12.6)$$

where S_0 is the entropy of the substance at absolute zero and S is the entropy of the substance at temperature T.

According to the third law of thermodynamics, $S_0 = 0$

$\therefore$ $$S_T = \int_0^T C_p \frac{dT}{T}$$

$$= \int_0^T C_p d\ln T \qquad \ldots(12.7)$$

Thus, the entropy (S) of the substance at the temperature T can be calculated from measurements of heat capacities (C_p), at a number of temperatures between 0 K to T K. The integral in Eq. (12.7) can be evaluated by plotting C_p *vs.* ln T, i.e. 2.303 log T and then measuring the area under the curve between $T = 0$ to $T = T$ as shown in Fig. 12.2.

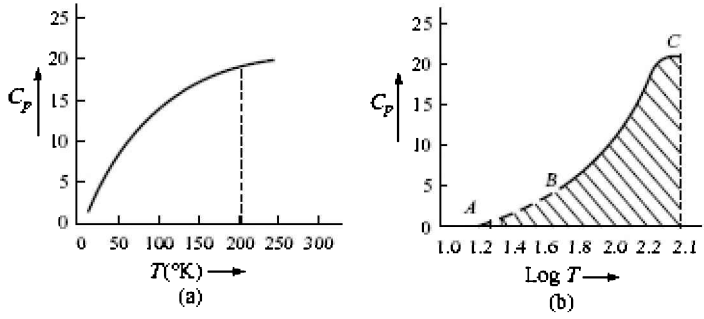


Fig. 12.2 *Plot of heat capacities (C_p) vs T in the first case and vs log T in the second case*

If C_p is supposed to remain almost constant in the temperature range 0 to T K, Eq. (12.7) can be simplified to,

$$S = C_p \ln T = 2.303\, C_p \log T \qquad \ldots(12.8)$$

This equation helps to calculate the value of S directly from the values of C_p and T.

However, heat capacities cannot be measured with accuracy below the temperature of 15 K. Thus, the part CB of the curve is an experimental curve using values of C_p. The curve is extrapolated to A to get the complete area under the curve from T to 0 K.

Between the range 0-15 K, heat capacity is obtained by Debye T-cubed law,

$$C_p = aT^3 \qquad \ldots(12.9a)$$

where, a is a constant. It is determined from the value of C_p at some low temperature.

Let T_1 be the temperature above which heat capacity can be measured experimentally. In Fig. 12.2(b), it corresponds to the point B. Point C corresponds to the temperature T at which the entropy of the solid is to be determined. In Fig. 12.2(b), the point A corresponds to 0 K. The integral in Eq. (12.7) can be split as under

$$S_T = \int_0^{T_1} C_p \frac{dT}{T} + \int_{T_1}^{T} C_p \frac{dT}{T} \qquad \ldots(12.9b)$$

The first integral in Eq. (12.9b) can be calculated using Eq. (12.9a),

$$\int_0^{T_1} C_p \frac{dT}{T} = \int_0^{T_1} aT^3 \frac{dT}{T} = \int_0^{T_1} aT^2 dT = \frac{1}{3} aT_1^3$$

or
$$\Delta S_1 = \frac{1}{3} C_p (\text{at } T_1) \qquad \text{(From Eq. 12.9a)}$$

The second integral in Eq. (12.9b) can be evaluated by the graphical method. C_p is plotted versus ln T. The area under the curve between the limits T_1 and T gives the value of the integral. Therefore, the entropy of the solid between 0 K and T K is given by,

$$S_T = \frac{1}{3} C_p (\text{at } T_1) + \int_{T_1}^{T} C_p \, d \ln T \qquad (12.10)$$

If there is some allotropic change between the temperature range 0 K–T K then the entropy of transition $\Delta H_t/T_t$ is added to Eq. (12.10.)

Thus, we have

$$S_T = \frac{1}{3}C_p(\text{at } T_1) + \int_{T_1}^{T} C_p d\ln T + \frac{\Delta H_t}{T_t}$$

For liquid and gaseous substances, the total absolute entropy of the substance at a given temperature is the total of all entropy change which the substance undergoes in order to reach that particular state starting from the crystalline solid at absolute zero. Thus, if the substance is gaseous at 1 atm pressure and 25°C, the entropy of the gas at 25°C will be the sum of the following entropies involved at different stages:

1. The entropy of heating a crystalline solid from $T = 0$ to $T = T_m$, the melting point.

2. The entropy of melting, $\frac{\Delta H_m}{T_m}$ where ΔH_m is the latent heat of melting.

3. The entropy of heating the liquid from T_m to T_b, the boiling point.

4. The entropy of vaporisation, $\frac{\Delta H_v}{T_b}$, where ΔH_v is the latent heat of vaporisation.

5. The entropy of heating the gas from T_b to 25°C (i.e. 298 K).

The complete expression for the calculation of entropy at the temperature T may be expressed as

$$S = \underbrace{\int_0^{T_m} C_{p(s)} d\ln T}_{\text{I}} + \underbrace{\frac{\Delta H_m}{T_m}}_{\text{II}} + \underbrace{\int_{T_m}^{T_b} C_{p(l)} d\ln T}_{\text{III}} + \underbrace{\frac{\Delta H_v}{T_b}}_{\text{IV}} + \underbrace{\int_{T_b}^{T} C_{p(g)} d\ln T}_{\text{V}}$$

Example 1 *C_V for a metal is 3.04 J KT^{-1} mol^{-1} at 20 K. Calculate the absolute entropy of the metal in J K^{-1} mol^{-1} at 20 K.*

Solution: At low temperature, $C_p = C_V = aT^3$ (Debye law)

$$a = \frac{C_v}{T^3} = 3.04 \text{ J K}^{-1} \text{ mol}^{-1}/(20 \text{ K})^3 = 38.03 \times 10^{-5} \text{ J K}^{-4} \text{ mol}^{-1}$$

Hence,
$$C_p = aT^3 = (38.03 \times 10^{-5} \text{ J mol}^{-1} \text{ K}^{-4})\, T^3$$

$$dS = \frac{C_p}{T} dT = 38.05 \times 10^{-5} \text{ J mol}^{-1} \text{K}^{-4}\, T^2 dT$$

or
$$S_{20} - S_0 = 38.03 \times 10^{-5} \text{ J K}^{-1} \text{mol}^{-1}\, (20 \text{ K})^3/3$$

or
$$S_{20} = 1.01 \text{ J K}^{-1} \text{mol}^{-1} \quad [\because S_0 = 0]$$

12.2.2 Testing Validity of the Third Law of Thermodynamics

Validity of the third law can be tested as under:

1. By Calculation of Equilibrium Constants The equilibrium constant (K) is related to standard free-energy change ($\Delta G°$) according to the equation

$$-\Delta G^\circ = RT \ln K \qquad (12.11a)$$

Also, the standard free-energy change is related to the standard enthalpy change (ΔH°) and standard entropy change (ΔS°) according to the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (12.11b)$$

Substituting the experimental value of ΔH° and calculated value of ΔS°, using the absolute values of entropies obtained from the third law of thermodynamics and applying the relation,

$$\Delta S^\circ = \Sigma S^\circ_{(\text{products})} - \Sigma S^\circ_{\text{reactants}} \qquad (12.11c)$$

ΔG° can be calculated for the reaction. Putting the value of ΔG° in Eq. (12.11a), the equilibrium constant 'K' can be calculated. The value of the equilibrium constant as calculated above comes to be in close arrangement with the experimental value. That proves the validity of the third law.

2. By Comparing with Entropies Calculated from Statistical Mechanics The absolute entropies calculated on the basis of the third law compare very well with those calculated from statistical mechanics. This further lends support to the validity of the third law of thermodynamics.

Entropy Changes in a Chemical Reaction We can calculate the ΔS° value of a chemical reaction from the standard entropy values for the reactants and products. This is one of the most important applications of the third law of thermodynamics. For a reaction,

$$aA + bB + \ldots \rightarrow lL + mM + \ldots$$

occurring in a standard state, the standard entropy change is given by

$$\Delta S^\circ = [lS^\circ_L + mS^\circ_m + \ldots] - [aS^\circ_A + bS^\circ_B + \ldots]$$
$$= \Sigma S^\circ_{(\text{products})} - \Sigma S^\circ_{\text{reactants}}$$

From the values of S°, we can obtain the value of ΔS° at 298 K. ΔS° values at other temperatures can be obtained from the Kirchoff type equation.

$$\left[\frac{d(\Delta S^\circ)}{dT}\right]_P = \sum\left(\frac{\partial S^\circ_{\text{products}}}{\partial T}\right)_P - \sum\left(\frac{\partial S^\circ_{\text{reactants}}}{\partial T}\right)_P$$

Since $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$, we have

$$\left[\frac{d(\Delta S^\circ)}{dT}\right]_P = \sum\left(\frac{C_p}{T}\right)_{\text{products}} - \sum\left(\frac{C_p}{T}\right)_{\text{reactants}}$$

Integrating the above equation between 298 K and T K, we have

$$\int_{298}^{T} d(\Delta S^\circ) = \int_{298}^{T} \left(\frac{\Delta C_p}{T}\right) dT + \int_{298}^{T} \Delta C_p d\ln T$$

or $$\Delta S_T^\circ = \Delta S_{298}^\circ + \int_{298}^{T} \Delta C_p d\ln T$$

This equation is applicable to solids, liquids and gases.

Example 2 *Calculate the standard entropy change of the reaction*

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Given that standard entropies per mole at 25°C are as under (in J KT^{-1} mot^{-1}):

$$N_2 = 191.62,\ O_2 = 205.01,\ NO = 210.45$$

Solution: The standard entropy change at 25°C for the reaction can be computed as under:

$$\Delta S^\circ = \Sigma S^\circ_{(\text{products})} - \Sigma S^\circ_{\text{reactants}}$$

$$= (2 \text{ mol} \times 210.45 \text{ J K}^{-1} \text{mol}^{-1}) - (1 \text{ mol} \times 191.62 \text{ J K}^{-1} \text{mol}^{-1} + 1 \text{ mol} \times 205.01 \text{ J K}^{-1} \text{mol}^{-1})$$

$$= 24.27 \text{ J K}^{-1}$$

Example 3 *Calculate the entropy change that takes place during the conversion of 1 mole of ice at 273.1 K and one atm, pressure into steam at 373.1 K and one atm pressure. Given that molar heat of fusion of ice, ΔH_f, is 6.00 kJ mot^{-1} at 273.1 K and molar heat of vaporisation of water, ΔH_v, at 373.1 K is 40.60 kJ mot. Assume that molar heat capacity C_p in this temperature range is constant at 75.2 J K^{-1} mol^{-1}.*

Solution: The entropy change would consist of three components.

ΔS_1, i.e. entropy change due to fusion of ice

ΔS_2, i.e. entropy change for heating 1 mole of water from 273.1 K to 373.1 K, and

ΔS_3, i.e. entropy change due to conversion of water at 373.1 K into steam.

Each one of these is computed as under:

$$\Delta S_1 = \frac{\Delta H_f}{T_f} = \frac{6000 \text{ J mol}^{-1}}{273.1 \text{ K}} = 22.0 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{C_p}{T} dT = \int_{273.1}^{371.1} \frac{75.2 \text{ J K}^{-1}\text{mol}^{-1}}{T} dT$$

$$= 75.2 \text{ J K}^{-1} \times 2.303 \times \log(373.1 \text{ K}/273.1 \text{ K})$$

$$= 23.5 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\Delta S_3 = \frac{\Delta H_v}{T_b} = \frac{40600 \text{ J mol}^{-1}}{373.1 \text{ K}} = 108.8 \text{ J K}^{-1} \text{mol}^{-1}$$

Total entropy change, $\Delta S = 22.0 + 23.5 + 108.8$

$$= 154.3 \text{ J K}^{-1} \text{mol}^{-1}$$

12.3 RESIDUAL ENTROPY

Entropy calculated by using the third law of thermodynamics as given in the pervious section is called ***thermal entropy.*** We can also calculate the entropy of a substance by using the following relation of statistical mechanics:

$$S = k \ln W$$

where, S = Statistical entropy

W = Number of possible arrangements of atoms, molecules or ions in a crystal (also called thermodynamic probability)

k = Boltzmann constant

We observe that, in some cases, the experimental values of thermal entropy (obtained from the third law of thermodynamics) are not in perfect agreement with those calculated from statistical methods. Thermal entropies are found to be slightly lower than statistical entropies. The lower values of third-law entropies are due to the fact that even at $T = 0$, there is some disorder in the solid and it possesses a finite value of entropy.

The entropy which the crystal of a substance possesses at T = 0 K is called residual entropy.

Some of the crystals which do not show zero entropy at 0 K are CO, NO, H_2 crystals and crystalline ice.

1. Calculation of Residual Entropy Residual entropy can be calculated using the relation,

$$S = k \ln W \qquad \ldots(12.12)$$

If W at 0 K is known, we can calculate residual entropy.

2. Residual Entropy of CO Suppose a sample of CO contains Nmolecules. Each molecule of CO can have two orientations.

CO or **OC**

Let there be N molecules in one mole of substance. Therefore, N molecules can have 2^N orientations, i.e. $W = 2^N$

Applying Eq. (12.12) above, the entropy can be calculated as

$$S = k \ln 2^N \quad \text{or} \quad S = kN \ln 2 \qquad (12.13)$$

k and N can be written as equal to R.

Thus, for 1 mole of the substance, the expression would be

$$S = R \ln 2 = 2.303 \times 8.314 \times 0.3010 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$= 5.85 \text{ J K}^{-1} \text{ mol}^{-1}$$

The number of orientations for a molecule of the type ABO_3 (A and B are two different elements, O is oxygen) is 4. Hence, $W = 4$ in this case.

In general, if there are x possible orientations of a molecule with nearly the same energy, the residual molar entropy will be

$$S = R \ln x$$

Example 4 *The $ClBrO_3$ molecule can have four possible arrangements with nearly the same energy. Calculate the residual entropy of the $ClBrO_3$ molecule.*

Solution: Residual entropy

$$S = R \ln W = 2.303 R \log W$$

In this case, $W = 4$, $R = 8.314$

Substituting the values in the above equation,

$$S = 2.303 \times 8.314 \times 0.6021$$
$$= 11.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example 5 *What is the difficulty in determining absolute entropy of the substance? How was the problem solved by Debye?*

Solution: In determination of absolute entropy of a substance, heat capacity values are required at different temperatures, starting from 0 K. But, heat capacities at low temperature (<15 K) cannot be determined experimentally. The problem was solved by Debye who gave the third power law for heat capacities of solids, according to which $C_p = aT^3$ below 15 K.

12.4 PARTIAL MOLAR PROPERTIES (OPEN SYSTEMS)

In the derivation of various thermodynamic equations so far, we have assumed that change of state has occurred due to change of pressure and temperature only. In the case of open systems containing two or more components, there could be a change in the number of moles of various components as well. In such a situation, an extensive property, say X, is a function of not only pressure and temperature, but also the number of moles of various components.

Consider a system at pressure P, temperature T and number of moles of components as n_1, n_2, n_3 ... Then we may write

$$X = f(T, P, n_1, n_2, n_3, \ldots n_j)$$

when $n_1 + n_2 + \ldots n_j$ = Total number of moles = N (say)

For a small change in T, P and n_1, n_2,. · · etc., dX is given by

$$dX = \left(\frac{\partial X}{\partial T}\right)_{P,N} dT + \left(\frac{\partial X}{\partial P}\right)_{T,N} dP + \left(\frac{\partial X}{\partial n_1}\right)_{T,P,n_2,\ldots n_j} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{T,P,n_1,n_3\ldots n_j} dn_2$$

$$+ \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_1,n_2\ldots n_j} dn_i + \left(\frac{\partial X}{\partial n_j}\right)_{T,P,n_1,n_2\ldots n_i} dn_j \qquad \ldots(12.14)$$

The quantity $\left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_1,n_2\ldots n_j} dn_i$ is called partial molar property of the concerned component. It is represented by $\overline{X}_i$.

For the *i*th component in a system,

$$\text{Partial molar internal energy} = \left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \overline{U}_i$$

$$\text{Partial molar enthalpy} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \overline{H}_i$$

$$\text{Partial molar entropy} = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \overline{S}_i \quad \text{Partial molar volume} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \overline{V}_i$$

12.4.1 Partial Molar Free Energy (Chemical Potential)

Partial molar free energy is the most important partial molar quantity. It is also called the chemical potential and written as μ_i. Thus,

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,\ldots n_j} dn_i = \overline{G}_i = \mu_i \qquad \ldots(12.15)$$

μ_i represents the change in free energy that results in the addition of 1 mole of that particular substance at a constant temperature and pressure to such a large quantity of the system that there is no appreciable change in the overall composition of the system.

For a small free energy change, Eq. (12.14) may be written as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \mu_1 dn_1 + \mu_2 dn_2 + \ldots \mu_j dn_j \qquad \ldots(12.16)$$

If P and T remain constant, Eq. (12.16) reduces to

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots \mu_j dn_j \qquad \ldots(12.17a)$$

If the system has definite composition, we have

$$(G)_{T,P,N} = n_1\mu_1 + n_2\mu_2 + \ldots + n_j\mu_j \qquad \ldots(12.17b)$$

Thus, from the above equation, ***chemical potential may be defined as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under conditions of constant temperature and pressure.***

For a total of one mole of the pure substance, $G = \mu$, i.e. free energy is identical with chemical potential.

It may be noted that while free energy is an *extensive* property, the chemical potential is an *intensive* property because it refers to one mole of the substance.

The Gibbs-Duhem Equation

The total differential of Eq. (12.17b) may be written as

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \ldots + \mu_j dn_j + n_j d\mu_j$$
$$- (\mu_1 dn_1 + \mu_2 dn_2 + \ldots \mu_j dn_j) + (n_1 d\mu_1 + n_2 d\mu_2 + \ldots n_j d\mu_j) \quad \ldots(12.18)$$

According to Eq. (12.17a), the first term in Eq. (12.18) is equal to dG at constant temperature and pressure. Therefore, it follows that

$$n_1 d\mu_1 + n_2 d\mu_2 + \ldots + n_j d\mu_j - 0$$

or
$$\Sigma n_i d\mu_i = 0 \quad \ldots(12.19)$$

This relation is known as Gibbs-Duhem equation.

If there are only two components 1 and 2, Eq. (12.19) may be written as

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{or} \quad d\mu_1 = -\frac{n_2}{n_1} d\mu_2 \quad \ldots(12.20)$$

Equation (12.20) shows that if the chemical potential of Component 1 ($d\mu_1$) is positive, that of Component 2 ($d\mu_2$) must be negative.

12.4.2 Variation of Chemical Potential with Temperature

We shall first derive the expressions for variation of free energy with temperature.

$$G = f(T, P, n_1, n_2, n_3 \ldots)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3} dn_2 + \ldots \quad \ldots(12.21)$$

For a closed system, there is no change in the number of moles of various constituents present, i.e., dn_1, dn_2, dn_3, etc., will be zero, so that the above equation reduces to

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP \quad \ldots(12.22)$$

For a closed system, we have the ***total differential equation***

$$dG = VdP - SdT$$

or
$$dG = -SdT + VdP \quad \ldots(12.23)$$

Comparing Eqs (12.22) and (12.23), we get

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \qquad \ldots(12.24)$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \qquad \ldots(12.25)$$

These two equations give the variation of free energy with temperature and pressure. By definition, chemical potential of a constituent in a system is given by

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2\ldots}$$

Differentiating the equation with respect to temperature, we get

$$\left[\frac{\partial \mu_i}{\partial T}\right]_{P,N} = \frac{\partial^2 G}{\partial n_i \partial T} \qquad \ldots(12.26)$$

Differentiating Eq. (12.24) with respect to n_i, we get

$$\frac{\partial^2 G}{\partial T \partial n_i} = -\left[\frac{\partial S}{\partial n_i}\right]_{T,P,n_1,n_2} = -\overline{S}_i \qquad \ldots(12.27)$$

where $\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_1,n_2} = -\overline{S}_i$ is the partial molar entropy of *i*th component.

Combining (12.26) and (12.27), we get

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\overline{S}_i \qquad \ldots(12.28)$$

Thus, the rate of variation of chemical potential, of any component i of a system with temperature at constant pressure and composition is equal to the partial molar entropy of that component with negative sign.

12.4.3 Variation of Chemical Potential with Pressure

Chemical potential of a component *i* is given by

$$\mu_i = \left(\frac{\partial \mu_i}{\partial n_i}\right)_{T,P,n_1,n_2\ldots}$$

Differentiating this equation with respect to pressure, we get

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \frac{\partial^2 G}{\partial n_i \partial P} \qquad \ldots(12.29)$$

Differentiating Eq. (12.25) with respect to n_i, we get

$$\frac{\partial^2 G}{\partial P \partial n_i} = \left[\frac{\partial V}{\partial n_i}\right]_{T,P,n_1,n_2,\ldots} \qquad \ldots(12.30)$$

where $= \left[\frac{\partial V}{\partial n_i}\right]_{T,P,n_1,n_2,\ldots} = \overline{V}_i$ represents the partial molar volume of the ith component. Combining equations (12.29) and (12.30), we get

$$\left[\frac{\partial \mu_i}{\partial P}\right]_{T,N} = \overline{V}_i$$

Thus, ***the rate of variation of chemical potential of any constituent i of the system with pressure is equal to the partial molar volume of that constituent.***

12.4.4 Chemical Potential in a System of Ideal Gases

For an ideal gas,

$$PV = nRT \qquad \ldots(12.31)$$

As the system consists of n_1, n_2, n_3, etc., moles of different gases,

$$n = n_1 + n_2 + n_3 + \ldots n_i + \ldots \qquad \ldots(12.32)$$

Substituting the value of n in Eq. (12.31),

$$PV = (n_1 + n_2 + \ldots n_i + \ldots)RT \qquad \ldots(12.33)$$

or
$$V = (n_1 + n_2 + \ldots n_i + \ldots)\frac{RT}{P} \qquad \ldots(12.34)$$

Differentiating this equation w.r.t n_i, keeping all other n's constant as well as temperature and pressure constant, we get

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_1,n_2,\ldots} = \frac{RT}{P} \qquad \ldots(12.35)$$

or
$$\overline{V}_i = \frac{RT}{P} \qquad \ldots(12.36)$$

We have another relation (from the previous article), showing change of chemical potential with pressure:

$$\left[\frac{\partial \mu_i}{\partial P}\right]_{T,N} = \overline{V}_i \qquad \ldots(12.37)$$

From Eqs (12.36) and (12.37),

$$\left[\frac{\partial \mu_i}{\partial P}\right]_{T,N} = \frac{RT}{P} \qquad \ldots(12.38)$$

This equation can be rewritten as

$$d\mu_i - \frac{RT}{P}dP = RTd\ln P \qquad \ldots(12.39)$$

In a mixture of gases, if p_i is the partial pressure of the ith component, we have

$$P_iV = n_iRT \qquad \ldots(12.40)$$

where n_i is the number of moles of the ith constituent.

For the complete mixture of gases containing n moles, for ideal behaviour, we have

$$PV = nRT \qquad \ldots(12.41)$$

$$\frac{p_i}{p} = \frac{n_i}{n}$$

or

$$p_i = \frac{n_i}{n}P = K.P \qquad \ldots(12.42)$$

where $K\left(=\frac{n_i}{n}\right)$ is a constant.

Taking logarithm of both sides of Eq. (12.42),

$$\ln p_i = \ln K + \ln P$$

Hence.

$$d\ln p_i = d\ln P \quad (\because d\ln K = 0) \qquad \ldots(12.43)$$

From Eqs (12.39) and (12.43), we have

$$d\mu_i = RTd\ln p_i$$

Integrating this equation, we get

$$\mu_i = \mu_i^\circ + RT\ln p_i \qquad \ldots(12.44)$$

Here, μ°_i is the constant of integration. Its value depends upon the nature of the gas and temperature. From Eq. (12.44), it is obvious that when $p_i = 1$ atm, $\mu_i = \mu^\circ_i$.

Therefore, μ°_i is the chemical potential of the ith constituent when its partial pressure is unity in the mixture of ideal gases.

12.5 CLAUSIUS-CLAPEYRON EQUATION

An important equation which finds application in a one-component, two-phase system is Clausius-Cla-peyron equation. The two phases could be solid-liquid, liquid-vapour, solid-vapour or two crystalline forms of the same substance at their transformation point.

It is possible to transfer any definite amount of the substance from one phase to the other in a thermodynamically reversible manner, i.e. infinitesimally slowly, the system remaining in a state of equilibrium all along. Since the system remains in a state of equilibrium, the free-energy change of phase change will be zero. We may, therefore, say that ***equal amounts of a given substance must have exactly the same free energy in the two phases at equilibrium with each other.***

Let us consider the change of a pure substance from Phase I to Phase II in equilibrium with

each other at a given temperature and pressure. If G_1 is the free energy per mole of the substance in Phase A and G_2 is the value in Phase B, since $G_1 = G_2$,

$$\Delta G = G_2 - G_1 = 0 \qquad \ldots(12.45)$$

The variation of free energy with temperature and pressure is given by the total differential equation,

$$dG = VdP - SdT \qquad \ldots(12.46)$$

Now suppose that the temperature changes from T to $T + dT$ and pressure from P to $P + dP$, keeping the phases in equilibrium. Let the change in free energy of Phase I be dG_1 and that of Phase II be dG_2 (see Fig. 12.3).

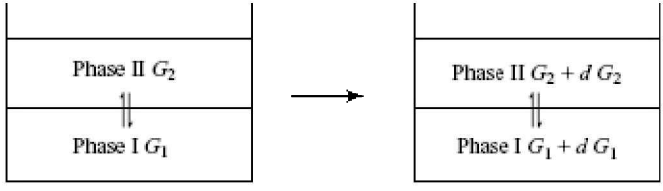


Fig. 12.3 *Phase equilibria at T and P, and at T + dT and P + dP*

According to Eq. (12.46),

$$dG_1 = V_1 dP - S_1 dT \qquad \ldots(12.47a)$$

and

$$dG_2 = V_2 dP - S_2 dT \qquad \ldots(12.47b)$$

where V_1 and S_1 are molar volume and molar entropy of Phase I. V_2 and S_2 are the corresponding values in Phase II.

When the two phases are in equilibrium at temperature T and pressure P, we have

$$\Delta G = 0$$

or

$$G_2 - G_1 = 0$$

For the equilibrium at the temperature $T + dT$ and pressure $P + dP$, we must have

$$(G_2 + dG_2) - (G_1 + dG_1) = 0$$

But

$$G_2 = G_1$$

$\therefore$

$$dG_2 - dG_1 = 0$$

or

$$dG_2 = dG_1 \qquad \ldots(12.48)$$

Substituting the value of dG_1 and dG_2 from equations (12.47a) and (12.47b), we have

$$V_2 dP - S_2 dT = V_1 dP - S_1 dT$$

or

$$(V_2 - V_1)\,dP = (S_2 - S_1)\,dT$$

or

$$\Delta V dP = \Delta S dT$$

or

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

where $\Delta V = V_2 - V_1$ = Molar volume change and $\Delta S = S_2 - S_1$ = Molar entropy change

If this change occurs at the temperature T (i.e. melting point, boiling point, etc.) and ΔH is the latent heat of transformation then

$$\Delta S = \frac{\Delta H}{T} \qquad (12.49)$$

Putting this value in (12.49), we get

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}} \qquad \ldots(12.50)$$

This equation was first derived by Clapeyron in 1934 and is known as the Clapeyron equation.

1. Applications of Clapeyron Equation This relation can be applied to physical equilibria like melting, vaporisation, sublimation and allotropic changes.

For the melting equilibrium, Solid $\rightleftharpoons$ Liquid

$\Delta H = \Delta H_m$, latent heat of melting

and $T = T_m$, the melting point

Equation (12.50) may then be written as

$$\frac{dP}{dT} = \frac{\Delta H_m}{T_m \Delta V} \qquad \ldots(12.51)$$

Further, $\Delta V = V_l - V_s$

where V_s = Molar volume of the solid

V_l = Molar volume of the liquid (melt)

Hence, Eq. (12.51) may be written as

$$\frac{dP}{dT} = \frac{\Delta H_m}{T_m(V_l - V_s)}$$

or

$$\frac{dT}{dP} = \frac{T_m(V_l - V_s)}{\Delta H_m} \qquad \ldots(12.52)$$

This equation gives the variation of melting point with pressure.

2. For the Vaporisation Equilibrium

Liquid $\rightleftharpoons$ Vapour

The Clapeyron equation, i.e. Eq. (12.50) takes the form

$$\frac{dP}{dT} = \frac{\Delta H_v}{T_b(V_v - V_l)} \qquad \ldots(12.53)$$

where

ΔH_v = Latent heat of vaporisation $\quad T_b$ = Boiling temperature of the liquid

V_l = Molar volume of the liquid $\quad V_v$ = Molar volume of the vapour

Volume of the liquid (V_l) is very small compared to the volume of the vapour (V_v). V_l can be neglected compared to V_v. Hence, Eq. (12.53) may be written as (omitting the subscript in T_b)

$$\frac{dP}{dT} = \frac{\Delta H_v}{TV_v} \qquad \ldots(12.54)$$

Assuming that the vapour behaves as an ideal gas, we have

$$PV_v = RT$$

or
$$V_v = \frac{RT}{P} \qquad \ldots(12.55)$$

Substituting this value in equation Eq. (12.54), we have

$$\frac{dP}{dT} = \frac{\Delta H_v}{RT^2} \cdot P \quad \text{or} \quad \frac{1}{P}\frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

or
$$\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2} \qquad \ldots(12.56)$$

This equation is called Clausius-Clapeyron equation as it was derived by Clausius during a detailed study of the Clapeyron equation. Commonly, Eq. (12.56) is written in integrated form. This may be obtained as follows:

Rewriting Eq. (12.56) as

$$d \ln P = \frac{\Delta H_v}{RT^2} \cdot dT \qquad \ldots(12.57)$$

If the temperature changes from T_1 to T_2 when the vapour pressure changes from P_1 to P_2 then integrating Eq. (12.57) between the limits, we get

$$\int_{P_1}^{P_2} d \ln P = \int_{T_1}^{T_2} \frac{\Delta H_v}{RT^2} dT \quad \text{or} \quad \ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

or
$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Changing the natural logarithm to logarithm to the base 10, we get

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

or
$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \qquad \ldots(12.58)$$

This relation is known as integrated form of Clausius-Clayperon equation. It has a number of applications as given below.

Applications of Clausius-Clayperon Equation

1. If the vapour pressure of a liquid is known at one particular temperature, the value at any other temperature can be calculated, if the latent heat of vaporisation of the liquid is known.
2. If the vapour pressures of a liquid at two different temperatures are known, the latent heat of vaporisation of the liquid can be calculated.
3. If the boiling point of a liquid is known at some particular pressure, the boiling point at any other pressure can be calculated, provided the latent heat of vaporisation of the liquid is known.

As we move towards higher altitudes, boiling point of water decreases as expected from the Clausius-Clapeyron equation. That is why it takes a longer time to cook on hills and mountains.

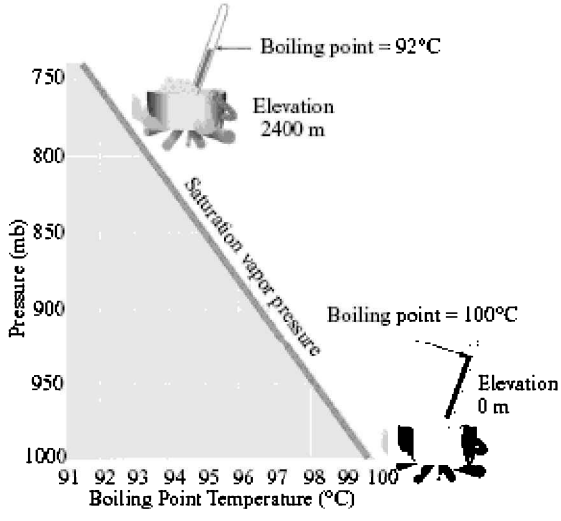


Fig. 12.4 *Boiling point vs pressure*

Example 6 *Water boils at 373 K at one atmosphere pressure. At what temperature will it boil when atmospheric pressure becomes 528 mm of Hg at some space station? Latent heat of H_2O = 2.28 k J^{-1} g and R = 8.314 J $K^{-1}mol^{-1}$.*

Solution: We are given that

$$T_1 = 373 \text{ K}, P_1 = 1 \text{ atm} = 760 \text{ mm}, P_2 = 528 \text{ mm}$$

T_2 to be calculated $\quad \Delta H_v = 2.28 \text{ k J/g} = 2.28 \times 18 \text{ kJ mol}^{-1} = 41040 \text{ J mol}^{-1}$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Substituting the values in the equation,

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \text{ or } \log \frac{521}{760} = \frac{41040}{2.303 \times 8.314}\left[\frac{T_2 - 373}{373 T_2}\right]$$

or $$-0.1582 = 2143.4 \times \left[\frac{T_2 - 373}{373 T_2}\right]$$

or $$-59.0\ T_2 = 2143.4\ T_2 - 799488.2$$

or $$2204.4\ T_2 = 799488.2$$

or $$T_2 = 363 \text{ K}$$

Example 7 *The normal boiling point of water is 100°C. Its vapour pressure at 80°C is 0.4672 atmosphere. Calculate the enthalpy of vaporisation per mole of water. Given that R = 8.314 J K^{-1} mol^{-1}.*

Solution: It is given that

T_1 = 100°C = 373 K, T_2 = 80°C = 353 K, P_1 = 1 atm, P_2 = 0.4672 atm
Using the Clausius-Clayperon equation,

$$\log\frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Substituting the values in the equation above, we have

$$\log\frac{0.4672}{1} = \frac{\Delta H_v}{2.303 \times 8.314}\left[\frac{353 - 373}{353 \times 373}\right] \text{ or } -0.3305 = \frac{\Delta H_v}{2.303 \times 8.314}\left[\frac{-20}{353 \times 373}\right]$$

On simplifying, we get

$$\Delta H_v = 41.66 \text{ kJ mol}^{-1}$$

Example 8 *Water boils at 100°C at a pressure of 1 atm. Calculate the vapour pressure of water at 90°C. The heat of vaporisation of water is 9.80 kcal mol^{-1}. Given that R = 1.987 cal deg^{-1} mol^{-1}.*

Solution: Given that H_v = 9.80 kcal mol^{-1} = 9800 cal mol^{-1}

Using the integrated form of Clausius-Clayperon equation

$$\log\frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Substituting the values, we get

$$\log P_2 = \frac{9800}{2.303 \times 1.987}\left[\frac{363 - 373}{363 \times 373}\right]$$

On simplifying, we get

$$\log P_2 = -0.1582 = \bar{1}.8418$$

or

$$P_2 = 0.6947 \text{ atm}$$

Example 9 *Calculate the value of $\partial T/\partial P$ for a water $\rightleftharpoons$ ice system at 0°C. ΔH_f for water is 6007.8 J mol^{-1}. Molar volume of water is 18.00 cm^3, molar volume of ice is 19.63 cm. Given that 1 J = 9.87 × 10^{-3}dm^3 atm.*

Solution: Using the following form of Clayperon-Clausius equation,

$$\frac{dP}{dT} = \frac{\Delta H_f}{T_f(V_l - V_s)}$$

Convert the data as given below:

$$V_l = 18.0\ \text{cm}^3\,\text{mol}^{-1} = 0.01800\ \text{dm}^3\,\text{mol}^{-1},\ V_s = 19.63\ \text{cm}^3\,\text{mol}^{-1}$$
$$= 0.01963\ \text{dm}^3\,\text{mol}^{-1}$$

Hence, $\dfrac{dT}{dP} = \dfrac{T_f(V_l - V_s)}{\Delta H_f}$ (Reversing the above equation)

Substituting the values,

$$\frac{dT}{dP} = \frac{(273\ \text{K})(0.01800\,\text{dm}^3\text{mol}^{-1} - 0.01963\,\text{dm}^3\text{mol}^{-1})}{(6007.8\ \text{J mol}^{-1})(9.87 \times 10^{-3}\ \text{dm}^3\text{atm J}^{-1})}$$
$$= -0.0075\ \text{K atm}^{-1}$$

Thus, the melting point of ice decreases by 0.0075° if the pressure is increased by 1 atm.

Applying Chemistry to Life

Ice skating becomes possible because of decrease of melting point when pressure is applied. The mass of the skates exerts appreciable pressure on the ice due to a very small area of the blades of the skates. If the temperature is not too low, ice would melt and the layer of water produced would act as a lubricant between the ice and the skates for smooth skating.



Fig. 12.5 *Ice skating*

12.6 FUGACITY AND ACTIVITY

Fugacity may be defined as a substitute for pressure to explain the behaviour of real gases and activity may be defined as the substitute for the concentration to explain the behaviour of a non-ideal solution.

Variation of free energy with pressure at constant temperature T is given by the equation

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \ldots(12.59)$$

This equation applies to ideal and real gases both.

For ***one mole*** of a gas, the molar volume is V. For an ideal gas, the above equation may be

written as

$$(dG)_T = \frac{RT}{P} dP \qquad \ldots(12.60)$$

And for n moles of the gas, the equation may be written as

$$(dG)_T = \frac{nRT}{P} dP = nRT d(\ln P) \qquad \ldots(12.61)$$

Integration of the above equation gives

$$G = G^* + nRT \ln P \qquad \ldots(12.62)$$

where G^*, the integration constant, is the free energy of n moles of the ideal gas at temperature T when the pressure P is unity. Equation (12.62) gives the free energy of an ideal gas at temperature T and pressure P.

Integration of Eq. (12.61) between the pressures P_1 and P_2 at constant temperature T yields

$$\Delta G = \int_{P_1}^{P_2} nRT \frac{dP}{P} = nRT \ln \frac{P_2}{P_1} \qquad \ldots(12.63)$$

And for one mole of the gas, the equation will be

$$\Delta G = RT \ln \frac{P_2}{P_1} \qquad \ldots(12.64)$$

Equations (12.62) and (12.64) are not valid for real gases because V is not ***exactly*** equal to $\frac{RT}{P}$.

Lewis introduced a new function, f called ***fugacity*** to make these simple equations applicable to ***real gases.***

Equation (12.61) for real gases may be expressed as

$$(dG)_T = nRT d(\ln f) \qquad \ldots(12.65)$$

And Eq. (12.62) for real gases may be expressed as

$$G = G^* + nRT \ln f \qquad \ldots(12.66)$$

Note that in equations (12.65) and (12.66), P has been replaced by f where G^* is the free energy of n moles of a ***real gas*** when its fugacity is equal to unity.

Thus, fugacity is the ***substitute for pressure*** which is used in order to retain simple equations applicable to ideal gases.

Equation (12.65) on integration between fugacities f_1 and f_2 at constant temperature T yields

$$\Delta G = nRT \ln \frac{f_2}{f_1} \qquad \ldots(12.67)$$

And for 1 mole of the gas, the corresponding equation would be

$$\Delta G = RT \ln \frac{f_2}{f_1} \quad \ldots(12.68)$$

Equations (12.67) and (12.68) are applicable to ***real gases.***
Fugacity of a gas can be determined by using the equation

$$\ln \frac{f}{P} = -\frac{1}{RT} \int_0^P \alpha dP \quad \ldots(12.69)$$

where α is the departure from ideal behaviour at a given temperature,

$$\alpha = \frac{RT}{P} - V \quad \ldots(12.70)$$

It has been found that at ***low*** pressure, the fugacity of a gas can be obtained from the relation

$$f = \frac{P^2 V}{RT} \quad \ldots(12.71)$$

Example 10 *Calculate the free-energy change accompanying the compression of 1 mole of an ideal gas at 57°C from 25 to 175 atm. Also calculate the free-energy change of a real gas at the same temperature. Given that the fugacities of the real gas at 57°C may be taken as 23 and 92 atm.*

Solution:

(a) For the ideal gas,

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

Substituting the values, we have

$$\Delta G = (1 \text{ mol})(8.314 \text{ J K}^{-1} \text{mol}^{-1})(330 \text{ K}) \times 2.303 \times \log \frac{175}{25}$$
$$= 1 \times 8.314 \times 330 \times 2.303 \times 0.8451 \text{ J} = 5340 \text{ J}$$

(b) For the real gas,

$$\Delta G = nRT \ln \frac{f_2}{f_1}$$

Substituting the values,

$$\Delta G = (1 \text{ mol})(8.314 \text{ J K}^{-1} \text{mol}^{-1})(330 \text{ K}) \times 2.303 \times \log \frac{92}{23}$$
$$= 1 \times 8.314 \times 330 \times 2.303 \times 0.6021 \text{ J} = 3804 \text{ J}$$

Activity and Activity Coefficient

Activity of a substance in any given state is defined as ***the ratio of the fugacity of the substance in that state to the fugacity of the same substance in the pure state.*** Thus, the activity of a substance represented by a is given by the equation

$$a = \frac{f}{f^\circ} \qquad \ldots(12.72)$$

Similarly, in a non-ideal solution, the concentration has to be corrected to give the activity as follows:

$$a = \gamma \times C \qquad \ldots(12.73)$$

where γ represents the ***activity coefficient*** of that component in the solution whose concentration is C Equation (12.73) may be written as

$$\gamma = \frac{a}{C}$$

Hence, activity coefficient of any component in the solution may be defined as the ratio of the activity of the component in the solution to the concentration of the same component in the solution.

SUMMARY

1. The Nernst heat theorem gives the variation of enthalpy change and energy change with decrease of temperature.
2. The third law of thermodynamics originates from the Nernst heat theorem.
3. The third law of thermodynamics can be stated in either of the following ways:
   (a) The entropy of all perfectly crystalline solids may be taken as zero at the absolute zero temperature.
   (b) Every substance has finite positive entropy but at absolute zero of temperature, the entropy may become zero and, in fact, it does become zero in case of perfectly crystalline solids.
4. The entropy which the crystal of a substance possesses at $T = 0$ K is called residual entropy.
5. The quantity $(\partial X/\partial n_i)_{T,P,n_1,n_2\ldots n_j} dn_i$ is called the partial molar quantity of the concerned component i. It is represented as $\overline{X}_i$.
6. We have the partial molar internal energy ($\overline{U}_i$), partial molar enthalpy ($\overline{H}_i$), partial molar entropy ($\overline{S}_i$) and partial molar volume ($\overline{V}_i$).
7. μ_i, the partial molar free energy of the component i, represents the change in free energy that results on the addition of 1 mole of that particular substance, i at a constant temperature and pressure to such a large quantity of the system that there is no appreciable change in the overall composition of the system.
8. Chemical potential may be defined as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under conditions of constant temperature and pressure.
9. While free energy is an extensive property, chemical potential is an intensive property because it refers to one mole of the substance.
10. Variation of chemical potential of any constituent i of the system with pressure at constant temperature and composition is equal to the partial molar volume of that component.
11. Variation of chemical potential of any component i of a system with temperature at constant pressure and composition is equal to the partial molar entropy of that component with negative sign.

12. Equal amounts of a given substance must have exactly the same free energy in the two phases at equilibrium with each other.

13. The Clausius-Clapeyron equation has the following applications:

(a) If V.P. of a liquid is known at one particular temperature, that at another temperature can be calculated if heat of vaporisation is known.

(b) If V.P. of a liquid at two different temperatures is known, the latent heat of vaporisation can be calculated.

(c) If b.p of a liquid at some particular pressure is known, that at another pressure can be calculated.

KEY RELATIONS

1. $C_p = aT^3$ Debye T-cubed law

2. $$S_T = \frac{1}{3}C_p(\text{at } T_1) + \int_{T_t}^{T} C_p d\ln T + \frac{\Delta H_t}{T_t}$$

3. $S = kN \ln 2$ (Residual entropy of CO)

and $$n_1 + n_2 + n_3 + \ldots n_j = N$$

Then

$$dX = \left(\frac{\partial X}{\partial T}\right)_{P,N} dT + \left(\frac{\partial X}{\partial P}\right)_{T,N} dP + \left(\frac{\partial X}{\partial n_1}\right)_{T,P,n_2 \ldots n_j} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{T,P,n_1 n_3 \ldots n_j} dn_2 + \left(\frac{\partial X}{\partial n_j}\right)_{T,P,n_1 n_2 \ldots} dn_j$$

4. If $X = f(T, P, n_1, n_2, n_3, \ldots n_j)$

5. $$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1 \ldots n_j} dn_i = \bar{G}_i = \mu_i$$

6. $(G)_{T,P,N} = n_1\mu_1 + n_2\mu_2 + \ldots + n_j\mu_j$

7. $\Sigma n_i d\mu_i = 0$ (Gibbs–Duhem equation)

8. $$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$$

9. $$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

10. $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2 \ldots}$$

11. $$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\bar{S}_i$$

12. $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \bar{V}_i$

13. $\mu_i = \mu_i^\circ + RT \ln P_i$

14. $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$ (Clausius equation)

15. $\frac{dT}{dP} = \frac{T_m(V_l - V_s)}{\Delta H_m}$

16. $\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2}$

17. $\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. At very low temperatures near the range of 0 K, the C_p of a solid can be calculated using the equation

   (a) $C_p \approx aT^3$

   (b) $C_p = aT^2$

   (c) $C_p = \frac{1}{3}aT^3$

   (d) $C_p = \frac{1}{3}aT$

2. Residual entropy is

   (a) the entropy possessed by the crystalline substance at $T = 0$

   (b) the entropy arising out of defects in crystalline substance

   (c) the entropy which is in excess over the normal value

   (d) the remaining entropy of a substance Residual molar entropy is given by the expression

3. Residual molar entropy is given by the expression

   (a) $S = R \ln W$

   (b) $S = N \ln W$

   (c) $S = \frac{R}{N} \ln W$

   (d) $S = nR \ln W$

4. The limit $T \rightarrow 0$, the entropy of a crystalline solid is approximately equal to

   (a) $\frac{1}{2}C_p$

(b) $\frac{2}{3}C_P$

(c) $\frac{1}{3}C_P$

(d) $\frac{1}{5}C_P$

5. The Boltzmann entropy equation is

(a) $S = \frac{K}{\ln W}$

(b) $S = K \ln \frac{P_2}{P_1}$

(c) $S = K \ln \frac{V_1}{V_2}$

(d) $S = K \ln W$

6. The third law of thermodynamics may be stated as follows:

(a) At absolute zero the entropy of all perfectly crystalline solids tends to decrease.

(b) The entropy of a perfectly crystalline solid may be taken as zero at absolute zero.

(c) The entropy of every substance is zero at 0 K.

(d) The entropy of a substance is related to its heat capacity.

7. From the third law, the entropy of a substance at temperature T is given as,

(a) $S_T = \frac{1}{3}C_P(\text{at } T_1) + \int_{T_1}^{T} \frac{C_P}{T} dT$

(b) $S = C_p(\text{at } T_1) + \int_{T_1}^{T} C_p \ln dT$

(c) $S = C_p \ln T + \int_{T_1}^{T} \frac{C_P}{T} dT$

(d) none of the above

8. The Nernst heat theorem can be mathematically stated as

(a) $\lim_{T \to 0} \frac{d(\Delta G)}{dT} = \lim_{T \to 0} \frac{d(\Delta H)}{dT} = 0$

(b) $\lim_{T \to 0} \frac{d(\Delta H)}{dT} = \lim_{T \to 0} \frac{d(\Delta S)}{dT} = 0$

(c) $\lim_{T \to 0} \frac{d(\Delta V)}{dT} = \lim_{T \to 0} \frac{d(\Delta A)}{dT} = 0$

(d) $\lim_{T \to 0} \frac{d(\Delta A)}{dT} = \lim_{T \to 0} \frac{d(\Delta H)}{dT}$

Answers

1. (a)
2. (a)
3. (a)
4. (c)
5. (c)
6. (b)
7. (a)
8. (a)

SHORT-ANSWER QUESTIONS

1. State and explain the Nernst heat theorem.
2. How did the results of Nernst theorem lead to the enunciation of the third law of thermodynamics?
3. The first law of thermodynamics leads to the concept of energy content and the second law leads to the concept of entropy. Does the third law lead to any new concept? If not, then why is it called a law?
4. How can you test the validity of the third law of thermodynamics?
5. Prove that the entropy of a substance at very low temperature is one-third of its molar heat capacity at that temperature.
6. State the third law of thermodynamics. How does this law help in the determination of absolute entropies of chemical compounds at any desired temperature?
7. What is residual entropy? How did the concept of residual entropy originate? How is it calculated?
8. Define the term *chemical potential*. Write an expression for it. Write an expression for the total free energy in terms of chemical potentials at constant composition for a system consisting of a number of components.
9. Write Gibbs-Duhem equation. What important conclusions can you draw from it by applying it to a system consisting of two components, i.e. a binary solution?
10. Show that the rate of variation of chemical potential of any constituent *i* of a system, with temperature at constant pressure and composition, is equal to partial molar entropy of that constituent with a negative sign.
11. How does chemical potential of the *i*th component in a gaseous mixture of ideal gases vary with its partial pressure?
12. Show that the variation of chemical potential of any constituent *i* of the system with pressure at constant temperature and composition is equal to the partial molar volume of that constituent.

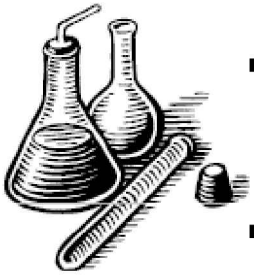
GENERAL QUESTIONS

1. What is the Nernst heat theorem? What result follows from it regarding entropy change and heat capacity change? State the 'third law of thermodynamics'. Briefly describe its importance
2. What is residual entropy? What is its origin and how can it be calculated? Explain taking suitable examples.
3. Write complete expression for the calculation of entropy of any substance in the gaseous state at

temperature T starting from 0 K and assuming that a solid undergoes a polymorphic transition at temperature T_{tr}. Represent the various changes graphically (entropy versus temperature).

4. What do you understand by the term *chemical potential?* Derive an expression for the variation of chemical potential with (a) temperature, and (b) pressure
5. What are partial molar quantities? How do you arrive at the general expression for partial molar quantities? Write expressions for three different partial molar quantities.
6. Derive Gibbs-Duhem equation.
7. Prove that in a mixture of ideal gases, the chemical potential of the *i*th component is given by

$$\mu_i = \mu_i^{\circ} + RT \ln P_i$$



Chemical Equilibrium

13

LEARNING OBJECTIVES

- Establish dynamic nature of equilibrium in physical and chemical processes
- State the law of equilibrium
- Explain the characteristics of equilibria involved in physical and chemical processes
- Write the expressions for equilibrium constants in terms of concentration, partial pressure and activity
- Establish a relation between K_P and K_c
- Learn the applications of equilibrium constant
- Understand the concept of partial molal quantities and chemical potential
- Derive Gibbs-Duhem equation
- Establish free-energy change as a criterion of spontaneity
- Derive the law of chemical equilibrium thermodynamically
- Understand van't Hoff reaction isotherm
- Derive van't Hoff equation for temperature dependence of equilibrium constant
- Understand Le Chatelier principle and study the effect of concentration, temperature, pressure, catalyst on the equilibrium of a reaction.
- Derive Clausius–Clayperon equation

13.1 INTRODUCTION

We have been treating reactions as though they proceed only from left to right (reactants to products) and end up giving the products in totality. But this is not so with most reactions. We find that as the reaction progresses, the concentration of the reactants decreases and the concentration of the products increases. Then the reverse reaction starts taking place, i.e. the products become the reactants and reactants become the products. At the end, the concentrations of reactants and products stop changing although the reaction continues in both directions at the same rate. This state is called the ***state of equilibrium.*** Chemical equilibria are important in a number of biological, chemical and environmental processes. We can explain the toxicity of CO in the reaction between CO molecules and haemoglobin and the transport of O_2 from our lungs to the muscles with the help of chemical equilibrium.

We give here the example of the equilibrium reaction $N_2O_4 \rightleftharpoons 2NO_2$.

N_2O_4 is a colourless gas at 0°C. At the temperature of boiling water, this gas changes to NO_2 and adopts a red-brown colour. At room temperature (around 25°C), a mixture of NO_2 + N_2O_4 exists in pale brown colour as shown below.

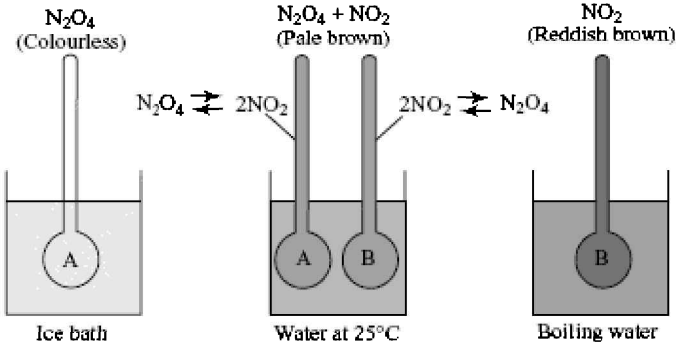


Fig. 13.1 *Equilibrium reaction:* $N_2O_4 \rightleftharpoons 2NO_2$

We have the relation $\Delta G = \Delta H - T\Delta S$ from thermodynamics. ΔG refers to the change in free energy. If ΔG for a process is negative, the process will take place. If ΔG is positive, the process will not take place. If $\Delta G = 0$, the process will be in a state of equilibrium.

Most chemical reactions, when carried out in closed vessels, do not go to completion. A process starts on its own or on initiation, continues for some time with falling rate and appears to have stopped. Although reactants are still present, they don't appear to react anymore. The process or the reaction is then said to be in a state of ***equilibrium.*** The composition of the reaction mixture at equilibrium at a given temperature is the same, irrespective of whether we start from the reactants side or product side.

This may be illustrated with the help of the following examples:

1. Evaporation of Water in a Closed Vessel If a small amount of water is placed in a closed vessel at room temperature, evaporation starts. A pressure due to water vapour is built up in the vessel, which can be recorded with the help of an attached manometer. After some time, we find that the pressure of water vapour remains constant if the temperature does not change. Sufficient water is still present, but it does not appear to evaporate further. We say that a state of equilibrium between evaporation of water and condensation of vapours has been established. This can be represented as

$$H_2O(l) \rightleftharpoons H_2O(g)$$

2. Decomposition of Calcium Carbonate Solid calcium carbonate on heating in a closed vessel starts decomposing into solid calcium oxide and gaseous carbon dioxide. Pressure built up due to carbon dioxide can be recorded on a manometer attached to a vessel. The pressure goes on increasing and it becomes constant. After that, calcium carbonate is still present in the reaction mixture but does not appear to decompose further. A state of equilibrium, as represented by the following equation, is attained.

$$CaCO_3(S) \rightleftharpoons CaO(s) + CO_2(g)$$

3. A Catalyst can Hasten the Approach of Equilibrium but does not Alter the State of Equilibrium In other words, the relative concentrations of the products and reactants remain the same irrespective of the presence or absence of a catalyst.

Based on the extent to which the reactions proceed, the state of equilibrium in a chemical reaction may be classified into three types. Correspondingly we have three types of reactions.

(i) The reactions that proceed nearly to completion and only negligible amounts of the reactants are left

(ii) The reactions in which only small amounts of products are formed and most of the reactants remain unchanged

(iii) The reactions in which the concentrations of reactants and products are comparable

The stage of equilibrium in a reaction varies with the experimental conditions such as concentration of reactants, temperature, pressure, etc. We need to optimise the operational conditions in order to obtain the desired products in laboratory and industry.

13.1.1 Characteristics of Chemical Equilibrium

1. Chemical Equilibrium At given temperature, chemical equilibrium is characterised by constant values of certain observable properties such as pressure, concentration or colour. Hydrogen gas and iodine vapours react at high temperature to give hydrogen iodide gas as per the following equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

It is also known that hydrogen iodide gas is not very stable and it dissociates into hydrogen and iodine as follows:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The composition of the reaction mixture at equilibrium is 1.56 ***moles*** of HI, 0.22 ***mole*** of H_2 and 0.22 ***mole*** of I_2 whether we carry out the reaction by taking one mole each of H_2 and Cl_2 as the reactants or two moles of HI as the reactant at 448°C.

This shows that ***when equilibrium is attained at a given temperature, each reactant and each product has fixed concentration and this is independent of the fact whether we start the reaction with the reactants or with the products. Thus, equilibrium can be attained from either side.***

2. Chemical Equilibrium is Dynamic in Nature Equilibrium involves two reactions proceeding in opposite directions. One of these reactions proceeds from the reactants towards the products and is known as the forward reaction. The other proceeds from the products to the reactants and is known as the reverse reaction. When equilibrium is attained, there is no further change in the concentration of the products or the reactants. This gives the impression that the reaction has come to a standstill. But this is not the case. Actually, the two opposing reactions, the forward reaction and the reverse reaction, are proceeding simultaneously at equal rates.

13.1.2 Experimental Proof of Dynamic Nature of Chemical Equilibrium

Consider the following reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

When the equilibrium is attained at 448°C, a small amount of radioactive isotope of iodine is introduced into the reaction mixture. Radioactive isotopes have the same ***chemical*** properties as their non-radioactive counterparts. After some time, if the mixture is examined, it will be seen that HI ***contains radioactive iodine.*** There is, however, no change in the relative amounts of HI, H_2 and I_2. This shows that although there has been no change in the relative amounts of the reactants and the products, ***chemical reaction has been taking place from left to right.*** But, since there has been no increase whatsoever in the amount of HI, it is evident that the ***reaction has been taking place from right to the left as well, at the same rate.*** Thus, the two opposing reactions have been proceeding. This proves the dynamic nature of equilibrium.

13.2 THE STATE OF CHEMICAL EQUILIBRIUM

Consider a general reversible reaction,

$$A + B \rightleftharpoons C + D$$

The reactants A and B react to form the products. With the passage of time, the concentrations of

reactants decrease. Therefore, the rate of forward reaction decreases. On the other hand, the concentrations of C and D increase. Therefore, rate of backward reaction increases. A stage is reached when the rate of backward reaction becomes equal to the rate of forward reaction and the system attains a state of equilibrium. The variation of rate of forward and backward reaction is shown. In Fig. 13.2.

Thus, the state of equilibrium is a state in which the measurable properties of the system do not undergo any noticeable change under a given set of conditions. That means the properties like concentration, pressure, etc., of the system become constant. But this does not mean that the reaction has stopped. In fact, both the backward and forward reactions carry on even after attainment of equilibrium. However, the rates of forward and backward reactions become equal as shown in Fig. 13.2. Thus, ***the equilibrium is dynamic in nature.***

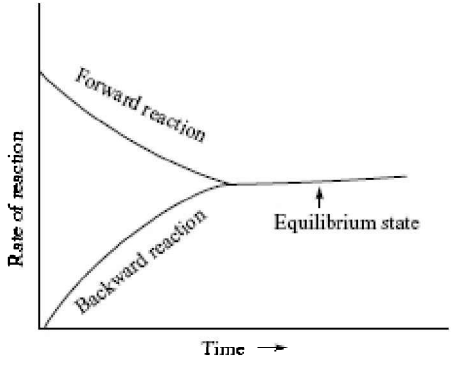


Fig. 13.2 *Variation of rate of forward and backward reaction with time*

A reaction in equilibrium may not be construed as if it has stopped. It is still taking place in forward and backward directions in such a way that the concentrations of the reactants and products remain constant. The situation may be likened to a bucket containing water, if the volumes of water that are added per unit time and removed from the bucket are the same.

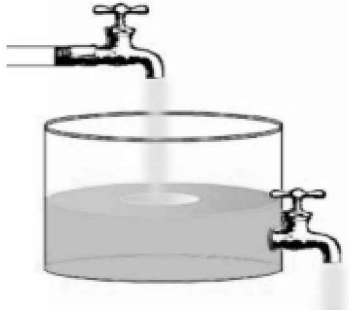


Fig. 13.3 *Chemical equilibrium is analogous to this*

13.3 LAW OF MASS ACTION

According to the law of mass action, ***the rate at which a substance reacts is proportional to its 'active mass' and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances.***

The term ***active mass*** used in the above statement implies ***activity*** which, for the sake of simplicity, may be taken as equal to ***molar concentration.***

Consider the following reversible reaction, taking place at a constant temperature:

$$A + B \rightleftharpoons C + D$$

According to the law of mass action, the rate (r_1) at which A and B react is given by the equation

$$r_1 = k_1[A][B] \qquad \ldots(13.1)$$

where, k_1 is the proportionality constant, known as the ***rate constant*** of the reaction and square brackets indicate molar concentrations. As the reaction proceeds further, the molar concentrations of A and B continue to decrease. Consequently, the velocity of the forward reaction goes on decreasing with time. The rate of back reaction (r_2) is given by the equation,

$$r_2 = k_2[C][D] \qquad \ldots(13.2)$$

where, k_2 is the rate constant of reverse reaction.

Ultimately, a dynamic equilibrium is attained when the rate of forward reaction becomes equal to that of the reverse reaction, i.e. $r_1 = r_2$.

13.3.1 Law of Chemical Equilibrium

Consider the reaction,

$$aA + bB \rightleftharpoons cC + dD$$

Rate of forward reaction, $r_1 = k_1[A]^a[B]^b$

Rate of backward reaction, $r_2 = k_2[C]^c[D]^d$

Since at equilibrium, $r_1 = r_2$ it follows that,

$$k_1[A]^a[B]^b = k_2[C]^c[D]^d$$

or

$$\frac{k_1}{k_2} = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \ldots(13.3)$$

K_c is known as the ***equilibrium constant.*** It is simply the ratio of the ***rate constants*** of the ***two opposing reactions.*** It is ***constant at given temperature.*** It has the same value at a given temperature ***irrespective of the direction*** from which the equilibrium is reached. It has also the same value ***irrespective of the pressure*** on the system or the concentrations of the reactants and products.

Thus, equilibrium constant for the reverse reaction is the inverse of equilibrium constant for the forward reaction.

This may be illustrated by taking the example of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. The equilibrium constant K_c for the reaction is

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

The equilibrium constant K'_c for the reverse reaction may be written as

$$K_c' = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{\frac{[HI]^2}{[H_2][I_2]}} = \frac{1}{K_c}$$

If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. Thus, if the reaction is written as

$$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$$

The equilibrium constant for the above reaction is given by

$$K_c'' = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}} = \left[\frac{[HI]^2}{[H_2][I_2]}\right]^{\frac{1}{2}} = K_c^{\frac{1}{2}}$$

In general, if the equation is multiplied by n then we have

$$nH_2 + nI_2 \rightleftharpoons 2nHI,$$

Then the equilibrium constant for the reaction is K^n_c.

In a general reaction represented by the equation $aA + bB + cC + \ldots \rightleftharpoons lL + mM + nN + \ldots$, the equilibrium constant is given by,

$$K_c = \frac{[L]^l[M]^m[N]^n\ldots}{[A]^a[B]^b[C]^c\ldots} \qquad \ldots(13.4)$$

The magnitude of an equilibrium constant reveals whether products or reactants are favoured. A very large value of K_c indicates that the product is favoured. For example, the value of K_c for the reaction between H^+(aq) and OH^-(aq) is 1×10^{14} which is very large.

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)\ K_c = 1 \times 10^{14}$$

This indicates that the reaction will proceed almost completely to the RHS, i.e. to the products.

On the other hand, if we consider the ionisation of liquid water into H^+(aq.) and OH^-(aq.), the value of K_c comes out to be $1/K_c$, i.e. 1×10^{-14}. This indicates that neutral water has tendency to ionise into H^+ and OH^-ions.

For gaseous reactions, it is more convenient to use partial pressures instead of concentrations. The equilibrium constant in that case is represented by K_p. Thus, for the general gaseous reaction,

$$aA + bB + cC + \ldots \rightleftharpoons lL + mM + \ldots,$$

$$Kp = \frac{[p_L]^l \times [p_M]^m\ldots}{[p_A]^a \times [p_B]^b\ldots}$$

where, p_L and p_M, etc., stand for partial pressures of the products and p_A, p_B, etc., for the partial pressures of the reactants.

13.3.2 Types of Equilibrium Constants and their Units

In Eq. (13.3), the concentrations of reactants and products are generally expressed in terms of moles/ litre.

1. The equilibrium constant is then written as K_c where the subscript c refers to the equilibrium constant expressed in terms of molar concentrations.
2. When the molar concentrations are replaced by activities of reactants and products then the equilibrium constant is written in terms of activities and is called K_a,

   i.e. $$K_a = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}, \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

   As activity is dimensionless, K_a has no units.
3. In gaseous reactions, the concentration terms in Eq. (13.3) are replaced by the partial pressure. Then, the equilibrium constant may be expressed as,

   $$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

   where, P_A, P_B, P_C and P_D are the partial pressures of gases A, B, C, and D respectively. K_p may not always be equal to K_c. Units of K_p are (atmospheres)$^{\Delta n}$.

   As concentrations are expressed in moles-litre, according to Eq. (13.3), dimensions of K_c are given by

   $$\left(\frac{\text{moles}}{\text{litre}}\right)^{\Delta n}$$

   where Δn is the difference is the number of moles of products and the reactants [say $\Delta n = (c + d) - (a + b)$].
   When $\Delta n = 0$, K_c and K_p both will become dimensionless, i.e. will have no units, simply numbers.
4. When the equilibrium constant is expressed in terms of mole fractions of reactants and products, it is expressed as K_x.

   $$K_x = \frac{(x_C)^c (x_D)^d}{(x_A)^a (x_B)^b}$$

   where, x_A, x_B, x_C and x_D represent the mole fractions of A, B, C and D.

13.3.3 Relationship between K_p and K_c

For a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant in terms of concentrations (moles/litre) is

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \ldots(13.5)$$

If the reactants and products are gaseous then the concentration terms may be replaced by partial pressure. The equilibrium constant K_p is written as

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \qquad \ldots(13.6)$$

For an ideal gas, $PV = nRT$ or $P = \frac{n}{V} RT = CRT$, where C = molar concentration,

For different gases A, B, C and D we may write,

$$P_A = C_A RT, \quad P_B = C_B RT, \quad P_C = C_C RT, \quad P_D = C_D RT$$

Putting these values in Eq. (13.6), we get,

$$K_p = \frac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a (C_B RT)^b}$$

or
$$K_p = \frac{C_C^c C_D^d}{C_A^a C_B^b} (RT)^{(c+d)-(a+b)}$$

or
$$\boxed{K_p = K_c (RT)^{\Delta n}} \qquad \ldots(13.7)$$

where, $\Delta n = (c + d) - (a + b)$

= [Number of moles of products] – [Number of moles of reactants]

It is necessary that while calculating the value of K_p, pressure should be expressed in bar as the standard state is 1 bar.

1 pascal, Pa = 1 Nm^{-2} and 1 bar = 10^5 Pa

Example 1 *For the equilibrium* $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, *the value of the equilibrium constant* K_c *is* 3.75×10^{-6} *at 1069 K. Calculate* K_p *for the reaction at this temperature.*

Solution: $K_p = K_c [RT]^{\Delta n}$

For this reaction, $\Delta n = (2 + 1) - 2 = 1$, $R = 0.0831$ m^3 atm in S.I. units

$\therefore$ $K_p = 3.75 \times 10^{-6} [0.0831 \times 1069]$

$= 0.033$

Units of Equilibrium Constant

The value of equilibrium constant can be calculated by substituting the concentration terms in mol/L and for K_p, the partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure unless the exponents of both the numerator and denomenator are same.

Thus, for the reactions

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_c and K_p have no units

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, K_c has unit of mol/L and K_p has the units bar

13.3.4 Relationship between K_x, K_p and K_c

The partial pressure p of a gas in an ideal gaseous mixture is related to total pressure P as

$$p = xP$$

where x is the mole fraction of the gas in the mixture. Substituting for the partial pressure of A, B, C and D in Eq. (13.6), we get

$$K_p = \frac{p_C^c\, p_D^d}{p_A^a\, p_B^b} = \left[\frac{x_C^c\, x_D^d}{x_A^a\, x_B^b}\right] \times P^{(c+d)-(a+b)} \quad \text{[After substituting } p = xP \text{ for } A, B, C, D\text{]}$$

or
$$K_p = K_x (P)^{\Delta n} \qquad \ldots(13.8)$$

From Eq. (13.7) and (13.8), we have

$$K_c (RT)^{\Delta n} = K_x P^{\Delta n}$$

or
$$K_c = K_x \left(\frac{P}{RT}\right)^{\Delta n}$$

or
$$\boxed{K_c = K_x V^{\Delta n}}$$

where V is the volume of the system containing 1 mole of an ideal gas.

When $\Delta n = 0$, K_p, K_c and K_x become equal.

or
$$K_p = K_x = K_c$$

13.3.5 Relationship between K_a and K_p or K_c

Activity and molar concentration are related as

$$a = \gamma C \qquad \ldots(13.9)$$

where γ is activitis coefficient.

$$K_a = \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b} \qquad \ldots(13.10)$$

Substituting, for activities of A, B, C and D in Eq. (13.10), we have

$$K_a = \left(\frac{\gamma_C^c\, \gamma_D^d}{\gamma_A^a\, \gamma_B^b}\right)\left(\frac{C_C^c\, C_D^d}{C_A^a\, C_B^b}\right) = K_\gamma \cdot K_c$$

or
$$\boxed{K_a = K_\gamma K_c} \qquad \ldots(13.11)$$

For very dilute solutions as $C \to 0$, $\gamma \to 1$

Then, $K_a \to K_c$

The activity of any gaseous component is related to its partial pressure as

$$a = \gamma_p \qquad \ldots(13.12)$$

Substituting (13.12) in Eq. (13.10), we get

$$K_a = K_\gamma K_p$$

For gases at very low pressure, $\gamma = 1$

$\therefore$ $K_\gamma = 1$

Hence, $K_a = K_p$

Example 2 *The value of K_p for the reaction $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ is 3.0 at 1000 K. If initially $P_{CO2} = 0.48$ bar and $P_{CO} = 0$ bar and pure graphite (carbon) is present, calculate the equilibrium partial pressure of CO and CO_2.*

Solution: Let x be the amount of CO_2 reacted,

Then	$CO_2(g) + C(s) \rightleftharpoons$	$2CO(g)$
Initial pressure	0.48 bar	0 bar
At equilibrium	$(0.48 - x)$ bar	$2x$ bar

$$K_p = \frac{p_{CO}^2}{p_{CO_2}}$$

or
$$K_p = \frac{(2x)^2}{0.48 - x} = 3$$

or
$$4x^2 = 3(0.48 - x)$$

or
$$4x^2 + 3x - 1.44 = 0$$

Solving the quadratic equation using the formula,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{(-3 \pm 5.66)}{8}$$

Taking only +ve sign as that above gives the +ve value for x,

$$x = \frac{(-3 + 5.66)}{8} = 0.33$$

The equilibrium pressures are

$$p_{CO} = 2x = 0.66 \text{ bar}$$

$$p_{CO2} = 0.48 - x = 0.15 \text{ bar}$$

13.4 APPLICATIONS OF EQUILIBRIUM CONSTANT

Equilibrium constant has applications in the

(1) prediction of extent of reactions on the basis of magnitude

(2) prediction of the direction of the reaction

(3) calculation of equilibrium concentrations

These are discussed separately as under:

1. Prediction of the Extent of Reaction on the Basis of Magnitude A high value of K_c or K_p suggests a high concentration of the products. We can make the following generalisations regarding the composition of the equilibrium mixtures.

(a) If $K_c > 10^3$, the products predominate over the reactants, i.e. the reaction proceeds nearly to completion. For example, the reaction

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl \text{ at } 300 \text{ K has } K_c = 4.0 \times 10^{31}$$

(b) If $K_c < 10^{-3}$, reactants predominate over the products, i.e. the reaction proceeds rarely. It is mostly the reactants in the reaction mixture. Consider the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

At 298 K, it has $K_c = 4.8 \times 10^{-31}$

(c) If K_c lies in the range 10^{-3} to 10^3, both reactants and products are present in appreciable concentration. Consider the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

It has a K_c value of 57.0 at 700 K.

Thus, both the reactants and products are present in the equilibrium mixture.

2. Predicting the Direction of the Reaction We calculate the reaction quotient Q of the reaction. The reaction quotient is similar to the equilibrium constant except that the concentrations (or pressure) are not necessarily equilibrium values. For a general reaction $aA + bB \rightleftharpoons cC + dD$,

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

(a) If $Q_c > K_c$, the reaction will proceed in the direction of the reactants, i.e. reverse reaction will take place.

(b) If $Q_c < K_c$, the reaction will proceed in the direction of the products, i.e. forward reaction will take place.

(c) If $Q_c = K_c$, the reaction is already in equilibrium.

To explain it further, let us say at any random time if Q_c is greater than K_c, it has to ultimately move lower to the equilibrium value, that is, the reaction will proceed backwards.

Similarly, if $Q_c < K_c$, it has ultimately to move higher to the equilibrium value. That is, the reaction will proceed forward to the products.

Example 3 *The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the concentration of the reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction will the reaction proceed?*

Solution: The reaction quotient for the given reaction is given by

$$Q = \frac{[B][C]}{[A]^2}$$

Substituting the values of $[A]$, $[B]$ and $[C]$ in the equation, we get

$$Q = \frac{[3 \times 10^{-4}][3 \times 10^{-4}]}{[3 \times 10^{-4}]^2} = 1$$

As $Q > K_c$, the reaction will proceed in the backward reaction.

3. Calculation of the Equilibrium Concentration The equilibrium concentrations of different species in a reaction can be calculated using the equilibrium constant.

We first write the balanced equation for the reaction. We write the initial concentration of the reactants. Assume that the amount x changes to the product. Using the stoichiometry of the reaction, find out the relative amounts of the reactants and products. Then substitute the equilibrium concentrations into the equation for equilibrium constant. Solve the equation to calculate actual equilibrium concentrations. An example to find out equilibrium pressures has already been given.

Example 4 *3.00 moles of PCl_5 kept in a 1 L closed reaction vessel was allowed to attain equilibrium at 380 K. Calculate the composition of the mixture at equilibrium K_c = 1.80*

Solution:

	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$		
Initial conc.	3.0	0	0
Equilibrium conc.	$3-x$	x	x

where x is the number of moles that decompose. Remember x moles on decomposition will give x mole of PCl_3 and x moles of Cl_2.

$$K_c = \frac{[PCl_3][Cl_2]}{PCl_5}$$

Substituting the values, we have

$$K_c = \frac{x^2}{3-x}$$

$$1.8 = \frac{x^2}{3-x}$$

or $x = 1.59$

Thus, $[PCl_3] = [Cl_2] = 1.59$ M

and $[PCl_5] = 3 - 1.59 = 1.41$ M

PROBLEMS FOR PRACTICE

1. The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500 K: $[N_2] = 1.5 \times 10^{-2}$ M, $[H_2] = 3.0 \times 10^{-2}$ M and $[NH_3] = 1.2 \times 10^{-2}$ M. Calculate the equilibrium constant.

[Ans. 1.06×10^3**]**

2. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K and having concentrations 1.59 M PCl_3, 1.59 M Cl_2 and 1.41 M PCl_5. Calculate K_c for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.

[Ans. 1.79**]**

3. At equilibrium, the concentrations of $N_2 = 3.0 \times 10^{-3}$ M, $O_2 = 4.2 \times 10^{-3}$ M and NO = 2.8×10^{-3} M in a sealed vessel at 800 K. What will be K_c for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.

[Ans. 0.622**]**

4. For the equilibrium $2NOCl \rightleftharpoons 2NO(g) + Cl_2(g)$, the value of equilibrium constant K_c is 3.75×10^{-6} at 1069 K. Calculate K_p for the reaction at this temperature.

[Ans. 0.033]

5. 13.8 g of N_2O_4 was placed in a 1 L reaction vessel at 400 K and allowed to attain equilibrium.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The total pressure at equilibrium was found to be 9.15 bar. Calculate K_c, K_p and partial pressures at equilibrium.

Given

$$R = 0.083 \text{ bar L mol}^{-1} \text{ K}^{-1}$$

[Ans. $p_{N2O4} = 0.81$ bar
$p_{NO2} = 8.34$ bar
$K_p = 85.87$, $K_c = 2.6$]

Hint: Use $PV = nRT$ to obtain initial pressure

13.5 PARTIAL MOLAR QUANTITIES

The thermodynamic properties such as free energy, enthalpy, entropy, etc. are extensive properties. Their values change with change in mass of the system. Consider an open system containing n_1, n_2, n_3 ... moles of various components. Let the entropy 'X' be a function of temperature, pressure, and the number of moles of various constituents, i.e.

$$X = f(T, P, n_1, n_2, n_3 \ldots n_i) \qquad \ldots(13.13)$$

where, $n_1 + n_2 + n_3 + \ldots n_i = N$

For a small change in temperature, pressure and the number of moles of constituents, the change dX in property X will be given by the following equation:

$$dX = \left(\frac{\partial X}{\partial T}\right)_{P,n_1,n_2\ldots} dT + \left(\frac{\partial X}{\partial P}\right)_{T,n_1,n_2\ldots} dP + \left(\frac{\partial X}{\partial n_1}\right)_{T,P,n_2,n_3\ldots} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{T,P,n_1,n_3\ldots} dn_2 + \ldots \qquad \ldots(13.14)$$

At constant temperature and pressure of the system, $dT = 0$, $dP = 0$
Equation (13.14), then becomes,

$$(dX)_{T,P} = \left[\frac{\partial X}{\partial n_1}\right]_{T,P,n_2,n_3\ldots} dn_1 + \left[\frac{\partial X}{\partial n_2}\right]_{T,P,n_1,n_3\ldots} dn_2 + \ldots \qquad \ldots(13.15)$$

Each term on the right-hand side of Eq. (13.15) is called ***partial molar property*** of that particular component. It is represented by putting a bar over the concerned property, i.e., $\overline{X}_1$, $\overline{X}_2$, for the first and second component respectively.

$$\left[\frac{\partial X}{\partial n_1}\right]_{T,P,n_2,n_3\ldots} = \overline{X}_1$$

$$\left[\frac{\partial X}{\partial n_2}\right]_{T,P,n_1,n_3\ldots} = \overline{X}_2$$

In general, for an *i*th constituent, we can write

$$\left[\frac{\partial X}{\partial n_i}\right]_{T,P,n_1,n_2\ldots} = \bar{X}_i$$

13.5.1 Partial Molar Free Energy*

Concept of Chemical Potential The most important partial molar property is partial molar free energy. It is also called chemical potential and represented by the symbol μ. For an ith component, it is written as

$$\mu = \bar{G}_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_1,n_2\ldots} \quad \ldots(13.16a)$$

Suppose dn_i is taken as 1 mole.

Then, $$\mu = (dG)_{T,P,n_1,n_2\ldots} \quad \ldots(13.16b)$$

The chemical potential of a given substance may be defined as the change in the free energy of the system which results in the addition of one mole of that particular substance at constant temperature and pressure, to such a large quantity of the system such that there is no appreciable change in overall composition of the system.

Taking free energy as the extensive property, change in property, i.e. dG, may be written as

$$(dG)_{T,P} = \left[\frac{\partial G}{\partial n_1}\right]_{T,P,n_2,n_3\ldots} dn_1 + \left[\frac{\partial G}{\partial n_2}\right]_{T,P,n_1,n_3\ldots} dn_2 + \ldots \quad (13.17)$$

or $$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots$$

where μ_1, μ_2. are chemical potentials of constituents 1, 2,...

For a system of definite composition having n_1, n_2, ... moles of components, Eq. (13.17) on integration gives,

$$G_{T,P,N} = n_1\mu_1 + n_2\mu_2 + \ldots$$

The subscript '*N*' stands for total number of moles.

Here, μ_1, μ_2, etc., give the contribution per mole of components 1, 2, etc to the total free energy of the system under conditions of constant temperature and pressure.

Thus, ***the chemical potential of a constituent in a mixture is its contribution per mole to the total free energy of the system of a constant composition at constant temperature and pressure.***

It is observed that for one mole of pure component $G = \mu$, i.e. free energy, is the same as chemical potential.

13.5.2 Gibbs-DuhemEquation

Free energy is an extensive property. Besides temperature and pressure, it also depends on the composition of the system. For a system having n_1, n_2,... moles of components 1,2,..., we can write

$$G = f(T, P, n_1, n_2, \ldots) \quad \ldots(13.18)$$

where, $$n_1 + n_2 + n_3 + \ldots = N$$

A small change in free energy with change in temperature pressure and number of moles of various components can be obtained by partial differentiation of Eq. (13.18)

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\ldots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\ldots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3,\ldots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3,\ldots} dn_2 + \ldots\ldots (13.19)$$

At constant temperature and pressure,

$$dT = 0 \quad \text{and} \quad dP = 0$$

---

* *IUPAC recommends the use of Gibbs energy in place of the term Gibbs free energy*

Equation (13.19) becomes,

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3,\ldots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_2,\ldots} dn_2 + \ldots \quad \ldots(13.20)$$

We can write,

$$\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3,\ldots} = \mu_1$$

$$\left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3,\ldots} = \mu_2$$

Thus, $$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots \quad \ldots(13.21)$$

For a system having definite composition, Eq. (13.21) on integration gives

$$G_{T,P,N} = n_1\mu_1 + n_2\mu_2 + \ldots \quad \ldots(13.22)$$

The total differential of G in Eq. (13.22) gives

$$\begin{aligned} dG &= \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \ldots \\ &= (\mu_1 dn_1 + \mu_2 dn_2 + \ldots) + (n_1 d\mu_1 + n_2 d\mu_2 + \ldots) \end{aligned}$$

From equations (13.21) and (13.23), we have

$$n_1 d\mu_1 + n_2 d\mu_2 + \ldots = 0 \quad \ldots(13.23)$$

or $$\boxed{\Sigma n_i d\mu_i = 0}$$

The relationship is called ***Gibbs-Duhem equation.***

13.5.3 Variation of Chemical Potential with Temperature and Pressure

To study the variation of chemical potential with temperature and pressure, we need to derive some results for the variation of free energy with temperature and pressure.

Free energy is an extensive property. Free energy is function of temperature, pressure and composition of a system. Therefore, we can write,

$$G = f(T, P, n_1, n_2, n_3 \ldots)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial T}\right)_{T,N} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3} dn_2 + \ldots \quad \ldots(13.24)$$

In a closed system, there is no change in the number of moles of various components in the system,
i.e.

$$dn_1, dn_2, dn_3 \ldots = 0$$

Equation (13.24) takes the form

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP \qquad \ldots(13.25)$$

For a closed system,

$$dG = VdP - SdT$$

or

$$dG = -SdT + VdP \qquad \ldots(13.26)$$

Equating coefficients of dT and dP in equations (13.25) and (13.26), we get,

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \qquad (13.27a)$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \qquad \ldots(13.27b)$$

Variation of free energy with temperature and pressure respectively for a closed system is thus provided by equations (13.27a) and (13.27b),

13.5.4 Variation of Chemical Potential with Temperature

The chemical potential of a component i in a system is given by,

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} \qquad \ldots(13.28)$$

Differentiating this equation with respect to temperature,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} - \frac{\partial^2 G}{\partial n_i \partial T} \qquad \ldots(13.29)$$

Differentiating Eq. (13.29) with respect to n_i,

$$\frac{\partial^2 G}{\partial T \partial n_i} = -\left[\frac{\partial S}{\partial n_i}\right]_{T,P,n_1,n_2\ldots} \qquad \ldots(13.30)$$

$$= -\overline{S_i}$$

The term $\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_1,n_2\ldots} = \overline{S_i}$ is the partial entropy of the ith component.

From equations (13.29) and (13.30), we have

$$\boxed{\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\overline{S}_i} \qquad \ldots(13.31)$$

Thus, ***the variation of chemical potential of a component of a system with temperature at constant pressure and composition is equal to the partial molar entropy of that component.***

13.5.6 Variation of Chemical Potential with Pressure

The expression for chemical potential is

$$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_1,n_2,\ldots} \qquad \ldots(13.32)$$

Differentiating μ_i with respect to pressure,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \frac{\partial^2 G}{\partial n_i \partial P} \qquad \ldots(13.33)$$

The variation of free energy with pressure at constant T and V is expressed as

$$\left[\frac{\partial G}{\partial P}\right]_{T,N} = V \qquad \ldots(13.34)$$

Differentiating Eq. (13.34) with respect to n_i

$$\frac{\partial^2 G}{\partial P \partial n_i} = \left[\frac{\partial V}{\partial n_i}\right]_{T,P,n_1,n_2,\ldots} \qquad \ldots(13.35)$$

But $$\left[\frac{\partial V}{\partial n_i}\right]_{T,P,n_1,n_2,\ldots} = \overline{V}_i \qquad \ldots(13.36)$$

$\overline{V}_i$ is the partial molar volume of the ith component.

From equations (13.33) and (13.35), we get

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \overline{V}_i \qquad \ldots(13.37)$$

Thus, the variation of chemical potential of a component of a system with pressure at constant temperature and composition is equal to the partial molar volume of that component.

13.5.7 Chemical Potential in a System of Ideal Gases

For an ideal gas,

$$PV = nRT \qquad \ldots(13.38)$$

Consider a system consisting of a number of ideal gases 1, 2, 3, … etc.

Let n_1, n_2, … be the number of moles of various constituents present in the mixture and n is the total number of moles.

Then, $n = n_1 + n_2 + n_3 + \ldots + n_i$

Substituting this value of 'n' in Eq. (13.38), we get

$$PV = (n_1 + n_2 + n_3 + \ldots)RT$$

or $$V = (n_1 + n_2 + \ldots)\frac{RT}{P} \qquad \ldots(13.39)$$

Differentiating V with respect to n_i at constant temperature and pressure,

$$\left[\frac{\partial \mu_i}{\partial n_i}\right]_{T,P,n_1,n_2,\ldots} = \bar{V}_i = \frac{RT}{P} \qquad \ldots(13.40)$$

Substituting the values of $\bar{V}_i$ in Eq. (13.37), we have

$$\left[\frac{\partial \mu_i}{\partial P}\right]_{T,\mathbf{v}} = \frac{RT}{P} \qquad \ldots(13.41)$$

Equation (13.41) may be expressed in the form,

$$d\mu_i = \left(\frac{RT}{P}\right)dP = RT\,d\ln P \qquad \ldots(13.42)$$

In a mixture of ideal gases, let p_i be the partial pressure of the ith component in the mixture. Therefore,

$$p_i V = n_i RT \qquad \ldots(13.43)$$

For a mixture of ideal gases having n moles, we have the relation,

$$PV = nRT$$

From equations (13.43) and (13.44), we have

$$\frac{p_i}{P} = \frac{n_i}{n}$$

or $$p_i = \frac{n_i}{n}P$$

$$p_i = K.P \qquad \ldots(13.45)$$

where, $K = \frac{n_i}{n}$ is a constant as both n_i and n are constants for the given system.

Taking logarithms of both sides of Eq. (13.45), we get

$$\ln p_i = \ln K + \ln P$$

On differentiating the above equation,

$$d\ln p_i = d\ln P \qquad (\because d\ln K = 0) \qquad \ldots(13.46)$$

From Eq. (13.42) and (13.46), we get

$$d\mu_i = RT\,d\ln p_i \qquad \ldots(13.47)$$

Integrating Eq. (13.47), we get

$$\boxed{\mu_i = \mu_i^0 + RT \ln p_i} \qquad \ldots(13.48)$$

where μ^0_i is the integration constant, the value of which depends upon the nature of gas and the temperature.

It is evident from Eq. (13.48) that the chemical potential of a component in a mixture of ideal gases is determined by the partial pressure of the component in the mixture. If the partial pressure is unity, i.e., $p_i = 1$

then $$\mu_i = \mu_i^0$$

Thus, μ°_i gives the chemical potential of a gaseous component *i*, when the partial pressure of the component is unity. It is called the chemical potential of the *i*th the component in the standard state.

13.5.8 The Free-Energy Change of a Reaction

For a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

the free energy change is give by the relation

$$\Delta G = \text{Free energy of products} - \text{Free energy of reactants}$$

In terms of chemical potentials of reactants and products, the free-energy change is given by the following equation:

$$\Delta G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$$

where μ_A, μ_B, μ_C and μ_D are the chemical potentials of reactants and products,

Standard Free-Energy Change of a Reaction When all the reactants and products of a chemical reaction are taken in their standard state, the free-energy change accompanying the reaction is called standard free energy change.

It is represented by ΔG°. Thus,

$$\Delta G^\circ = G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$$

In terms of chemical potential, this can be written in the form,

$$\Delta G^\circ = (c\mu_C^\circ + d\mu_D^\circ) - (a\mu_A^\circ + b\mu_B^\circ)$$

where, μ°_A, μ°_B μ°_C μ°_D are the standard chemical potentials of *A*, *B*, *C* and *D* respectively.

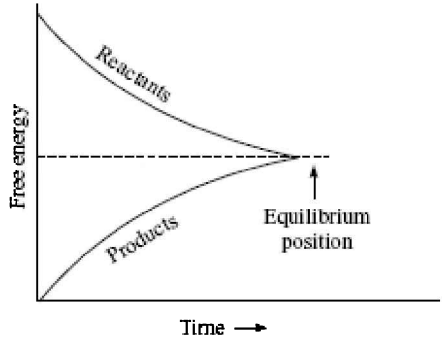


Fig. 13.4 *Free-energy change when reactants are converted into products.*

13.6 FREE-ENERGY CHANGE AS A CRITERION OF SPONTANEITY

It has been discussed in the chapter on thermodynamics that change in free energy can be used as a criterion of feasibility of a process.

1. If $\Delta G > 0$, the process is spontaneous in the forward direction.
2. If $\Delta G > 0$, the process is non-spontaneous in the forward direction.

   In fact, it will proceed in the backward direction, i.e. products will get converted into reactants.
3. If $\Delta G = 0$, the reaction will be at equilibrium.

Consider a reversible reaction, Reactants $\rightleftharpoons$ Products.

Free-energy change that takes place when the reaction is in progress is depicted in Fig. 13.4.

In the beginning, the concentration of the reactants is maximum. Therefore, the free energy associated with them is also maximum while the free energy associated with the products is minimum. As the reaction proceeds, the concentration of reactants decreases and concentration of products increases. Hence, the free energy associated with products increases.

Equilibrium is reached with the concentrations of reactants and products become constant and the free energy of reactants is equal to the free energy of products. Thus, at equilibrium, $\Delta G = 0$.

In a reversible reaction, both forward and backward reactions take place. The condition of spontaneity is that ΔG should be negative. Thus, ΔG is negative for forward as well as backward reaction. This is explained with the help of the following example.

Consider the following gaseous reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

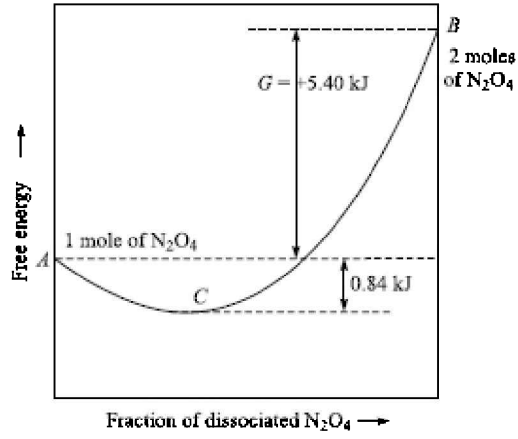


Fig. 13.5 *Graph of free energy of system showing spontaneity of forward as well as backward reaction.*

The variation of free energy of N_2O_4 and NO_2 versus the extent of reaction at constant temperature and pressure is shown in Fig. 13.5. At the point *A* (where the extent of reaction is zero), only the reactant N_2O_4 is present. Point *A* represents standard free energy of the reactant.

At the point *B*, only products, i.e. 2 moles of NO_2 are present. Point *B*, therefore, represents standard free energy of products. Point *C* is the equilibrium state where 16.6% of N_2O_4 and 83.40% of NO_2 exist together. At this point, the $\Delta G = 0$. The difference between the standard free energy of products (Point B), and the standard free energy of the reactants (Point A) is ΔG = +5.40 kJ. The free energy of equilibrium mixture (Point *C)* is 0.84 kJ lower than the point A. This implies that when 1 mole of $N_2O_4(g)$ changes into equilibrium mixture, the value of ΔG° = −0.84 kJ. Similarly, when 2 moles of NO_2 change into equilibrium mixture, the value of ΔG°

$$= -0.54 + (-0.84) = -6.24 \text{ kJ}$$

Thus, we find that in both cases, the value of ΔG° is negative. Therefore, both the processes are spontaneous.

13.6.1 Calculation of Standard Free-Energy Change in a Reaction

The standard free-energy change in a reaction may be calculated by one of the following methods.

1. Using the Relation: $\Delta G^\circ = \Delta H^\circ - \Delta TDS^\circ$

Heat of reaction ΔH° is determined experimentally and entropy change ΔS° is calculated from the absolute entropies of the reactants and products using the relation

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{Reactants})$$

2. Using the Relation: $\Delta G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{Reactants})$

Standard free energy of forward reaction is define as the free-energy change accompanying a reaction in which one mole of the substance in its standard state is formed from its elements in their standard states. Free energy of formation of an element in its standard state is taken as zero.

3. Using the relation: $\Delta G^\circ = -RT \ln K_p$ or $\Delta G^\circ = -RT \ln K_c$

Knowing the values of K_p or K_c, it is possible to calculate standard free energy change using the above relationships.

4. Free-energy Change ΔG of a Gaseous Reaction, at constant temperature can be obtained, using the following relation:

$$\Delta G = nRT \ln \frac{p_2}{p_1}$$

where p_1 and p_2 are initial and final pressures respectively.

Example 5 *Calculate the standard free-energy change of the reaction*

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$$

Standard free energies of formation of NO(g) and NO_2(g) are 87 kJ and 52 kJ mol^{-1}.

Solution:

$$\Delta_f G^\circ = \Sigma \Delta_f G^\circ(\text{products}) - \Sigma \Delta_f G^\circ(\text{Reactants})$$

$$\Delta_f G^\circ = \Delta_f G^\circ(NO_2) - \left[\Delta_f G^\circ(NO) + \frac{1}{2}\Delta_f G^\circ(O_2)\right]$$

Substituting the values, we have

$$\Delta_f G^\circ = 52 - \left[87 + \frac{1}{2}(0)\right] \qquad [\because \Delta_f G^\circ_{(O_2)} = 0]$$

or $$\Delta_f G^\circ = -35 \text{ kJ}$$

Example 6 *Calculate the standard free-energy change for the reaction*

$$CO + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = 270 \text{ kJ}$$

Standard entropies of CO_2, CO and O_2 are 205, 190 and 200 J/degree mole respectively. Predict whether the reaction is feasible or not.

Solution: Standard change in entropy ΔS° is given by,

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{Reactants})$$

$$\Delta S^\circ = S^\circ(CO_2) - \left[S^\circ(CO) + \frac{1}{2}S^\circ(O_2)\right]$$

Substituting the values, we have

$$\Delta S^\circ = 205 - \left[190 + \frac{1}{2} \times 200\right] = -85 \text{ J/degree/mole}$$

Apply the relation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Here,

$$\Delta H^\circ = -270 \text{ kJ} = -270000 \text{ J}$$
$$T = 25 + 273 = 298 \text{ K}$$
$$\Delta S^\circ = -85 \text{ J/degree/mole}$$
$$\Delta G^\circ = -270000 - 298(-85) \text{ J}$$
$$= -244670 \text{ J} = -244.67 \text{ kJ}$$

Since ΔG° is negative, the relation is feasible.

Example 7 *Calculate ΔG° for the reaction: $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$. The standard free energies offormation of glucose, $CO_2(g)$ and $H_2O(l)$ are −910.5, −394.4 and −237.2 kJ mol^{-1} respectively.*

Solution:

$$\Delta G^\circ = [\Delta G_f^\circ]\text{products} - [\Delta G_f^\circ]\text{Reactants}$$
$$= [6 \text{ mol}(-394.4 \text{ kJ mol}^{-1}) + (6 \text{ mol})(-237.2 \text{ kJ mol}^{-1})] - [(1 \text{ mol})(-910.5 \text{ kJ mol}^{-1})]$$
$$= -2879.1 \text{ kJ} \quad \text{(we take } \Delta^\circ G_f \text{ of } O_2 \text{ as zero)}$$

PROBLEMS FOR PRACTICE

1. Calculate the standard free-energy change of the reaction

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

Given that the standard free energies of formation ($\Delta_f G^\circ$) for $NH_3(g)$, NO(g) and $H_2O(l)$ are −16.74, 86.61 and −237.23 kJ mol^{-1} respectively.

Predict the feasibility (or spontaneity) of the above reaction at the standard state.

[Ans. ΔG° = −1009.98 kJ, Feasible]

2. Calculate the standard free energy for the reaction

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$$

Given that the standard free energies of formation of Fe_2O_3 and H_2O are −741.0 kJ and 237.2 kJ per mole respectively. Can the above reaction occur at the standard state?

[Ans. ΔG° = +29.4 kJ, No]

3. Calculate the standard free-energy change at 25°C for the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H^\circ = -22.08 \text{ kcal}$$

Given that ΔS° for the reaction is −47.4 cal/degree. Predict the feasibility of the above reaction at the given state.

[Ans. ΔG° = −7954.8 kcal/Feasible]

13.7 THERMODYNAMIC DERIVATION OF THE LAW OF CHEMICAL EQUILIBRIUM

Consider a general reversible reaction,

$$aA + bB \rightleftharpoons cC + dD$$

where the reactants and products are taken to be ideal gases. If μ_A, μ_B, μ_C, μ_D are the chemical potentials of *A*, *B*, *C*, and *D* respectively at constant temperature and pressure then,

Total free energy of reactants = $G_{\text{reactants}} = a\mu_A + b\mu_B$

Total free energy of products = $G_{\text{products}} = c\mu_C + d\mu_D$

At constant temperature and pressure, the free-energy change of the reaction is given by.

$$\Delta G = G_{(\text{products})} - G_{(\text{Reactants})}$$

or
$$\Delta G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \quad \ldots(13.49)$$

When the system is in equilibrium state at constant temperature and pressure, $\Delta G = 0$, Therefore, Eq. (13.49) can be written as

$$(c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) = 0$$

or
$$c\mu_C + d\mu_D = a\mu_A + b\mu_B \quad \ldots(13.50)$$

Chemical potential of any component in an ideal gas mixture is given by the relation

$$\mu = \mu^\circ + RT \ln p \quad \ldots(13.51)$$

where p is the partial pressure of the component and μ° is the chemical potential in the standard state (i.e. at 1 atm pressure). μ° depends only on temperature.

Substituting the value of μ from Eq. (13.51) into Eq. (13.50), we get

$$c(\mu_C^\circ + RT \ln p_C) + d(\mu_D^\circ + RT \ln p_D) = a(\mu_A^\circ + RT \ln p_A) + b(\mu_B^\circ + RT \ln p_B)$$

$$RT(c \ln p_C + d \ln p_D) + (c\mu_C^\circ + d\mu_D^\circ) = RT(a \ln p_A + b \ln p_B) + (a\mu_A^\circ + b\mu_B^\circ)$$

$$RT[(\ln p_C^c + \ln p_D^d) - (\ln p_A^a + \ln p_B^b)] = (a\mu_A^\circ + b\mu_B^\circ) - (c\mu_C^\circ + d\mu_D^\circ)$$

or
$$RT \ln \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = G^\circ_{\text{Reactants}} - G^\circ_{\text{Products}}$$

$$= -(G^\circ_{\text{Products}} - G^\circ_{\text{Reactants}}) \quad \ldots(13.52)$$

$$= -\Delta G^\circ \quad \ldots(13.53)$$

or
$$\ln \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = \frac{-\Delta G^\circ}{RT}$$

or
$$\frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = e^{-\Delta G^\circ / RT} \quad \ldots(13.54)$$

The standard free-energy change of a reaction ΔG° depends only on temperature. Hence, at constant temperature, the term $e^{-\Delta G^\circ/RT}$ is constant. Thus, Eq. (13.54) can be written as

$$\frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} = \text{constant } (K_p) \quad \ldots(13.55)$$

This is the thermodynamic derivation of the law of chemical equilibrium in terms of partial pressure. From equations (13.54) and (13.55), we arrive at a result,

$$\boxed{\Delta G^\circ = -RT \ln K_p} \quad \ldots(13.56)$$

If molar concentrations are taken in place of partial pressures, the chemical potential of a component may be expressed as

$$\mu = \mu^\circ + RT \ln C$$

where C is the molar concentration of a given component in the reaction mixture and μ° is the chemical potential of the substance in the standard state (when the concentration is unity). Repeating the same steps as described above, we can show that

$$\frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} = \text{constant } (K_c) \quad \text{or} \quad \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_c$$

Similarly, we can obtain a relation between ΔG° and K_c as under:

$$\boxed{\Delta G^\circ = -RT \ln K_c} \qquad \ldots(13.57)$$

To derive the law of equilibrium in terms of activities, we write the chemical potential of each component at

$$\mu = \mu_x^\circ + RT \ln a$$

where a is the activity of the component and μ°_x depends both on temperature and pressure.

Substituting the values of μ in Eq. (13.50), we get

$$\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} = \text{constant } (K_a)$$

Also, $$\boxed{\Delta G^\circ = -RT \ln K_a}$$

By knowing ΔG° of the reaction, we can calculate K_P, K_a, or K_x and vice versa $K_P = K_c$ only when the number of moles of reactants and products are equal. Therefore, the value of ΔG° obtained in equations (13.55) and (13.57) are different.

13.7.1 Free Energy (or Gibbs Energy) (ΔG), Equilibrium Constant (K) and Spontaneity of a Reaction

1. If ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
2. If ΔG is positive then the reaction is considered non-spontaneous. Instead as the reverse process will have a positive ΔG, the reverse reaction would be spontaneous and products of the forward reaction would be converted into reactants.
3. If $\Delta G = 0$, the reaction has achieved equilibrium.

But how do we arrive at these conclusions? For a reaction in equilibrium, we have derived the following relation in the previous section

$$\Delta G^\circ = -RT \ln K \qquad \ldots(13.58)$$

where ΔG° = standard Gibb's (Free) energy

K = equilibrium constant

Equation (13.58) can be written as

$$\ln K = -\frac{\Delta G^\circ}{RT} \qquad \ldots(13.59)$$

Taking antilog of both sides, we get

$$K = e^{-\Delta G^\circ/RT} \qquad \ldots(13.60)$$

Using Eq. (13.60), reaction spontaneity can be interpreted in terms of the value of ΔG°.

(a) If $\Delta G^\circ < 0$ then $-\Delta G^\circ/RT$ is positive and $e^{-\Delta G^\circ/RT} > 1$ which makes $K > 1$. This implies that the reaction proceeds in the forward direction or is spontaneous and the products are present predominantly.

(b) If $\Delta G^\circ > 0$ then $-\Delta G^\circ/RT$ is negative and $e^{-\Delta G^\circ/RT} < 1$, i.e. $K < 1$ which means it is a non-spontaneous reaction.

In such a reaction, the products are present only to a very small extent.

Example 8 *The value of K_p, for the water gas reaction*

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is 1.06×10^5 at 25°C. Calculate the standard state free-energy change (ΔG°) of the reaction at 25°C ($R = 8.314\ J\ K^{-1}\ mol^{-1}$)

Solution:

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_p = -2.303 RT \log K_p \\ &= -(2.303)(8.314\ JK^{-1})(298\ K) \log(1.06 \times 10^{-5}) \\ &= -28673.65 = -28.674\ kJ\end{aligned}$$

Example 9 *Calculate the standard state free-energy change (ΔG°) of the reaction*

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

given that at 1000 K, water vapour at 1 atmosphere pressure has a degree of dissociation = 3×10^{-5} per cent ($R = 8.314\ J\ K^{-1}\ mol^{-1}$).

Solution: The partial pressures of various reactants in the equilibrium mixture will be evidently as below:

$$pH_2 = 3 \times 10^{-7}\ atm,\ pO_2 = \frac{3}{2} \times 10^{-7}\ atm$$

$$K_p = \frac{p^2_{H_2} \times pO_2}{p_{H_2}O} = \frac{9 \times 10^{14} \times \frac{3}{2} \times 10^{-7}}{1} = 13.5 \times 10^{-21}\ atm$$

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_p = -2.303 RT \log K_p \\ &= -2.303\,(8.314\ J\ K^{-1}mol^{-1})(1000\ K) \log(13.5 \times 10^{-21}) \\ &= 3804.48\ J = 380.45\ kJ\end{aligned}$$

Example 10 *At 2000 K, the standard state free-energy change (ΔG°) for the reaction $N_2 + O_2 \rightleftharpoons$*

2NO is given by $\Delta G^\circ = 92048 - 10.46\,T$ J. Calculate K_p for the reaction at 2000 K ($R = 8.314\ JK^{-1}\ mol^{-1}$)

Solution:

$$\Delta G^\circ = -RT \ln K_p = -2.303\,RT \log K_p$$

$$\log K_p = -\frac{\Delta G^\circ}{2.303RT}$$

$$= \frac{(-92048) + 10.46 \times 2000\ \text{J mol}^{-1}}{(2.303)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(2000\ \text{K})} = 1.857$$

$$K_p = 1.39 \times 10^{-2}\ \text{atm.}$$

Example 11 *At 2000 K, the standard free-energy change (ΔG°) for the reaction*

$$N_2 + O_2 \rightleftharpoons 2NO$$

is given by, $\Delta G^\circ = 22000 - 2.0\,T$ cal.

Calculate K_p for the reaction at 2000 K ($R = 1.98$ calories).

Solution: Given

$$\Delta G^\circ = 22000 - 2.0\,T \text{ and } T = 2000\ \text{K}$$

$$\Delta G^\circ = 220000 - 2.0 \times 2000 = 18000\ \text{cal}$$

Using the relationship between ΔG° and K_p,

$$\Delta G^\circ = -RT \ln K_p = -2.303\,RT \log K_p$$

Substituting the values we have,

$$18000 = -2.303 \times 1.98 \times 2000 \times \log K_p$$

or $$K_p = -1.9737 \quad \text{or} \quad \log K_p = \bar{2}.0263$$

or $$K_p = \text{antilog}(\bar{2}.0263) = 1.063 \times 10^{-2}$$

Example 12 *The value of ΔG° for phosphorylation of glucose in glucolysis is 13.8 kJ/mol. Find the value of K_c at 298 K.*

Solution: $\Delta G^\circ = 13.8$ kJ/mol $= 13.8 \times 10^3$ J/mol

We have the relation

$$\Delta G^\circ = -RT \ln K_c$$

Substituting the value, we have

$$13.8 \times 10^3\ \text{J/mol} = -8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K} \times \ln K_c$$

or $$\ln K_c = -5.569$$

or $$\log K_c = -\frac{5.569}{2.303}$$

or $$K_c = 3.81 \times 10^{-3}$$

Example 13 *Hydrolysis of sucrose gives: Sucrose + Water* $\rightleftharpoons$ *Glucose + Fructose Equilibrium constant* K_c *for the reaction is* 2×10^{13} *at 300 K. Calculate* $\Delta G°$ *at 300 K.*

Solution: $\Delta G° = -RT \ln K_c$

Substituting the values, we have

$$\Delta G° = -8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 300 \text{ K} \times 2.303 \log (2 \times 10^{13})$$
$$= -7.64 \times 10^4 \text{ J mol}^{-1}$$

PROBLEMS FOR PRACTICE

1. The standard state free energy of a reaction at 298.15 K is −16.65 kJ. Calculate the value of equilibrium constant of the reaction at 298.15 K.

[Ans. 8.252×10^2**]**

2. The values of standard state free energy for a gaseous reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

at 298 K is 28.53 kJ.

Calculate the value of the equilibrium constant K_P (R = 8.314 $JK^{-1}mol^{-1}$)

[Ans. 1.0×10^5**]**

3. At 27°C, the standard free-energy change for the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is −6909 cal. Calculate K_P for the equilibrium.

[Ans. 1.078×10^5**]**

4. For the reaction

$$CCl_4(l) + H_2(g) \rightarrow HCl(g) + CHCl_3(l)$$

at 25°C, $\Delta H°$ = −21.83 kcal/mol and $\Delta S°$ = 9.92 kcal K^{-1} mol^{-1}.

Determine whether the reaction is favourable at 25°C under standard conditions.

Calculate the value of K_P at 25°C.

[Ans. $\Delta G°$ = −24.79 kcal, Reaction is favourable, $K_P = 1.5 \times 10^{18}$**]**

5. Calculate K_P for the following reaction at 25°C.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
$$\Delta_f G°_{(SO_2)} = -71.79 \text{ kcal/mol}$$
$$\Delta_f G°_{(SO_3)} = -88.52 \text{ kcal/mol}$$

[Ans. 1.2×10^{22}**]**

6. Calculate (a) $\Delta G°$, and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K.

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

Given
$$\Delta_f G°(NO_2) = 52.0 \text{ kJ/mol}$$
$$\Delta_f G°(NO) = 87.0 \text{ kJ/mol}$$
$$\Delta_f G°_{(O2)} = 0 \text{ kJ/mol}$$

[Ans. (i) –35.0 kJ, (ii) 1.365×10^6]

13.8 VAIM'T HOFF REACTION ISOTHERM

Consider the following reaction,

$$aA + bB + \ldots \rightleftharpoons lL + mM + \ldots$$

taking place under any conditions of temperature, pressure and composition. The free-energy change of the reaction is given by the following expression

$$\Delta G = (G)_{\text{products}} - (G)_{\text{Reactants}} \qquad \ldots(13.61)$$
$$= (l\mu_L + m\mu_M + \ldots) - (a\mu_A + b\mu_B + \ldots)$$

where μ_A, μ_B, μ_L, μ_M ... etc., represent chemical potentials of the species concerned.

Let us suppose that various reactants and products are in gaseous state. Chemical potential of gaseous substance in ***any state*** is given by the equation

$$\mu i_{(p)} = \mu°_{i(p)} RT \ln p_i \qquad \ldots(13.62)$$

where $\mu°_{i(p)}$ is a chemical potential of a gaseous component *i*, in the ***standard state*** (partial pressure = 1 atmosphere) and $\mu i_{(p)}$ is the chemical potential of the gaseous component '*i*' in any state of partial pressure p_i.

Substituting the values of chemical potentials of various species at their partial pressures from Eq. (13.62) in (13.61), we have,

$$\Delta G = \{l(\mu°_{L(p)} + RT \ln p_L) + m(\mu°_{M(p)} + RT \ln p_M) + \ldots\}$$
$$- \{a(\mu°_{A(p)} + RT \ln p_A) + b(\mu°_{B(p)} + RT \ln p_B) + \ldots\} \quad \ldots(13.63)$$

Rearranging, we have

$$\Delta G = \{(l\mu°_{L(p)} + m\mu°_{M(p)} + \ldots) - (a\mu°_{A(p)} + b\mu°_{B(p)} + \ldots)\}$$
$$+ RT \ln \frac{(p_L)^l (p_M)^m \ldots}{(p_A)^a (p_B)^b \ldots} \qquad \ldots(13.64)$$

The first expression on the right-hand side is the free-energy change of the reaction when the products and reactants are all in their respective standard states. This expression may be substituted by $\Delta G°$, Hence,

$$\Delta G = \Delta G° + RT \ln Q_p \qquad \ldots(13.65a)$$

where Q_p stands for the reaction quotient of partial pressures of the products and the reactants, viz.

$$\frac{(p_L)^l (p_M)^m \ldots}{(p_A)^a (p_B)^b \ldots}$$



Fig. 13.6 *Jacobus Henricus van't Hoff Jr. was a Dutch physicist and organic chemist and the first winner of the Nobel prize in chemistry. He is known for his work in chemical kinetics, chemical equilibrium and stereochemistry.*

Equation (13.65a) is known as ***van't Hoff reaction isotherm.*** This gives the ***free energy change of a reaction*** at a given temperature, pressure and composition of the reacting system.

Q_p is different from K_p. Here, the values p_L, p_M, p_A, p_B, etc., are not the partial pressures at equilibrium, but for any state. If the partial pressure values correspond to equilibrium state then Q_p will become equal to K_p. From Eq. (13.56), we have

$$\Delta G^\circ = -RT \ln K_p$$

Substituting for ΔG° in Eq. (13.65a), we have

$$\Delta G = -RT \ln K_p + RT \ln Q_p \qquad (13.65b)$$

Equations (13.65a) and (13.65b) are two forms of Van't Hoff reaction isotherm.

Example 14 *At 25°C, the ΔG° for the reaction*

$$H_2(g) + I_2(g) \rightarrow 2HI(g).$$

is −3.1 kcal. Calculate ΔG when hydrogen gas at 0.1 atm and iodine vapour at 0.1 atm react to form hydrogen iodide at 10 atm and 25°C.

Solution: For the given reaction,

$$K = \frac{p^2(\mathrm{HI})}{p(\mathrm{H_2})p(\mathrm{I_2})}$$

where p terms represent partial pressures of the various species in the reaction mixture.

$$\Delta G = \Delta G^\circ + RT \ln K = \Delta G^\circ + 2.303\, RT \log \frac{p^2(\mathrm{HI})}{p(\mathrm{H_2})\, p(\mathrm{I_2})}$$

$$= -3100 \text{ cal} + 2.303\,(1.987 \text{ cal K}^{-1}\text{ mol}^{-1})(298 \text{ K}) \log \frac{(10)^2}{(0.1)\,(0.1)}$$

$$= -3100 \text{ cal} + 1363.7 \log (10^4) \text{ cal}$$

$$= -3100 \text{ cal} + 4(1363.7) \text{cal}$$

$$= +2354.8 \text{ cal} = 2.355 \text{ kcal}$$

13.9 RELATION BETWEEN K_P AND K_C

The value of K_P for the reaction

$$aA + bB + cC + \ldots \rightleftharpoons lL + mM + \ldots$$

is given by the expression,

$$K_p = \left[\frac{(p_L)^l (p_M)^m \ldots}{(p_A)^a (p_B)^b \ldots}\right]_{eq} \qquad \ldots(13.66)$$

The value of K_c for above reaction would be given by the expression

$$K_c = \left[\frac{(c_L)^l (c_M)^m \ldots}{(c_A)^a (c_B)^b \ldots}\right]_{eq} \qquad \ldots(13.67)$$

where p and c stand for partial pressure and concentration, respectively. Now, for an ideal gas,

$$pV = nRT$$

or $$p = (n/V)RT = cRT$$

or $$c = p/RT \qquad \ldots(13.68)$$

where c is the concentration. Thus, for any component i whose partial pressure is P_i,

$$c_i = p_i/RT \qquad \ldots(13.69)$$

Substituting the concentration of various species in terms of their partial pressures in Eq. (13.67), we get

$$K_c = \left\{\frac{\left(\frac{p_L}{RT}\right)^l \left(\frac{p_M}{RT}\right)^m \ldots}{\left(\frac{p_A}{RT}\right)^a \left(\frac{p_B}{RT}\right)^b \ldots}\right\}_{eq}$$

$$= \left[\frac{(p_L)^l (p_M)^m \ldots}{(p_A)^a (p_B)^b \ldots}\right]_{eq} \times \left[\frac{1}{RT}\right]^{\{(l+m+\ldots)-(a+b+\ldots)\}}$$

$$= K_p \left(\frac{1}{RT}\right)^{\Delta n} \qquad \ldots(13.70)$$

where Δn = Number of moles of products − Number of moles of reactants

or
$$K_p = K_c(RT)^{\Delta n} \qquad \ldots(13.71)$$

Example 15 *The value of K_p for the equilibrium*

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$

is 0.035 atm at 400°C when the partia/pressures are expressed in atmospheres. Calculate the value of K_c for the same reaction.

Solution: $\Delta n = 4 + 1 - 2 - 2 = 1$
$\therefore$ we shall use the relation,

$$K_p = K_c(RT)^{\Delta n}$$

or
$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

Substituting the values,

$$K_c = \frac{0.035\,\text{atm}}{(0.0820\ \text{Latm K}^{-1}\,\text{mol}^{-1} \times 673\ \text{K})} = 6.342 \times 10^{-4}\ \text{mol L}^{-1}$$

13.10 VAN'T HOFF EQUATION FOR TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT (VAN'T HOFF REACTION ISOCHORE)

The equation for reaction isotherm when the reactants as well as products are ***gaseous*** and are also in their ***standard states*** is represented as

$$\Delta G^\circ = -RT \ln K_p$$

Differentiating with respect to temperature at constant pressure, we have

$$\left\{\frac{\partial(\Delta G^\circ)}{\partial T}\right\}_p = -R \ln K_p - RT\frac{d(\ln K_p)}{dT} \qquad \ldots(13.72)$$

Multiplying throughout by T, we get

$$T\left\{\frac{\partial(\Delta G^\circ)}{\partial T}\right\}_p = -RT \ln K_p - RT^2\frac{d(\ln K_p)}{dT} \qquad \ldots(13.73)$$

Substituting ΔG° for $-RT \ln K_p$, we have

$$T\left\{\frac{\partial(\Delta G^\circ)}{\partial T}\right\}_p = \Delta G^\circ - RT^2 \ln K_p - RT^2\frac{d(\ln K_p)}{dT} \qquad \ldots(13.74)$$

The Gibbs-Helmholtz equation for substances in standard states may be written as,

$$\Delta G^\circ = \Delta H^\circ + T\left\{\frac{\partial(\Delta G^\circ)}{\partial T}\right\}_p \qquad \ldots(13.75)$$

Comparing Eqs. (13.74) and (13.75), we get

$$RT^2\frac{d(\ln K_p)}{dT} = \Delta H^\circ \qquad \ldots(13.76)$$

or
$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad \ldots(13.77)$$

Equation (13.77) is known as van't Hoff's equation, ΔH° is the enthalpy change for the reaction at constant pressure when the reactants as well as the products are in their standard states.

It is known from experiments that the enthalpy change, ΔH, accompanying a chemical reaction does not vary appreciably with change in partial pressures of reactants or products. Therefore, we may take ΔH° as equal to ΔH, the enthalpy change of the reaction whatever may be the partial pressures of the reactants as well as products. Hence, the van't Hoff equation may be written as

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2} \qquad \ldots(13.78)$$

Integrating Eq. (13.78) between temperatures T_1 and T_2 at which the equilibrium constants are K'_p and K''_p respectively and assuming that ΔH remains constant over this range of temperature, we get

$$\int_{K'_p}^{K''_p} d(\ln K_p) = \frac{\Delta H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

or
$$\ln K''_p - \ln K'_p = \frac{-\Delta H}{R}\left[\frac{1}{T_1} - \frac{T}{T_2}\right]$$

$$= \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \ldots(13.79)$$

or
$$\log K''_p - \log K'_p = \log\frac{K''_p}{K'_p} = \frac{\Delta H}{2.303}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \ldots(13.80)$$

Knowing the equilibrium constant at a temperature, it is possible to calculate the equilibrium constant at another temperature provided the heat of reaction *(ΔH)* is known.

Alternatively, if we know the equilibrium constants of a reaction at two temperatures, the heat of reaction *(ΔH)* can be calculated.

Example 16 The *equilibrium constant K_p for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} atm at 400°C. What will be the equilibrium constant at 500°C if the heat of reaction in this temperature range is −105185.8 J?*

Solution:

$$\log K_p'' - \log K_p' = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$T_1 = 400 + 273 = 673 \text{ K}$$

$$T_2 = 500 + 273 = 773 \text{ K}$$

$$\Delta H = -105185.8 \text{ J}$$

$$\log K_p'' = \log(1.64 \times 10^{-4}) + \frac{-105185.8 \text{ J mol}^{-1}}{(2.303)(8.314 \text{ J K}^{-1}\text{mol}^{-1})}\left(\frac{773 \text{ K} - 673 \text{ K}}{673 \text{ K} \times 773 \text{ K}}\right)$$

$$K_p' = 0.114 \times 10^{-4} \text{ atm}$$

Example 17 *Calculate K_p at 25°C and 325°C for the reaction: $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$, if at 25°C, $\Delta H° = -56.48$ kJ mol^{-1} and $\Delta G° = -34.85$ kJ mol^{-1}*

Solution:

$$\Delta G° = -RT \ln K_p$$

or

$$\ln K_p = \frac{\Delta G°}{RT} = \frac{34.85 \text{ kJ mol}^{-1}}{(8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1})(298 \text{ K})}$$

$$K_p \text{ at } 25°\text{C} = 1.28 \times 10^5$$

To calculate K_p at 325°C, use the equation

$$\ln \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H°}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

or

$$\ln (K_p)_2 = \ln (K_p)_1 + \frac{\Delta H°}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Substituting the values, we get $(K_p)_2$ at 325°C = 13.9

Example 18 *The equilibrium constant of a reaction doubles on raising the temperature from 25°C to 35°C. Calculate $\Delta H°$ for the reaction.*

Solution: Itegrated form of the Van't Hoff equation is

$$\ln \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H°}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Given

$$T_1 = 25°\text{C} = 298 \text{ K}, T_2 = 318 \text{ K}$$

$$\frac{(K_p)_2}{(K_p)_1} = 2, R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$$

$\therefore$

$$\Delta H° = R\left[\frac{T_1 T_2}{T_2 - T_1}\right]\ln 2$$

$$= 53137 \text{ J} = 53.141 \text{ k J mol}^{-1}$$

Example 19 *The equilibrium constant K_p for the reaction $H_2(g) + S_{(g)} \rightleftharpoons H_2S(g)$ is 20.2 atm at 945°C and 9.21 atm at 1065°C. Calculate the heat of reaction.*

Solution: Applying van't Hoff equation,

$$\log K_p'' - \log K_p' = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$T_1 = 945 + 273 = 1218 \text{ K}$$

$$T_2 = 1065 + 273 = 1338 \text{ K}$$

$$K_p' = 20.2 \text{ atm}$$

$$K_p'' = 9.21 \text{ atm}$$

Substituting the values, we have

$$\log 9.21 - \log 20.2 = \frac{\Delta H}{(2.303)(8.314 \text{ J K}^{-1}\text{mol}^{-1})}\left[\frac{1338 - 1218}{(1218 \text{ K})(1338 \text{ K})}\right]$$

$$\Delta H = -88126.3 \text{ J} = -88.826 \text{ kJ}$$

PROBLEMS FOR PRACTICE

1. For a certain reaction, $K_p = 1.21 \times 10^{-4}$ at 1800 K and 2.31×10^{-4} at 1900 K. Calculate K_p at 2000 K.

[Ans. 4.13×10^{-4}]

2. For the reaction $N_2O_4 \rightleftharpoons 2NO_2$, $\Delta H = 14.6$ kcal if $K_p = 0.141$ at 298 K, calculate K_p at 338 K.

[Ans. 2.607]

3. Calculate the enthalpy change for the reaction

$$N_2 + O_2 \text{ — } 2NO$$

Given that the equilibrium constant for this reaction is 4.08×10^{-4} at 2000 K and 3.60×10^{-3} at 2500 K.

[Ans. 181.1 kJ]

4. The equilibrium constant K_p for a reaction is 3.0 at 400°C and 4.0 at 500°C. Calculate the value of $\Delta H°$ for the reaction.($R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$)

[Ans. 12.44 kJ]

13.10.1 van't Hoff's Equation for Temperature Dependence of Equilibrium Constant in Terms of K_c

K_p and K_c are related by the expression

$$K_p = K_c(RT)^{\Delta n} \qquad \ldots(13.81)$$

Taking logarithm of the above equation, we have

$$\ln K = \ln K_c + \Delta n \ln RT \qquad \ldots(13.82)$$

Differentiating Eq. (13.82) with respect to temperature, we get

$$\frac{d(\ln K_p)}{dT} = \frac{d(\ln K_c)}{dT} + \frac{\Delta n}{T} \qquad \ldots(13.83)$$

or

$$\frac{d(\ln K_c)}{dT} = \frac{d(\ln K_p)}{dT} - \frac{\Delta n}{T}$$

$$= \frac{\Delta H^\circ}{RT^2} - \frac{n}{T}$$

$$= \frac{\Delta H^\circ}{RT^2} - \frac{nRT}{TRT} \qquad \text{Refer eq. (13.78)}$$

$$= \frac{\Delta H^\circ - nRT}{RT^2}$$

But $\Delta H - \Delta nRT = \Delta E$ (From thermodynamics)

$\therefore$

$$\left(\frac{d(\ln K_c)}{dT}\right) = \frac{\Delta E}{RT^2}$$

Example 20 *Explain the terms:*

(a) Homogeneous equi/ibrium

(b) Heterogeneous equi/ibrium

Solution:

(a) An equilibrium which has all the reactants and products in the same state is called a homogenous equilibrium. For example,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Here, H_2, I_2 and HI all exist in the same gaseous phase.

Similarly, $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

is also an example of homogenous equilibria as all the reactants and products are in the liquid phase.

(b) An equilibrium which has the reactants and products in two or more phases is called heterogeneous equilibrium. For example,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

13.11 LE CHATELIER'S PRINCIPLE

Le Chatelier, a noted French chemist, studied the effect of concentration, temperature and pressure on a large number of chemical equilibria. He summed up his observation in the form of a generalisation known as Le Chatelier's principle, which states as follows:

If an equilibrium is subjected to stress, the equilibrium shifts in such a way as to reduce the stress.

According to this principle, ***if a system at equilibrium is subjected to a change of concentration, pressure and temperature, the equilibrium shifts in the direction that tends to undo***

the effect of change.

1. Effect of Change of Concentration Consider the following equilibrium:

$$\underset{\text{Pale yellow}}{Fe^{3+}(aq)} + \underset{\text{Colourless}}{(SCN)^{-}(aq)} \rightleftharpoons \underset{\text{Dark brown}}{[Fe(SCN)]^{2+}(aq)}$$

Suppose some ferric salt is added to this equilibrium. The colour of the solution will darken immediately showing that there is increase in concentration of the coloured complex ion $[Fe(SCN)]^{2+}$. This change is in accordance with Le Chatelier's principle. Addition of more Fe^{3+} ions has resulted in increasing the concentration of the complex ferric sulphocyanide.

Now, suppose a small amount of potassium ferric sulphocyanide capable of giving complex ions, $[Fe(SCN)]^{2+}$ is added to the equilibrium. The solution will be seen to become less dark showing that the dark-coloured $[Fe(SCN)]^{2+}$ ion has been changed into Fe^{3+} and $(SCN)^{-}$ ions. Thus, increasing the concentration of the product shifts the equilibrium in favour of the reactants.



Fig. 13.7 *Henri Louis Le Chatelierwasan influential Fench chemist of late 19 th century and early 20th century*

2. Effect of Change of Pressure Consider another gaseous reaction involving combination of nitrogen and hydrogen to give ammonia.

$$\underset{\underbrace{\text{1 mole}\quad \text{3 moles}}_{\text{4 moles}}}{N_2(g) + 3H_2(g)} \rightleftharpoons \underset{\text{2 moles}}{2NH_3}$$

As is evident from the above equation, the forward reaction is accompanied by a decrease in the number of moles. If the pressure is increased, the volume will decrease. According to Le Chatelier's principle, therefore, the equilibrium will shift in the direction in which there is decrease in the number of moles, i.e. in favour of the formation of ammonia. Thus, the higher the pressure the greater would be the yield of ammonia. It is on account of this that the pressure of about 200 atmospheres is maintained in Haber's process for the manufacture of ammonia.

The combination of sulphur dioxide and oxygen to give sulphur trioxide is also accompanied by decrease in the number of moles.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

According to Le-Chatelier's principle, therefore, high pressure would give a better yield of sulphur trioxide.

The dissociation of calcium carbonate takes place as under:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

It is accompanied by an increase in the number of gaseous moles. The dissociation of calcium carbonate would, therefore, be suppressed by an increase of pressure.

3. Effect of Change of Temperature Consider the equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = +59.0 \text{ kJ}$$

In this equilibrium, the reaction favouring the product (NO_2) is seen to be endothermic. Therefore, the opposing reaction favouring the reactants (N_2O_4) must be exothermic. Now, suppose the system is heated and its temperature is allowed to rise then according to Le-Chatelier's principle, the equilibrium will shift in the direction which tends to undo the effect of heat, i.e. which tends to produce cooling.

Therefore, the equilibrium will shift in favour of NO_2, i.e. dissociation of N_2O_4 into NO_2 will increase. If the system is cooled, on the other hand, the equilibrium will shift in the direction which produces heat. Therefore, the equilibrium will shift in the reverse direction, i.e. in favour of N_2O_4. The dissociation of N_2O_4 will decrease.

The combination of nitrogen and hydrogen to give ammonia is represented by the following thermochemical equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H = -92.38 \text{ kJ}$$

The forward reaction is exothermic. Therefore, the back reaction must be endothermic. By Le Chatelier's principle, the increase of temperature will favour the back reaction, i.e. the dissociation of ammonia will occur. Therefore, in order to get better yield of ammonia, the temperature at equilibrium should be low. But since the reaction rate varies with the temperature, the time taken to reach the equilibrium state becomes very long if the temperature is kept low. Therefore, a temperature close to 500°C, which is neither too low nor too high, is maintained.

4. Effect of Addition of Inert Gas The effect of addition of an inert gas can be studied under two different conditions:

(a) Addition of an Inert Gas at Constant Volume When an inert gas is added to the equilibrium state at constant volume then the total pressure will increase. But, the partial pressure of each component will remain uncharged. Under these conditions, there will be no effect on the equilibrium on addition of the inert gas.

(b) Addition of an Inert Gas at Constant Pressure When an inert gas is added to the system at constant pressure, there will be an increase in the volume. As a result, the number of moles per unit volume of different components will decrease. The equilibrium will shift to the side where the number of moles are increased. For example, consider the following equilibrium:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ at constant pressure}$$

The addition of an inert gas at constant pressure will shift the equilibrium to the backward direction. For the equilibrium

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \text{ at constant pressure}$$

at constant pressure the addition of inert gas at constant pressure will shift the equilibrium to the forward direction. However, addition of an inert gas to the following equilibrium

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ at constant pressure will have no effect because the number of moles of reactants and products are same.

5. Effect of Catalyst There is no effect of addition of a catalyst on the equilibrium state. This is because a catalyst increases the rate of both forward as well as backward reaction to the same extent. It simply helps to achieve the equilibrium quickly. It may be further noted that a catalyst has no effect on the equilibrium concentration of a reaction mixture.

13.11.1 Applications of Le-chatelier's Principle to Physical Equilibrium

The following examples describe the applications of Le-Chatelier's principle to physical equilibrium.

1. Liquid-Vapour Equilibrium Consider the water-vapour equilibrium

$$\underset{\text{(Less volume)}}{H_2O(g)} \rightleftharpoons \underset{\text{(More volume)}}{H_2O(\text{vapour})} \quad \text{(Endothermic process)}$$

The conversion of water to water vapour is an endothermic process.

Also, as liquid water changes to vapour phase, it is accompanied by increase in volume. According to Le-Chatelier's principle, the increase in temperature shifts the equilibrium towards the right, i.e. more of liquid water will evaporate. This will absorb the heat supplied.

On increasing pressure, the equilibrium shifts in a direction so as to lower the pressure. Thus, increase of pressure favours the condensation of water vapour into liquid water. On the other hand, decreasing the pressure will favour the vaporisation of water into water vapour.

2. Effect of Pressure on Boiling Point of a Liquid Consider the equilibrium

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

The vaporisation of liquid is accompanied by increase of pressure. Thus, if pressure is increased, the equilibrium shifts towards condensation of vapour into liquid state at a given temperature. The vapour pressure will decrease. Higher temperature is thus needed to make the liquid boil. This is the reason that the boiling point of a liquid increases with increase in external pressure.

3. Effect of Pressure on Freezing Point of a Liquid or Melting Point of a Solid Consider the equilibrium,

$$\underset{\text{(More volume)}}{\text{Ice}} \rightleftharpoons \underset{\text{(Less volume)}}{\text{Water}} \quad \text{(Endothermic process)}$$

When a solid melts, there is a change in volume. For example, when ice melts, there is decrease in volume.

Increase of pressure on ice $\rightleftharpoons$ water equilibrium will cause the equilibrium to shift towards right. Thus, if at constant temperature, the pressure is increased, more of ice will melt. In order to retain ice in equilibrium with water, it is necessary to lower the temperature. Hence, the increase of pressure will lower the melting point of ice. As the process is endothermic, increase of temperature will shift the equilibrium to RHS. Thus, more ice will melt.

Most of the solids show increase in volume on melting, e.g. sulphur (solid) $\rightleftharpoons$ sulphur (liquid) equilibrium. Therefore, we can say that if the pressure on equilibrium is increased, the melting point of sulphur is raised.

4. Effect of Pressure on Solubility of Gases in Liquids Consider the equilibrium involving dissolution of CO_2 in water.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

On increasing the pressure of CO_2 gas, the equilibrium shifts in the direction which causes a decrease in the pressure of CO_2. The pressure of CO_2 will be lowered only if it dissolves more in

water to form CO_2(aq). Thus, according to Le-Chatelier's principle, the solubility of a gas in a liquid will increase with increase in pressure of the gas in equilibrium with its solution.

5. Effect of Temperature on Solubility We can explain the effect of temperature on solubility of solids with the help of Le Chatelier's principle. During the dissolution process, if heat is evolved, solubility decreases with increase in temperature. $CaCl_2$, NaOH, etc., are the examples of such solutes. The solubility of such substances decreases on increase of temperature. On the other hand, dissolution of substances like NH_4Cl, $NaNO_3$, etc., is accompanied by absorption of heat. Their solubility increases with increase in temperature as per Le Chatelier's principle.

Example 21 *State Le Chatelier's principle and apply it for the following equilibrium.*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \ldots 17\ kcal$$

The above reaction is endothermic and takes place with increase of pressure (number of gaseous product molecules is greater than the number of gaseous reactant molecules) in the forward direction.

6. Effect of Temperature On increasing the temperature, the reaction will shift in a direction where it is endothermic, i.e. heat can be absorbed. Thus, the reaction will shift in the forward direction. On decreasing the temperature, however, the reverse action will take place.

7. Effect of Pressure On increasing the pressure, the reaction will shift in a direction where the effect can be neutralised, i.e. in a direction where the pressure is decreased. Thus, the reaction will move in the backward direction. On decreasing the pressure, the reverse effect will be observed.

Le-Chatelier's principle comes to the rescue of people living on hills. People feel breathing problems because of lower pressure at high altitudes. The combination of oxygen with haemoglobin (Hb) molecule, which carries oxygen through the blood may be simplistically represented as

$$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq)$$

HbO_2 is oxyhaemoglobin which actually transports oxygen to tissues.

$$K_c = \frac{[HbO_2]}{[Hb][O_2]}$$

Partial pressure of oxygen is much less at high altitudes compared to that at sea level. Le-Chatelier's principle says that a decrease in the concentration of O_2 will shift the equilibrium to the left. This change will reduce the concentration of HbO_2 causing ***hypoxia.*** Over a period, the body copes with this situation by producing more haemoglobin. Studies show that longtime residents of high-altitude places have high haemoglobin levels in their blood compared to people living at sea level.

13.12 CLAUSIUS-CLAPEYRON EQUATION

When the system is in equilibrium, the free-energy change accompanying the process is zero, i.e.

$\Delta G = 0$, for a system in equilibrium ...(13.84)

The variation of free energy with temperature and pressure is given by the total differential equation, viz.

$$dG = VdP - SdT \qquad \ldots(13.85)$$

Consider a system consisting of two phases I and II in equilibrium at temperature T and pressure P. Under these conditions, suppose that free energy of Phase I is G_1 and that of Phase II is G_2. If the temperature of the system is changed from T to $T + dT$ and pressure from $P + dP$, suppose the corresponding change in free energy of Phase I is dG_1 and that of Phase II is dG_2 (Fig. 13.10). Then according to Eq. (13.85).

$$dG_1 = V_1 dP - S_1 dT \qquad \ldots(13.86)$$

and

$$dG_2 = V_2 dP - S_2 dT \qquad \ldots(13.87)$$

where V_1 and S_1 are the molar volume and entropy of Phase I, and V_2 and S_2 are the corresponding values of Phase II.

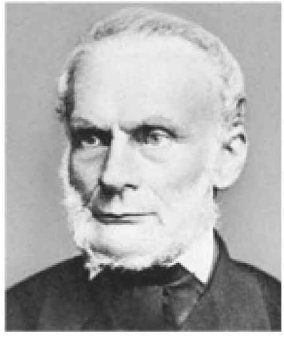


Fig. 13.8 *Rudolph Julius Emanuel Clausius was a German physicist and mathematician and is considered one of the central founders of the field of thermodynamics.*

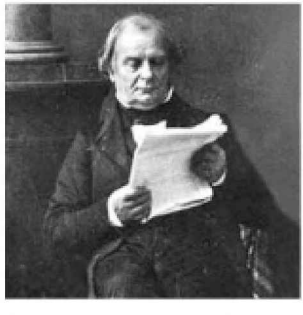


Fig. 13.9 *Benoit Paul Emile Clayperon was a French engineer and physicist. He was one of the founders of thermodynamics.*

But when Phase I is in equilibrium with Phase II,

$$\Delta G = 0$$

i.e.

$$G_2 - G_1 = 0$$

where G_1 is the molar free energy of Phase I and G_2, that of Phase II at temperature T and pressure

P.

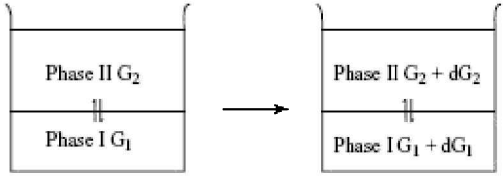


Fig. 13.10 *Phase equilibria at T and P and at T + dT and P + dP.*

Similarly, for the equilibrium at temperature $T + dT$ and pressure $P + dP$, we must have

$$(G_2 - dG_2) - (G_1 - dG_1) = 0$$

But $G_2 - G_1 = 0$ (as already stated above)

$\therefore$ $dG_2 - dG_1 = 0$

or $dG_2 = dG_1$ ...(13.88)

Substituting, the values of dG_1 and dG_2 from equations (13.86) and (13.87), we get

$$V_2 dP - S_2 dT = V_1 dP - S_1 dT$$

or $$(V_2 - V_1) dP = (S_2 - S_1) dT$$

or $$\Delta V - dP = \Delta S \cdot dT$$

or $$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$ ...(13.89)

where, $\Delta V = V_2 - V_1$ is molar volume change

and $\Delta S = S_2 - S_1$ is the molar entropy change

where Phase I changes into Phase II.

If this change occurs at temperature T (i.e. melting point, boiling point, etc.) and ΔH is the latent heat of transformation then

$$\Delta S = \frac{\Delta H}{T}$$

Putting this value in Eq. (13.89), we get

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}}$$ ...(13.90)

This equation was first derived by Clapeyron (1934) and is called ***Clapeyron equation.*** It can be applied to various physical equilibria like melting, vaporisation and sublimation.

For the melting equilibrium, i.e.

$$\text{Solid} \rightleftharpoons \text{Liquid}$$

$\Delta H = \Delta H_m$, latent heat of melting and $T = T_m$, the melting point.

Equation (13.90) may then be written as

$$\frac{dP}{dT} = \frac{\Delta H_m}{T_m \Delta V} \quad \ldots(13.91)$$

Also, $\Delta V = V_l - V_s$

where, V_s = molar volume of the solid

and V_l = molar volume of the liquid (melt)

Hence, Eq. (13.91) may be written in the form

$$\frac{dP}{dT} = \frac{\Delta H_m}{T_m (V_l - V_s)}$$

or
$$\frac{dT}{dP} = \frac{T_m (V_l - V_s)}{\Delta H_m} \quad \ldots(13.92)$$

This equation givens the variation of melting point with pressure.

For the vaporisation equilibrium, i.e.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

The Clapeyron equation, i.e. Eq. (13.91) takes the form

$$\frac{dP}{dT} = \frac{\Delta H_v}{T_b (V_v - V_l)} \quad \ldots(13.93)$$

where, ΔH_v = Latent heat of vaporisation

T_b = Boiling point of the liquid

V_l = Molar volume of the liquid

and V_v = Molar volume of the vapour

Volume of the liquid (V_l) is very small as compared to the volume of the vapour (V_v). Thus, V_l can be neglected in comparison to V_v. Hence, Eq. (13.93) may be written as (omitting the subscript in T_b)

$$\frac{dP}{dT} = \frac{\Delta H_v}{T V_v} \quad \ldots(13.94)$$

Further assuming that the vapour behave like an ideal gas, we have

$$PV_v = RT$$

or
$$V_v = \frac{RT}{P} \quad \ldots(13.95)$$

Substituting this value in Eq. (13.95), we get

$$\frac{dP}{dT} = \frac{\Delta H_v}{RT^2} P$$

or
$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

or
$$\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2} \quad \ldots(13.96)$$

This equation is called ***Clausius-Clapeyron equation*** as it was derived by Clausius during a detailed investigation of Clapeyron equation.

Equation (13.96) can also be written in integrated form as explained below.

Equation (13.96) may be rewritten as

$$d \ln P = \frac{\Delta H_v}{RT^2} dT \qquad \ldots(13.97)$$

If the temperature changes from T_1 to T_2 when the vapour pressure changes from P_1 to P_2 then integrating Eq. (13.97) between the appropriate limits, we get

$$\int_{P_1}^{P_2} d \ln P = \int_{T_1}^{T_2} \frac{\Delta H_v}{RT^2} dT$$

or

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

$$= \frac{\Delta H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Changing from natural logarithm to the logarithm to base 10, we obtain

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

or

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \qquad \ldots(13.98)$$

This is called the integrated form of ***Clausius-Clapeyron equation.*** It has a number of applications.

1. If the boiling point of a liquid is known at some particular pressure, the boiling point at any other pressure can be obtained, provided the latent heat of vaporisation of the liquid is known.
2. If the vapour pressure of the liquid is known at one particular temperature, the value at any other temperature can be calculated, if the latent heat of vaporisation of the liquid is known.
3. If the vapour pressure of liquids at two different temperatures are known, the latent heat of vaporisation of the liquid can be calculated from the equation.

Example 22 *Water boils at 373 K at one atmospheric pressure. At what temperature will it boil when atmospheric pressure becomes 528 mm of Hg at same space station?*

Latent heat of $H_2O = 2.28\ kJ^{-1} g$

$R = 8.314\ J\ K^{-1} mol^{-1}$

Solution: We are given that,

$T_1 = 373$ K

$P_1 = 1$ atm $= 760$ mm

$P_2 = 528$ mm

$T_2 =$ To be calculated

$$\Delta H_v = 2.28 \text{ kJ/g}$$
$$= 2.28 \times 18 \text{ kJ mol}^{-1}$$
$$= 41.04 \text{ kJ mol}^{-1}$$
$$= 41040 \text{ J mol}^{-1}$$
$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Substituting the values, in the integrated form of Clausius-Clapeyron equation, we have

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

we get $$\log \frac{528}{760} = \frac{41040}{2.303 \times 8.314} \times \left(\frac{T_2 - 373}{373 T_2}\right)$$

or $$-0.1582 = 2143.4 \times \left(\frac{T_2 - 373}{373 T_2}\right)$$

or $$-59.0\, T_2 = 2143\ T_2 - 799488.2$$

or $$2202.4\, T_2 = 799488.2$$

$\therefore$ $$T_2 = 363 \text{ K}$$

Example 23 *Water boils at 100°C at a pressure of 1 atm. Calculate the vapour pressure of water at 90°C. The heat of vaporisation of water is 9.80 kcal mol^{-1}.*

Solution: Given that

$$T_1 = 100 + 273 = 373 \text{ K}$$
$$P_1 = 1 \text{ atm}$$
$$T_2 = 90 + 273 = 363 \text{ K}$$
$$P_2 = \text{To be calculated}$$
$$\Delta H_v = 9.80 \text{ kcal mol}^{-1} = 9800 \text{ cal mol}^{-1}$$
$$R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

Substituting these values in the Clausius-Clapeyron equation,

$$\log \frac{P_2}{P_1} = \frac{9800}{2.303 \times 1.987} \times \frac{363 - 373}{363 \times 373}$$

or $$\log p_2 = -0.1582 = \bar{1}.8418$$

$\therefore$ $$P_2 = 0.6947 \text{ atm}$$

Example 24 *The normal boiling point of water is 100°C. Its vapour pressure at 80°C is 0.4672 atmosphere. Calculate the enthalpy of vaporisation per mole of water.*

Solution: Here, we have

$$T_1 = 100°\text{C} = 100 + 273 = 373 \text{ K}$$
$$P_1 = 1 \text{ atm}$$
$$T_2 = 80°\text{C} = 80 + 273 = 353 \text{ K}$$
$$P_2 = 0.4672 \text{ atm}$$
$$\Delta H_v = \text{To be calculated}$$

Substituting the values in the equation,

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

we get,
$$\log \frac{0.4672}{1} = \frac{\Delta H_v}{2.303 \times 8.314}\left(\frac{353 - 373}{353 \times 373}\right)$$

or
$$0.3305 = \frac{\Delta H_v}{2.303 \times 8.314} \times \frac{-20}{353 \times 373}$$

or
$$\Delta H_v = 41.66 \text{ kJ mol}^{-1}$$

PROBLEMS FOR PRACTICE

1. If the vapour pressure of toluene is 60 mm at 40.3°C and 20 mm at 18.4°C, calculate (a) the vapour pressure at 25°C, and (b) the heat or vaporization.

[Ans. (a) 28.4 mm. (b) 38.08 kJ mol^{-1}]

2. The vapour pressure of an organic liquid at 27°C and 37°C are 90 mm. and 110 mm ofmercury respectively. Calculate the molar enthalpy of vaporisation. (R = 1.987 cal $degree^{-1}$)

[Ans. 3711 cal mol^{-1}]

3. The vapour pressure of solid benzene is 2.24 mm at 243 K and 24.5 mm at 373 K. Calculate from these data the heat of fusion of benzene.

[Ans. 43.99 kJ/mol]

4. At 373.6 K and 372.6 K, the vapour pressures of water are 1.018 and 0.982 atm. respectively. Calculate the heat of vaporisation of water.

[Ans. 41.676 kJ/mol^{-1}]

5. The normal boiling point of cyclohexane is 80.7°C and heat of vaporisation is 30.08 kJ mol^{-1}. Calculate (a) the boiling point at 650 mm, and (b) the vapour pressure at 25°C.

[Ans. (a) 348.4 K (b) 0.1479 atm or 112.4 mm]

6. Using Clausius-Clapeyron equation, calculate the enthalpy of vaporisation of the liquid X.

P (torr)	40	60
T (K)	294	302

[Ans. 37.422 kJ]

13.13 HAMMETT EQUATION

Louis P Hammett of Columbia University (USA) observed that equilibrium constants and rates of polar organic reactions are strongly influenced by substituents on organic molecules. Hammett suggested in 1937 that the effects of ***meta*** and ***para*** substituents on the ionisation constants of benzoic acid could guide the course of other reactions involving these substituents. Only ***meta*** and ***para*** positions are chosen because substituents at these positions in benzene rings are held at fixed distances from the point of reaction. Hammett specifically excluded ***ortho*** positions from his studies because they could affect the reaction by steric hindrance or by hydrogen bonding. He introduced the following two quantities.

1. Substituent Constant, σ It is defined as the logarithm of the ratio of the ionisation constant of a substituted benzoic acid to that of benzoic acid itself in a water solution at 25°C.

$$\sigma = \log \frac{K_a}{K_{a,0}} \qquad \ldots(13.99)$$

where K_a is the dissociation constant of substituted benzoic acid and $K_{a,\,0}$ is the dissociation constant of benzoic acid.

From Eq. (13.99), $$\sigma = \log K_a - \log K_{a,0} = pK_{a,0} - pK_a \qquad \ldots(13.100)$$

Since the dissociation constants of meta and para-substituted benzoic acids differ from each other, each substituted has two sigma constants, σ_{meta} and σ_{para}. Strongly electron attracting groups like NO_2, ClF_3, etc., have large positive values, because $K_a > K_{a,\,0}$. On the other hand, strongly electron-donating groups such as NH_2, OH groups have large negative values of σ. This is because $K_a < K_{a,0}$. Logarithm of a quantity less than 1 is negative. Hydrogen has a value of 0 for σ.

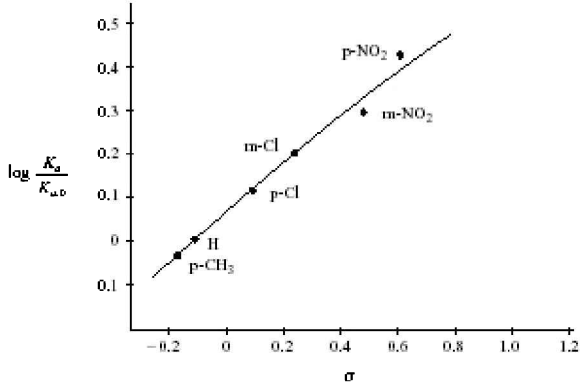


Fig. 13.11 *Hammettplotforthe dissociation ofphenylacetic acids*

We may also compare the two sig ma values (σ_{para} and σ_{meta} for the same substituent. Most substituents show greater value for (σ_{para} than for σ_{meta} However, we have to consider the resonance and inductive effects while studying the effect of substituents on the ionisation of the organic acids. For example, an amino group in the ***para*** position directly transmits electrons towards the carboxylic group making it difficult to ionise. However, this does not happen when the amino group is in the meta position. To make another comparison, OH and OCH_3 groups have the opposite signs for σ_{meta} and σ_{para}. Here, in addition to the resonance effect (in case of NH_2 group), the inductive effect also operates. The hammett plot for phen-ylacetic acid with different substituents and in different positions is given below (Fig. 13.11)

2. Reaction Constant, P Figure 13.11 shows a Hammett plot for ionisation constants of phenyl-acetic acid. The points fit a straight line which can be represented by the Hammett equation with good approximation ($y = mx$, equation of a straight line)

$$\log \frac{K_a}{K_{a,0}} = \sigma\rho \qquad \ldots(13.101)$$

Slope of the above straight line, P, is called ***reaction constant.*** The numerical value and sign of ρ differs from reaction to reaction and show how each reaction is affected by the nature of the

substituents on the aromatic rings. The value of ρ for the ionisation of phenylacetic acids in water at 25°C is only about half as large as the value of ρ for the ionisation of benzoic acid (which is supposed to have the value 1.00 as per the definition of σ). We explain it by saying that substituents in phenylacetic acids are farther from the carboxylic group.

A reaction with a positive ρ value takes place when electron-attracting substituents are present. The reverse is true for reactions with negative ρ values.

Example 25 *How is thermodynamic equilibrium constant in terms of activities (K_a) related to K_p or K_c? Under what condition does K_a become equal to K_p or K_c?*

Solution: For the reaction, $aA + bB + \ldots \rightleftharpoons mM + nN + \ldots$

$$K_a = \frac{a_M^m a_N^n \ldots}{a_A^a a_B^b \ldots}$$

Activity = Activity coefficient × Composition variable (Conc. or pressure)

i.e., $$a = \gamma X$$

Substituting the value of a in the above equation

$$K_a = \left(\frac{\gamma_M^m \gamma_N^n \ldots}{\gamma_A^a \gamma_B^b \ldots}\right)\left(\frac{X_M^m X_N^n \ldots}{X_A^a X_B^b \ldots}\right) = K_\gamma K_X$$

$\therefore$ $$K_a = K_\gamma K_C \quad \text{or} \quad K_a = K_\gamma K_P$$

For ideal gases or real gases at very low pressures, $\gamma = 1$ for each gas.

Then, $K_\gamma = 1$ and hence $K_a = K_p$

Similarly, for very dilute solutions, as $C \rightarrow 0$, $\gamma \rightarrow 1$ and $K_a \rightarrow K_c$

Example 26 *How is that a reversible reaction is spontaneous in the forward as well as backward direction?*

Solution: This is because the free energy of equilibrium mixture is lower than that of reactants as well as products. Hence, ΔG is negative both for forward direction and for the backward direction.

Example 27 *How is the free energy of gas determined (a) by studying its isothermal expansion, (b) from its equilibrium constant K_p, (c) from enthalpy change and entropy data?*

Solution:

(a) $\Delta G = nRT \ln \frac{P_2}{P_1}$ (b) $\Delta G^\circ = -RT \ln K_p$ (c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta S^\circ = \Sigma S^\circ_{(\text{products})} - \Sigma S^\circ_{(\text{Reactants})}$

Example 28 *Under what condition are K_p, K_c, K_a and K_x all equal?*

Solution: It is when $\Delta n = 0$, i.e. $n_p = n_r$ (gaseous)

Example 29 *Can the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ be attained in an open vessel? Why or why not?*

Solution: No, this equilibrium cannot be attained in an open vessel because one of the products, viz. CO_2, is gaseous which escapes out.

Example 30 *Give Clausius-Clapeyron equation for liquid $\rightleftharpoons$ vapour equilibrium and write its applications.*

Solution: The Clausius-Clapeyron equation for liquid $\rightleftharpoons$ vapour equilibrium is

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

This equation can be used to calculate the molar heat of vaporisation, ΔH_v of a liquid if the vapour pressure at two temperatures are known. Further, if the molar heat of vaporisation (enthalpy of vaporisation) is known and vapour pressure at one temperature is known then vapour pressure at another temperature can be calculated from the equation.

If the boiling point of a liquid at one pressure is known, that at any other pressure can also be calculated.

Example 31 *Write the Clausius-Clapeyron equation for solid $\rightleftharpoons$ vapour equilibria. What are applications of this equation for solid $\rightleftharpoons$ vapour equilibria?*

Solution: Clausius-Clapeyron equation for solid $\rightleftharpoons$ vapour equilibrium is written as

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_s}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

where ΔH_s is the molar enthalpy of sublimation of the solid.

This equation can be used to calculate the effect of pressure on melting point of a solid. Further, if vapour pressures at two temperatures are known then ΔH_3 can be calculated.

Example 32 *Which of the properties remain constant when equilibrium is attained?*

Solution: Temperature, pressure and chemical potential of a particular substance remain constant in all the phases.

Example 33 *Write the Clausius-Clapeyron equation both in differential form and in the integrated form.*

Solution: Differential form is $\dfrac{d \ln R}{dT} = \dfrac{\Delta_{vap} H}{RT^2}$

Integrated form is $$\log \frac{P_2}{P_1} = \frac{\Delta_{vap} H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Example 34 *What is van't Hoff reaction isotherm? Why is it so called?*

Solution: The van't Hoff reaction isotherm is $\Delta G = \Delta G^\circ + RT \ln Q_p$

It gives free-energy change of the reaction in terms of standard free-energy change and the value of the reaction quotient Q_p under the given state at constant temperature. That is why it is called reaction isotherm.

Example 35 *How is free-energy change of a reaction in a given state related to its reaction quotient (pressure quotient) Q_p in that state and the equilibrium constant K_p?*

Solution: $\Delta G = -RT \ln K_p + RT \ln Q_p$

Example 36 *Write the Van 't Hoff equation giving the variation of equilibrium constant with temperature both in the differential form and in the integrated form.*

Solution:

$$\text{Differential form is } \frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$\text{Integrated form is } \log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Example 37 *On the basis of Le-Chatelier's principle, discuss the favorable reaction conditions for the following reaction.*

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad (\Delta H = 180.5 \text{ kJ})$$

Solution: The given reaction is endothermic and, therefore, it will be favoured by high temperature. Δn for the reaction is zero and, therefore, increase of pressure has no effect on equilibrium.

Example 38 *Why does ΔG° obtained from K_p and K_c have different values?*

Solution: $\Delta G^\circ = -RT \ln K_p$. Also, $\Delta G^\circ = -RT \ln K_c$. As $K_p \neq K_c$ unless $\Delta n = 0$. Therefore, ΔG° values are different in the two cases.

Example 39 *Write the van't Hoff equation. Explain that it leads to the same effect of temperature on equilibrium constant as predicted by Le-Chatelier.*

Solution: van't Hoff equation is $\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$

For endothermic reaction, ΔH° is +ve. Hence, $d \ln K_p/dT$ is +ve.

This means that $\ln K_p$ and, hence, K_p increases with increase in temperature, i.e. equilibrium shifts towards products.

For exothermic reactions, ΔH° is − ve. Hence, $d \ln K_p/dT$ is –ve. This means that $\ln K_p$ and, hence, K_p decreases with increase in temperature, i.e. equilibrium shifts towards reactants. This is what is stated by Le-Chatelier's principle.

Example 40 *Explain why is it permissible to omit the concentrations of pure solids and liquids in calculating K_c for a homogeneous reaction.*

Solution: The standard state for a solid or liquid means the state of the substance in its pure form. We have the following relation for chemical potential μ of a substance:

$$\mu = \mu^\circ + RT \ln a$$

For a pure substance $\mu = \mu^\circ$, the above equation reduces to

$$RT \ln a = 0$$

R and T cannot be zero, hence $\ln a = 0$ or $a = 1$

Thus, we replace the activity of each pure substance by 1 in the equilibrium condition which is just like omitting it. But when the substance is impure, a first estimate of activity is the mole fraction and not concentration, as per Raoult's law.

SUMMARY

1. Criteria for a reaction in equilibrium in terms of free energy is $\Delta G = 0$
2. Criteria for the spontaneity of a reaction is $\Delta G < 0$. If $\Delta G > 0$, forward reaction does not take place.
3. For a reaction taking place under standard state (25°C, 1 atmosphere)

$$\Delta G^\circ = \Sigma \Delta G_f^\circ(\text{Products}) - \Sigma \Delta G_f^\circ(\text{Reactants})$$

   Thus, knowing the standard Gibbs free energies of formation of the reactants and products, ΔG° of the reaction can be calculated.
4. The relation between the equilibrium constant and Gibbs free energy is given by $\Delta G^\circ = -RT \ln K$. This equation is known as ***Van't Hoff reaction isotherm.***
5. There are three types of equilibrium constants, viz. K_p, K_c and K_x, depending upon the concentration units used.

   These are related as $K_p = K_c (RT)^{\Delta n}$ where Δn is the difference between the number of moles of the products and the reactants. If $\Delta n = 0$ then $K_p = K_c = K_x$
6. The temperature dependence of the equilibrium constant is given by the relation

$$\ln \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

7. For an exothermic reaction, increase of temperature decreases K_p and for endothermic reaction, increase of temperature increases K_p.
8. When a system in equilibrium is subjected to a stress, the equilibrium shifts in the direction which tends to undo the effect of the change. This is known as Le-Chatelier's principle.

EXERCISES

Based on Different University Papers
Multiple-Choice Questions

1. In which of the following reaction is K_p less than K_c?

   (a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

   (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

   (c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

   (d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

2. What will be the equilibrium constant at 717 K for the reaction

$$2HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$$

   if its value for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ at } 717 \text{ K is } 64?$$

   (a) 8

(b) 64

(c) $\frac{1}{64}$

(d) $\frac{1}{8}$

3. According to law of mass action, for the reaction $2A + B \rightarrow$ Products, which equation holds good?

(a) Rate $= k[A]^2[B]$

(b) Rate $= k[A][B]^2$

(c) Rate $= k[A][B]$

(d)

4. The relation between K_p and K_c for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ is

(a)

(b)

(c)

(d)

5. Which of the following equilibria will shift to the right side on increasing the temperature?

(a)

(b)

(c)

(d)

6. Consider the following reaction equilibrium:

On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is

(a) decreasing the temperature and increasing the pressure

(b) increasing temperature as well as pressure

(c) lowering of temperature as well as pressure

(d) any value of temperature and pressure.

7. With increase in temperature, equilibrium constant of a reaction

(a) always decreases

(b) always increases

(c) may increase or decrease depending upon whether $n_p < n_r$ or $n_p > n_r$.

8. K_1 and K_2 are equilibrium constants for reactions (1) and (2).

Then

(a)

(b)

(c)

(d)

9. At 490°C, the equilibrium constant for the synthesis of HI is 50. The value of K for the dissociation of HI will be

(a) 2.0

(b) 20.0

(c) 0.002

(d) 0.02

10. The degree of dissociation of dinitrogen tetraoxide $N_2O_4(g) \rightarrow 2NO_2(g)$ at temperature T and total pressure P is α. The equilibrium constant (k_p) at this temperature is given by

(a)

(b)

(c)

(d)

11. In which of the following cases does the reaction go farthest to completion?

(a) $K = 10$

(b) $K = 1$

(c) $K = 10^3$

(d) $K = 10^{-2}$

12. In a reaction

$$A + 2B \rightleftharpoons 2C,$$

2.0 moles of 'A', 3.0 moles of 'B' and 2.0 moles of 'C' are placed in a 2.0 L flask and the equilibrium concentration of 'C' is 0.5 mole/L. The equilibrium constant (K) for the reaction is

(a) 0.147

(b) 0.073

(c) 0.05

(d) 0.026

13. Which one of the following oxides of nitrogen will be the most stable one?

(a)

(b)

(c)

(d)

14. The rate of forward reaction is two times that of the backward reaction at a given temperature and identical concentration, $K_{\text{equilimbrium}}$ is,

(a) 1.5

(b) 0.5

(c) 2.5

(d) 2.0

15. For a reaction

The value of K_c is i6 at 250°C. The value of K_p at this temperature is

(a) 0.83

(b) 0.57

(c) 0.46

(d) 0.61

16. In a reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium concentrations of PC_5 and PCl_3 are 0.4 and 0.2 moles/litre respectively. If the value of K_c is 0.5, what is the concentration of $C1_2$ in mole/litre?

(a) 1.0

(b) 1.5

(c) 0.5

(d) 2.0

Answers

1. (a)
2. (d)
3. (a)
4. (b)
5. (b)
6. (a)
7. (d)
8. (c)
9. (d)
10. (d)
11. (c)
12. (c)
13. (a)
14. (d)
15. (d)
16. (a)

SHORT-ANSWER QUESTIONS

1. State the units in which K_p and K_c are expressed.
2. Explain the meaning of the term ***equilibrium constant.***
3. How is the standard free energy change of a chemical reaction related to its equilibrium constant?
4. Give two examples of each of the following:

(a) Reversible homogeneous reactions

(b) Reversible heterogeneous reactions

(c) Irreversible reactions

Represent graphically how equilibrium is attained.

5. Discuss any two applications of Le-Chatelier's principle as applied to physical equilibria.
6. Prove that K_c is independent of pressure at constant temperature.
7. Define the law of chemical equilibrium.
8. State the law of mass action.
9. Derive the relationship between K_p and K_c.
10. What do you understand by a reversible reaction? State with an example.
11. What are irreversible reactions? Give an example.
12. Derive the relationship between

(a) K_p and K_c

(b) K_a and K_p or K_c

(c) K_x with K_p and K_c

13. Write expressions for equilibrium constant for the following reactions:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

(c) $4Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

(d) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

14. Give an integrated from of the Clausius-Clapeyron equation and also list any two applications.
15. What do you understand by equilibrium state?
16. Derive the van't Hoff equation.

GENERAL QUESTIONS

1. With the help of Le-Chatelier'-Braun principle, explain the following:

(a) Effect of temperature on the solubility of sugar in water given that the dissolution of sugar in water is an endothermic process

(b) Effect of pressure on melting of ice

(c) Effect of temperature and pressure on solubility of gases in liquids

(d) Effect of pressure on the boiling point of a liquid

(e) Effect of pressure on the freezing point of a liquid

2. Derive van't Hoff equation,

For temperature dependence of equilibrium constant (K_p). What is the difference between ΔH and $\Delta H°$?

3. Derive van't Hoff equation (reaction isochore) giving the effect of temperature on equilibrium constant.
4. Discuss 'Chemical Equilibrium' in terms of free-energy change.

5. Starting from Clapeyron equation, how Clausius-Clapeyron equation is obtained? Express it in the integrated form.

6. Write the expression for equilibrium constant:

(a) in terms of pressure (K_p)

(b) in terms of concentrations (K_c)

(c) in terms of activities (K_a)

(d) in terms of moles fractions (K_x)

Derive the relationship between

(i) K_p and K_c

(ii) K_a and K_p or K_c

(iii) K_c and K_x

7. If K_1 and K_2 are the equilibrium constants of reaction at temperatures T_1 and T_2 respectively, derive thermodynamically the relation

8. Derive the Van't Hoff reaction isotherm. How is the free-energy change of reaction in any state other than the state of equilibrium related to reaction quotient Q_p and equilibrium constant K_p? Derive this relationship.

9. Derive Clausius-Clapeyron equation for liquid-vapour equilibrium. Show how the equation can be expressed in the integrated form. What are its important applications?

10. Derive the criteria for thermodynamic equilibrium in terms of temperature, pressure and chemical potential.

11. Derive the van't Hoff equation in the integrated form.

12. Write the Clausius-Clapeyron equation in the integrated form. What are its important applications?

13. Derive the van't Hoff equation giving the variation of equilibrium constant with temperature.

14. Define the law of chemical equilibrium. How can it be derived thermodynamically?

15. For a gaseous reaction in equilibrium, derive the reaction $\Delta G^\circ = -RT \ln K_p$.

16. Starting from basic principles, derive the relationship $\Delta G^\circ = -RT \ln K_p$.

17. For a gaseous reaction, derive the following relationship.

$$\Delta G = -RT \ln K_P + RT \ln Q_p$$

18. Apply Le-Chatelier's principle to predict suitable conditions for getting maximum yield of the product in each of the following cases:

(a) Manufacture of ammonia by Haber's process

(b) Manufacture of nitric oxide in Birkland-Eyde process for manufacture of nitric acid

(c) Manufacture of hydrogen by Bosch process

19. What do you understand by reversible and irreversible reactions? What do you mean by the saying that *equilibrium is dynamic in nature?* State the law of chemical equilibrium. Name at least three different types of equilibrium constants. Give the relationship between them. What are their units?

20. Derive the following for the gaseous reaction:

21. How is free energy-change and standard free-energy change of a reaction calculated from the chemical potentials of the reactants and products involved? Taking a suitable example, explain how free-energy change of forward and backward reactions of a reversible reaction takes place.
22. Briefly describe at least three different ways by means of which the standard free-energy change of a reaction can be calculated.
23. Derive the van't Hoff equation in terms of equilibrium constant K_c and standard internal energy, ΔU°.
24. A reversible reaction is spontaneous in a forward direction as well as in the backward direction (i.e. ΔG is negative for both). Explain with a suitable example.
25. For a gaseous reaction (not in equilibrium), derive the relationship $\Delta G = \Delta G^\circ + RT \ln Q_p$.



Phase Equilibria and Phase Rule

14

LEARNING OBJECTIVES

- Explain the terms *phase, component* and *degree offreedom*
- Define equilibrium and learn about true and metastable equilibrium, thermal, mechanical and chemical equilibrium
- Derive phase rule thermodynamically
- Learn different methods for the determination of transition point
- Understand the phase diagram of water and the meaning of different curves, areas and points
- Follow solid-liquid phase transition and heating curves from solid phase through liquid phase to the gaseous phase and solid-vapour phase transition
- Know how phase changes in nature could endanger lives
- Study phase diagram of the following system (one component)
  (a) Water system
  (b) Carbon dioxide system
  (c) Sulphur system
- Learn the experimental determination of phase diagram of two-component systems
- Study in detail the following two-component systems:
  - Bismuth-cadmium system
  - Lead-silver system
  - Kl-water system
  - Mg-Zn system
  - Ferric chloride-water system
  - Na_2SO_4–H_2O system
  - NaCl–H_2O system
  - $CuSO_4$–H_2O system

14.1 INTRODUCTION

A ***phase*** is a homogeneous part of a system that is separated from the rest of the system by a well-defined boundary. When an ice cube floats in a glass of water, solid water (ice) is one of the phases and liquid water is the other. Although ice and water show the same chemical properties, their physical properties are different. A phase change generally occurs by the addition or removal of heat energy.

Phase equilibrium is relevant to heterogeneous system. A heterogeneous system is defined as *a system consisting of a number of phases in equilibrium*. The number of phases that can exist together at equilibrium depends upon the conditions of temperature, pressure and concentration of different phases. A relationship governing all heterogeneous equilibria was first given by Willard Gibbs. It is known as Phase Rule.

Gibbs phase rule cannot be expressed in words. It is described by a mathematical equation as under:

For a heterogeneous system in equilibrium,

$$F = C - P + 2$$

where, F = Number of degrees of freedom
C = Number of components
P = Number of phases

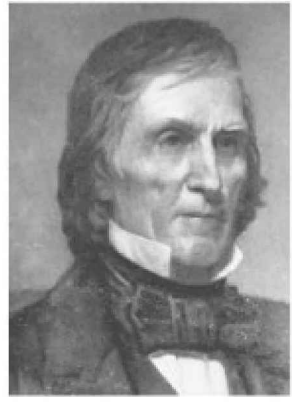


Fig. 14.1 *Willard Gibb's was the creator of the field of chemical thermodynamics. He formulated the phase rule.*

14.2 EXPLANATIONS OF TERMS

14.2.1 Phase

A phase may be defined as any part of a system which is

1. Homogeneous and separated from other part of the system by a distinct boundary.
2. Physically and chemical different from other parts of the same system.
3. Mechanically separable from other parts of the system

Examples illustrating phases are given in Table 14.1

Table 14.1 *Phases associated with different systems*

System	Phases

(i)	Ice and water	2 phases:	1 solid and 1 liquid
(ii)	Water and water vapour	2 phases:	1 liquid and 1 gaseous
(iii)	Ice, water and water vapour	3 phases:	1 solid, 1 liquid and 1 gaseous
(iv)	Two immiscible liquids, e.g. CS_2/H_2O, CCl_4/H_2O etc.	2 phases:	both liquids.
(v)	Two miscible liquids, i.e. water/alcohol	1 phase:	only liquid
(vi)	$CaCO_3$, CaO and CO_2	3 phases:	2 solids and 1 gaseous
(vii)	Monoclinic and rhomic sulphur	2 phases:	both solids

Miscible gases and miscible liquids constitute a single phase: solid + liquid, solid + gas liquid + gas. Two solids and two immiscible liquids constitute two phases.

Different solids are regarded as different phases, however intimately they may be mixed.

14.2.2 Components

The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation, negative and zero signs being permitted.

Examples

(a) Water System consists of the equilibrium

$$\underset{\text{(Solid)}}{\text{Ice}} \rightleftharpoons \underset{\text{(Liquid)}}{\text{Water}} \rightleftharpoons \underset{\text{(Gaseous)}}{\text{vapour}}$$

This system consists of one component only, i.e. it is a one-component system because the composition of each of the three phases present can be directly expressed as H_2O.

(b) Sulphur System consisting of four phases—monoclinic (s), rhombic (s), liquid (l) and vapour (g)—is also a ***one component system*** because the composition of each phase can be expressed in terms of one constituent-sulphur.

(c) Decomposition of $CaCO_3$ by Heat can be expressed according to the equilibrium

$$\underset{\text{(Solid)}}{CaCO_3} \rightleftharpoons \underset{\text{(Solid)}}{CaO} + \underset{\text{(Gas)}}{CO_2}$$

There are three different constituents forming three different phases. But the composition of

each phase can be expressed in terms of any two of the constituents. For example,

(i) If the constituents chosen are CaO and CO_2, then

Phase		Composition
$CaCO_3$	$\rightarrow$	$CaO + CO_2$
CaO	$\rightarrow$	$CaO + 0\,CO_2$
CO_2	$\rightarrow$	$0\,CaO + CO_2$

(ii) If the constituents chosen are $CaCO_3$ and CO_2 then

Phase		Composition
$CaCO_3$	$\rightarrow$	$CaCO_3 + 0\,CO_2$
CaO	$\rightarrow$	$CaCO_3 - CO_2$
CO_2	$\rightarrow$	$0\,CaCO_3 + CO_2$

Likewise, the composition of three phases can be expressed in terms of $CaCO_3$ and CaO. Thus, the ***dissociation of $CaCO_3$ by heat is a two component system.***

(d) Sodium Sulphate-Water System This system at equilibrium contains a number of phases like $Na_2SO_4 \cdot 10H_2O$, $Na_2SO_4 \cdot 7H_2O$, Na_2SO_4 solution, ice, water and vapour but the composition of each phase can be expressed by chemical equations, in terms of only anhydrous sodium sulphate (Na_2SO_4) and water (H_2O) as follows:

Phase	Composition
$Na_2SO_4 \cdot 10H_2O$	$\rightarrow Na_2SO_4 + 10H_2O$
$Na_2SO_4 \cdot 7H_2O$	$\rightarrow Na_2SO_4 + 7H_2O$
Na_2SO_4	$\rightarrow Na_2SO_4 + 0H_2O$
Na_2SO_4 solution	$\rightarrow x\,Na_2SO_4 + y\,H_2O$
Ice	$\rightarrow 0Na_2SO_4 + H_2O$
Water	$\rightarrow 0Na_2SO_4 + H_2O$
Vapour	$\rightarrow 0Na_2SO_4 + H_2O$

Thus, the smallest number of independently variable constituents by which the composition of the phases present at equilibrium can be expressed is two—Na_2SO_4 and H_2O. Hence, it is also a two-component system.

In a chemically reactive system, the number of components is calculated as follows:

Number of components (C) − Total number of constituents or species, S (already present as well as produced due to reaction)
− Number of equations (E) representing equilibrium between the constituents
− Number of restrictions (R) for electrical neutrality if ions are considered)

Mathematically, this may be written as $C = S - E - R$

The following examples will illustrate this

(a) $Na_2SO_4 - H_zO$

(i) Assuming no dissociation,

$S = 2$ (Na_2SO_4 and H_2O)

$E = 0$ (No chemical reaction/equilibrium)

$R = 0$ (No restriction of electrical neutrality or material balance)

$\therefore C = S - E - R = 2 - 0 - 0 = 2$

Thus, Number of components = 2.

(ii) Assuming complete dissociation of the salt

$S = 3$ (Na^+, SO_4^{2-} and H_2O)

$E = 0$

$R = 1$ (for electrical neutrality, $2Na^+ = SO_4^{2-}$)

$\therefore C = S - E - R = 3 - 0 - 1 = 2$

Thus, Number of components = 2.

(iii) Assuming dissociation of H_2O also.

$S = 6$ (Na_2SO_4, Na^+, SO_4^{2-}, H_2O, H^+, OH^-)

$E = 2$ ($Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$ and $H_2O = H^+ + OH^-$)

$R = 2$ ($2Na^+ = SO_4^{2-}$, i.e. number of moles of $Na^+ = 2 \times$ Number of moles of SO_4^{2-} and $H^+ = OH^-$)

$C = S - E - R = 6 - 2 - 2 = 2$. Thus, number of components = 2.

(b) KCl-NaBr-H_2O System

(i) Assuming no dissociation

$S = 5$[KCl, NaBr, H_2O (already present) NaCl, KBr (produced due to reaction.)]

$E = 1$ [KCl + NaBr $\rightleftharpoons$ KBr + NaCl]

$R = 0$ (No ions have been considered)

$\therefore C = S - E - R = 5 - 1 - 0 = 4$ or number of components = 4.

(ii) Assuming complete dissociation

$S = 11$ (KCl, K^+, Cl^-, NaBr, Na^+, Br^-, KBr, NaCl, H_2O, H^+, OH^-)

$E = 5$ ($KCl \rightleftharpoons K^+ + Cl^-$, $NaBr \rightleftharpoons Na^+ + Br^-$, $NaCl \rightleftharpoons Na^+ + Cl^-$ $KBr \rightleftharpoons K^+ + Br^-$, $H_2O \rightleftharpoons H^+ + OH^-$)

$R = 2$ (Electrical neutrality and $H^+ = OH^-$)

$\therefore C = S - E - R = 11 - 5 - 2 = 4$ or number of components = 4

Thus, KCl − NaBr − H_2O is a four-component system if salts are present in unequal amounts but it becomes a three-component system if the salts are taken in equal amounts.

(c). KCl-NaCl − H_2O system

(i) Assuming no dissociation

$$S = 3 \text{ (KCl, NaCl, } H_2O)$$
$$E = 0$$
$$R = 0$$
$$C = S - E - R = 3 - 0 - 0 = 3 \text{ (three components)}$$

(ii) Assuming complete dissociation

$$S = 8 \text{ (KCl, } K^+, Cl^-, \text{ NaCl, } Na^+, H_2O, H^+, OH^-)$$
$$E = 3 \text{ (KCl} \rightleftharpoons K^+ + Cl^-, \text{ NaCl} \rightleftharpoons Na^+ + Cl^-, H_2O \rightleftharpoons H^+ + OH^-)$$
$$R = 2 \text{ (Electrical neutrality and } H^+ = OH^-)$$
$$\therefore C = S - E - R = 8 - 3 - 2 = 3 \text{ (three components)}$$

If the salts KCl and NaCl are taken in equal amounts then there will be one more restriction ($Na^+ = K^+$) so that $R = 3$.

Hence,

$$C = S - E - R = 8 - 3 - 3 = 2 \text{ or number of components} = 2$$

From examples (b) and (c), we conclude that if the salts are taken in unequal amounts, KCl–NaBr–H_2O is a 4 component system and KCl–NaCl–H_2O is a three-component system and if they are taken in equal amounts in each case, the former is a 3-component system and the latter is a 2-component system.

14.2.3 Degree of Freedom or Variance

Degrees offreedom or variance of a system is the smallest number of variable factors, i.e. temperature, pressure and concentration of the components which must be arbitrarily fixed in order that the conditions of the system may be completely defined.

Examples

(a) Ice-Water-Vapour System In this system, there are three phases of one component (H_2O). These three phases can co-exist in equilibrium only at one particular temperature and under one particular pressure. Any variation in these factors will make one or more of the phases disappear and there fore will destroy the system. Hence this system has no degree of freedom or in other words it is ***invariant.*** The same result follows from phase rule, i.e.

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

(b) Water-Vapour System This system consists of two phases of one component. As the vapour pressure of water is definite at definite temperature, independent of the amount of water present, it follows that if the temperature is fixed, the vapour pressure is also fixed and conversely, fixing the pressure fixes the temperature. Thus, the system has only one degree of

freedom or in other words, it is ***univariant.***

(c) For a Gas The temperature, pressure and concentration (volume) are related according to the equation $PV = RT$. Thus, in order to completely define the system, any two factors out of P, V and T must be fixed. Hence, it follows that a gas has two degrees of freedom or it is ***blvariant.***

Example 1 *What are the number of components, phases and degrees of freedom in the following equilibrium system?*

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Solution: No. of components = 2

No. of phase = 3 (2 solids + 1 gas)

Degree of freedom $F = C - P + 2$ or $F = 2 - 3 + 2$

$F = 1$

14.3 EQUILIBRIUM

A system is said to be in equilibrium if the properties like temperature, composition, etc., of various phases do not undergo any change with time. This is of the following two types:

1. True Equilibrium A system is said to be in a state of true equilibrium if the same state can be achieved by approach from either direction. For example, the equilibrium between ice and water at 1 atm. pressure and 0°C is a true equilibrium, because it can be attained by melting of ice or by freezing of water.

2. Metastable Equilibrium If the state of system can be attained only from one direction and that too by very careful change of conditions, it is called a state of metastable equilibrium. For example, water at −2°C can be obtained only by very careful cooling of liquid water but not by melting of ice. Hence, water at −2°C is said to be in a state of metastable equilibrium.

Criteria for Phase Equilibrium

The following three equilibrium must exist in phase equilibria in a multicomponent system.

1. Thermal Equilibrium The temperature in every part of a system must be the same as otherwise heat may flow from one part of the system to another. We arrive at this condition as under:

Suppose a system consists of two phases A and B and their temperatures T_A and T_B respectively. Further suppose that at equilibrium, a small amount of heat δ_q flows from phase A to phase B.

Then,

Entropy change of phase A $(dS_A) = -\dfrac{\delta_q}{T_A}$

Entropy change of phase B $(dS_B) = +\dfrac{\delta_q}{T_B}$

$\therefore$ Total entropy change of the system $(dS) = -\dfrac{\delta_q}{T_A} + \dfrac{\delta_q}{T_B}$

The condition for equilibrium in terms of entropy change is

$$(dS)_{E,V} = 0$$

$\therefore$ $$-\frac{\delta_q}{T_A} + \frac{\delta_q}{T_B} = 0 \text{ or } \frac{\delta_q}{T_A} - \frac{\delta_q}{T_B} = 0 \text{ or } T_A = T_B$$

2. Mechanical Equilibrium The pressure in every part of the system must be same as otherwise matter may flow from one part of the system to another. We arrive at this condition as under.

Consider an isolated system consisting of two phases in equilibrium at constant volume and temperature. Suppose at equilibrium, a small amount of matter flows from Phase A to Phase B and as a result, the volume of Phase A decreases by small amount dV while that of Phase B increases by the same amount, dV. Let the pressure of two phases now be P_A and P_B respectively. Then,

Change in Helmholtz free energy of Phase A $(dA_A) = -P_A\, dV$

Change in Helmholtz free energy of Phase B $(dA_B) = +P_B\, dV$

But, in terms of Helmholtz free-energy change, the condition of equilibrium is $(dA)_{V,T} = 0$

$\therefore$ $$dA = dA_A + dA_B = -P_A\, dV + P_B\, dV = 0 \text{ or } P_A = P_B$$

3. Chemical Equilibrium At equilibrium, the chemical potential of any component in all the phases must be the same. This is called thermodynamic criteria or phase equilibrium.

For a solution (or a phase) containing a number of constituents, the chemical potential of any component is the increase or decrease of free energy that takes place, at constant temperature and pressure, for the addition and removal of one mole of that component, keeping the amount of all other components constant. It is usually represented by 'μ'.

As a system consisting of a number of phases in equilibrium constitutes a closed system, the total free energy of the whole system is constant at constant temperature and pressure. For any change in the composition of any component among the various phases, there is no change in the free energy of the whole system as long as temperature and pressure remain constant, i.e. $(\Delta G°)_{TP} = 0$

Consider a simple case consisting of only two phases, A and B (Fig. 14.2). Suppose a number of components (C_1, C_2, ... C_C) are distributed between them. Further, suppose that at constant temperature and pressure, a small amount δn_1 of the component 1 is transferred from Phase A to Phase B. If $(\mu_1)_A$ and $(\mu_1)_B$ represent the chemical potentials of the component 1 in Phase A and Phase B respectively,

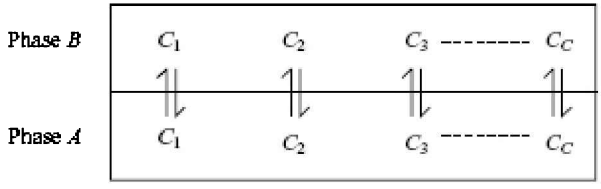


Fig. 14.2 *Distribution of a number ofcomponents between two phases*

we have,

Decrease in the free energy of Component 1 in Phase $A = (\mu_1)_A \, \delta n_1$

Increase in the free energy of Component 1 in Phase $B = (\mu_1)_B \, \delta n_1$

As the system is a closed one,

$$(\Delta G)_{T.P} = 0$$

$$-(\mu_1)_A \, \delta n_1 + (\mu_1)_B \, \delta n_1 = 0 \text{ (minus sign to represent the decrease)}$$

or

$$(\mu_1)_A = (\mu_1)_B$$

Thus, for a system consisting of two phases in equilibrium, the chemical potential of any given component is same in both the phases.

In general, for a system consisting of a number of phases P_1, P_2, P_3 in equilibrium (i.e. in multiphase equilibria) for any component *i*,

$$(\mu_i)P_1 = (\mu_i) \, P_2 = (\mu_i) \, P_3 \ldots$$

To Conclude ***For a multiphase equilibria containing a number of components distributed among them, the chemical potential of any component is the same in all the phases.***

Criteria for Two-phase Equilibria for One-component System If a system consists of one substance only which may exist in two different phases in equilibrium, e.g. liquid water $\rightleftharpoons$ water vapour or ice $\rightleftharpoons$ liquid water or sulphur (monoclinic) $\rightleftharpoons$ sulphur (rhombic), etc., the criterion is obtained in a simple manner in terms of ***free energy*** instead of chemical potential. Evidently, in such a case, if a certain amount of the substance is transferred from one phase to the other, the molar free energy of one phase decreases while that of the other phase increases by an equal amount. Hence, the net result is that there is no change in free energy, i.e.,

$$\Delta G = 0$$

This implies that if at equilibrium, G, is the molar free energy of Phase I and G_2 that of Phase II, we have

$$G_2 - G_1 = 0$$

$$G_1 = G_2$$

14.4 THERMODYNAMIC DERIVATION OF PHASE RULE

Let us consider a heterogeneous system consisting of C components (C_1, C_2, C_3, ... C_C) distributed among P phases (P_1, P_2, P_3, ... P_P) as shown in Fig. 14.3. Degree of freedom of a system is equal to the number of independent variables which must be fixed arbitrarily to define the system completely. Clearly, the number of these variables is equal to the total number of

variables of the system minus the number of variables which are defined by the system itself because of its being in equilibrium.

Thus,

Degree of freedom = Total number of variables − Number of variables defined by the system because of its being in equilibrium.

The total number of variables can be calculated as follows :

Suppose a phase contains two components. If the molar concentration of one component is known, that of the other can be obtained by difference. Thus, the phase containing two components can be defined completely by one concentration term.

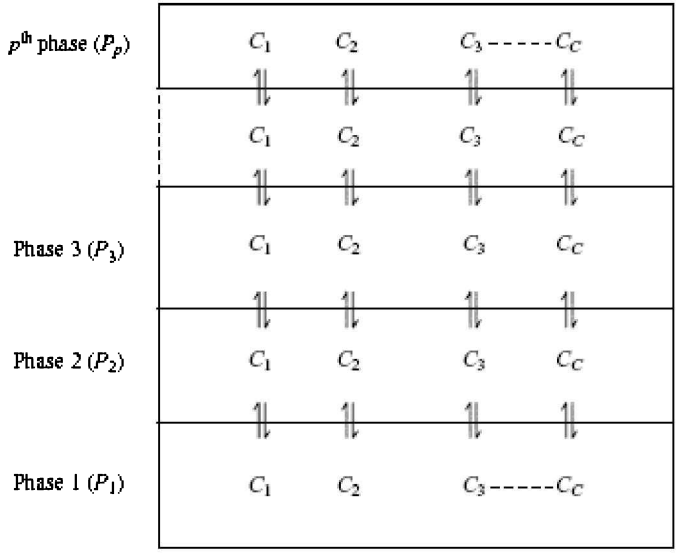


Fig. 14.3 *Distribution of C components among P phases*

Similarly, if a phase contains three components, two concentration terms should be known to define it (because then the concentration of the third can be found by difference). In general, if a phase contains C components, it can be defined completely by $(C - 1)$ concentration terms or variables. To define the system completely, i.e. all the P phases, the total number of concentration terms or variables required will be $P(C - 1)$. Besides these concentrations variables, the temperature and pressure of the system, which are the same for all the phases, are also variables. Therefore,

$$\text{Total number of variables} = P(C - 1) + 2$$

The number of variables defined by the system itself, because of its being in equilibrium can be calculated as follows.

For a system in equilibrium, the chemical potential of a component (μ) is the same in all P phases. Thus, if a system consists of three phases, say A, B and C then for any component i

$$(\mu_i)_A = (\mu_i)_B = (\mu_i)_C$$

These are in fact two equations, viz.,

$$\text{(i) } (\mu_i)_A = (\mu_i)_B \quad \text{and} \quad \text{(ii) } (\mu_i)_B = (\mu_i)_C$$

Thus, for a system of three phases, two equations are known for each component. In general, for a system of P phases, $(P - 1)$ equations are known for each component. Hence, for a system of P phases and C components, the number of equations known will be $C(P - 1)$. This is clearly the number of variables defined by the system itself. Thus, we have

Number of variables defined by the system itself = $C(P - 1)$

Hence, the degree of freedom F of the system is given by,

$$F = [P(C - 1) + 2] - [C(P - 1)]$$
$$= C - P + 2$$

14.5 DIFFERENT TECHNIQUES FOR THE DETERMINATION OF TRANSITION POINT

Transition temperature of a change can be obtained by observing the change in physical property such as colour, density, solubility, etc. Various methods that are employed to determine the transition temperature are discussed as under:

1. Colour Change If a little mercuric iodide is place in a melting point tube attached to a thermometer and heated in a conc. H_2SO_4 bath, it is possible to record temperature at which the red mercuric iodide changes to the yellow form.

2. Density Change As rhombic sulphur changes to monoclinic sulphur, there is a decrease in density and, therefore, an increase in volume. The change in volume is employed to measure the transition temperature by using an apparatus known as dilatometer, shown in Fig. 14.4.

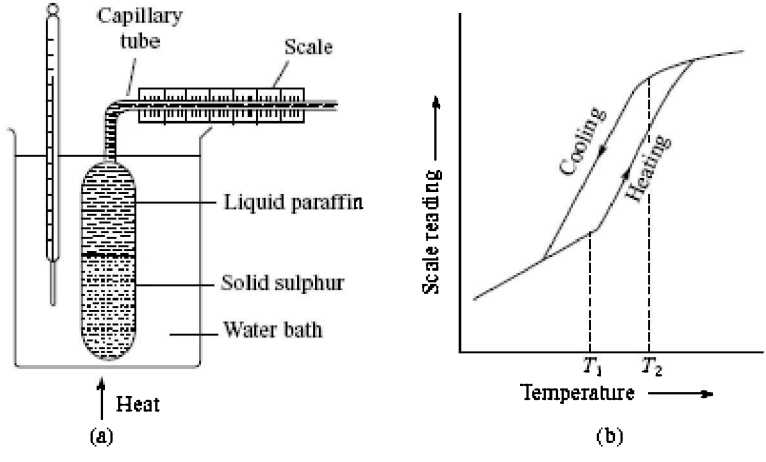


Fig. 14.4 *(a) A dilatometer (b) Plot of scale reading (volume) against temperature recorded with a dilatometer*

Some powdered rhombic sulphur is placed in the glass bulb and liquid paraffin (an inert liquid) is introduced above sulphur [Fig. 14.4(a)]. The apparatus is then immersed in a hot-water bath, the temperature of which is raised by heating. The scale reading and the temperature are recorded every minute. A plot of liquid level in a capillary against temperature is drawn [Fig.

14.4(b)]. On cooling of the dilatometer, reverse changes take place but due to thermal log, the curve takes a different route. The transition temperature is taken as the mean of the respective temperature where expansion starts (T_1) and contraction begins (T_2).

3. Solubility Change Two forms of the same substance may possess different solubilities but at the transition point, they have identical solubilities. Thus, if a solubility-temperature graph is plotted for the two forms, it is found to consist of two parts with a sharp break. While one form represents the solubility curve for one form, the second part represents that for the other. At the melting point of the two curves, the solubility of the two forms is the same. This is how the transition temperature is located.

For example, for the sodium sulphate-water system, the solubility curves of Na_2SO_4 (rhomic) and $Na_2SO_4 \cdot 10H_2O$ meet at 32.2°C. Thus, 32.2°C is the transition temperature where $Na_2SO_4 \cdot 10\ H_2O$ changes to Na_2SO_4.

4. Cooling Curve Method This is often an evolution or absorption of heat when one form changes into the other. Suppose Form *A* is converted into Form *B* on heating. Now, let *B* be allowed to cool and the curve is obtained by plotting the temperature against the time. The otherwise steady curve has a distinct break at a temperature which corresponds to the transition point.

The method is found to be suitable for determination of transition point for different hydrates of a salt or for a hydrate and anhydrous salt. The method can also be employed for different allotropes of a metal.

14.6 PHASE DIAGRAM

The number of phases that exist together when the system is in equilibrium are studied under the following variables conditions:

1. Temperature and pressure
2. Temperature and composition (pressure being constant)

The variables of temperature and pressure (or composition) governing the existence of various phases are obtained from the experiment. Then the temperature-pressure or temperature-composition diagrams are constructed for the different values of the variables.

The diagrams which give the conditions of equilibrium between differed phases of the system are called ***phase diagrams.*** Such a diagram contains a number of lines, points of intersection of lines and areas. Each of the above has a significance attached to it.

One-Component Systems

Phase Rule as Applied to a One-Component System

1. When number of phases in a one-component system is 1 then $C = 1$ and $P = 1$. Substituting the value in phase rule equation $F = C - P + 2$, we get $F = 2$.

   Thus, the degree of freedom is 2. It is known as a ***bivariant system.*** Hence, we can completely describe the system graphically with the help of two variables, viz. temperature and pressure, on *X* and *Y* axes.

2. When the number of phases in a one-component system is 2, the degree of freedom is given by

$$F = C - P + 2 \text{ or } F = 1 - 2 + 2 \text{ or } F = 1$$

The system possesses one degree of freedom. Such systems are called univariant. We need to mention only one variable in such a case. The other variable is automatically defined.

3. When the number of phases in a one-component system is 3, the degree of freedom is given by

$$F = C - P + 2 \text{ or } F = 1 - 3 + 2 \text{ or } F = 0$$

Such a system having no degree of freedom is called a ***non-variant system.*** Univariant systems are represented by lines, bivariant systems are represented by areas and non-variant systems are represented by points in a one-component system.

14.7 PHASE DIAGRAM OF THE WATER SYSTEM

The system consists of three phases:

$$\underset{(s)}{\text{Ice}} \rightleftharpoons \underset{(l)}{\text{water}} + \underset{(g)}{\text{vapour}}$$

These three single phases may occur in four possible combinations in equilibrium as

1. Liquid $\rightleftharpoons$ Vapour
2. Solid $\rightleftharpoons$ Vapour
3. Solid $\rightleftharpoons$ Liquid
4. Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

The number of phases that can exist in equilibrium at any point depends upon the conditions of temperature and pressure. These conditions have been determined experimentally and a phase diagram is constructed by plotting pressure against temperature (Fig. 14.5). The phase diagram consists of

1. Three stable curves *OA*, *OB* and *OC* and one metastable curve *OA'*
2. Three areas, and
3. Definite point, O.

These are separately discussed as under:

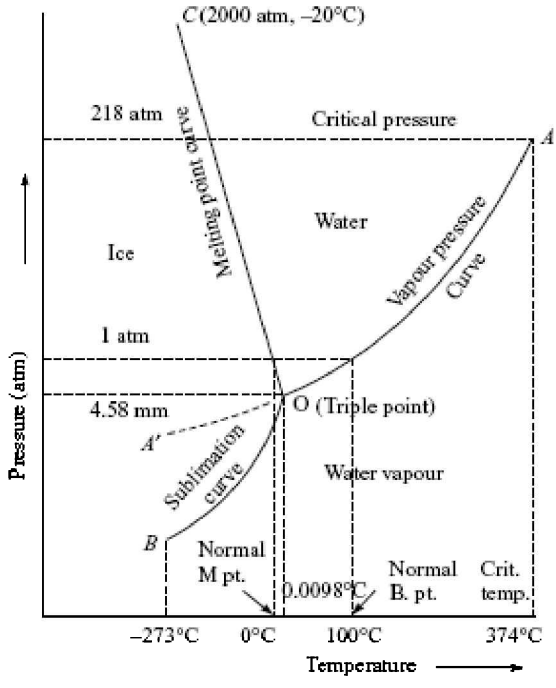


Fig. 14.5 *The water system (pressure and temperature indicated are not to scale)*

1. Curves

(a) OA This is a ***vapour pressure curve*** of water. It represents the equilibrium between liquid water and vapour at different temperatures. At any point on the curve, the two phases are present. The curve starts from the point O, the freezing point of water and ends at A, the critical temperature (374°C) beyond which the two phases merge into each other. Consider any point on the curve. For a fixed value of pressure, temperature also has a fixed value. If by keeping the pressure constant, an attempt is made to raise the temperature then the liquid phase will disappear and if the temperature is lowered then the vapour phase will disappear. Thus, to define the system completely at any time, it is necessary to mention either temperature or pressure. In other words, pressure being fixed, it is not necessary to mention temperature, it gets automatically fixed. Therefore, the water-vapour system is univariant, or it has one degree of freedom. It also follows from the phase rule equation,

$$F = C - P + 2$$

$$F = 1 - 2 + 2 = 1$$

(b) *OA'* The dotted curve *OA'*, a continuation of curve *OA* represents the vapour pressure curve of supercooled water. It is a metastable curve. On being disturbed, the supercooled phase at once changes to solid ice and the curve merges into *OB*.

(c) *OB* It is the ***sublimation curve*** or the vapour pressure curve of the ice. It gives values of temperature and pressure at which ice and vapours can exist together. It is obtained by studying the effect of pressure on the freezing point of water. The curve starts from the point *O*, the

freezing point of water and ends at B (−273°C). As temperature decreases, the vapour pressure of ice tends to become negligible. We find that for a particular temperature, there can be one and only one pressure value and vice versa. In other words, the ice-vapour system is univariant or has one degree of freedom.

(d) OC It is the ***melting point curve*** and represents the equilibrium between ice and liquid water at various pressures. In other words, it shows the effect of pressure on the melting point of ice. It should be noted that the line OC is inclined towards the pressure axis. The slope of the curve OC clearly indicates that the melting point of ice is lowered by increase of pressure. There is, however, no limit for the curve, OC. It goes up to a point corresponding to 2000 atmospheres and −20°C. At this point, one type of ice changes into another solid modification but the solid-liquid equilibrium still remains.

At any point of the curve OC, two phases (ice and liquid water) are present in equilibrium. Hence, the system is univariant or the degree of freedom is one.

2. Areas The areas, i.e. regions bounded by two lines give the conditions of temperature and pressure under which the single phase, i.e. ice or liquid water or vapour, is capable of stable existence. The area below AOB has water vapour, the area BOC has ice and the area COA has liquid water. These areas are bivariant because to locate any point in the area, temperature as well as pressure must be fixed, thus indicating two degrees of freedom. This also follows from phase-rule equation.

$$F = C - P + 2$$
$$F = 1 - 1 + 2 = 2$$

3. Triple Point It is a point where the three curves OA, OB and OC meet. At this point, the three phases—ice, water and vapour are in equilibrium. It should be noted that it is only a point indicating that there is only one set of conditions under which it is possible for the three phases to exist together. The point O is a self-defined point corresponding to a definite temperature of 0.0098°C and a definite pressure of 4.58 mm. If either pressure or temperature is changed then one of the three phases will disappear. Since on changing either pressure or temperature one of the phases disappear, therefore the system at the point O has no degree of freedom, that is it is invariant. The same result follows from phase rule equation.

$$F = C - P + 2$$
$$F = 1 - 3 + 2 = 0$$

It may be mentioned that triple point is different from normal melting point of ice, i.e. 0°C. At the normal melting point of ice at 0°C and 1 atmospheric pressure, only ice and water (no vapours) exist together.

Example 2 *Explain why the fusion curve of ice has a negative slope in the phase diagram of water.*

Solution: This is because the freezing point of water is depressed by the increase of pressure. Therefore, the fusion curve is inclined towards the pressure axis, i.e. it has a negative slope.

But the sublimation curve has a positive slope, i.e. it is inclined away from the pressure axis. This is because the vapour pressure of water increases with rise of temperature.

14.8 SOLID-LIQUID PHASE TRANSITION

Conversion of a solid into liquid is called ***melting,*** the reverse of it being ***freezing.*** The melting

point of a solid or the freezing point of a liquid is the temperature at which the solid and liquid phases of the substance coexist in equilibrium at 1 atm.

A common example of solid-liquid equilibrium is that of water:

$$\text{Ice} \rightleftharpoons \text{Water at } 0^\circ\text{C}$$

or

$$H_2O\,(s) \rightleftharpoons H_2O\,(l) \text{ at } 0^\circ\text{C}$$

It may look surprising that when we take out ice cubes from the refrigerator and keep them pressed together for a couple of minutes, they join together. This is because the melting and freezing phenomenon are in equilibrium. As the ice cubes melt, some of the water between them may freezes thus, joining the ice cubes (Fig. 14.6)



Fig. 14.6 *Ice cubes*

When a solid is heated, its temperature rises gradually until the point *A* is reached (see Fig. 14.7). Here, the solid begins to melt. During this span ($A \rightarrow B$), heat is absorbed by the system and the temperature does not change. The heat being supplied is used to overcome the attractive forces in the solid. Once complete melting has taken place (Point *B)*, further heat supplied increases the kinetic energy of the liquid molecule and the temperature starts rising *(*$B \rightarrow C$*)*. At *C*, the process of vaporisation starts and continues till *D*. Although heat is being supplied, the temperature does not change. The heat being supplied is used to overcome the cohesive forces between the molecules. At the point *D*, the process of vaporisation is complete. Further heating raises the temperature.

1. Molar Heat of Fusion, ΔH_{fus}, is the energy required to melt 1 mole of a solid. Its value for water is 6.01 kJ/mol.

2. Molar Heat of Vaporisation, ΔH_{vap}, is the energy required to boil 1 mole of a liquid. Its value for water is 40.79 kJ/mol.

How can we explain that ΔH_{vap} ***of a substance is much higher than its*** ΔH_{fus} ***value?***

During melting, the heat supplied displaces the molecules from their lattice positions but still there is some order left in the liquid. During vaporisation, the heat supplied separates the molecules completely and the molecules are quite apart from each other. In the vaporisation process, a lot more heat energy is consumed. Therefore, ΔH_v is much greater than ΔH_{fus}.

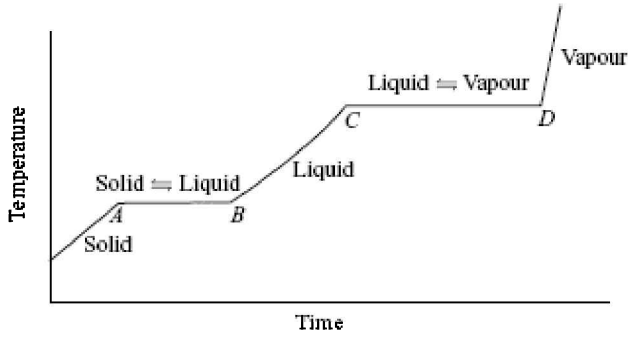


Fig. 14.7 *A typical heating curve from solid phase through liquid phase to the gas phase*

3. Supercooling It is a phenomenon in which a liquid can be cooled below its freezing point without change of state. Supercooling occurs when heat is removed from a liquid so rapidly that the molecules have no time to assume the lattice structure of the solid. Gentle shaking of the supercooled liquid converts it to the solid state.

4. Solid-Vapour Phase Transition

Sublimation It is the process by which a substance changes from the solid state to the vapour state directly without going through the liquid state. Reverse of sublimation in which a substance changes from the gaseous state to the solid state is called ***deposition.*** Iodine and naphthalene are some examples of substances that undergo sublimation.

Molar enthalpy of sublimation, ΔH_{sub}, is the energy required to sublime one mole of a substance. It is equal to the sum of the molar enthalpies of fusion and vaporisation.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

This is in accordance with Hess's law.

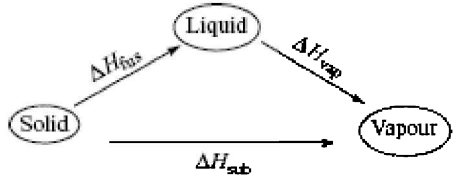


Fig. 14.8 *Sublimation*

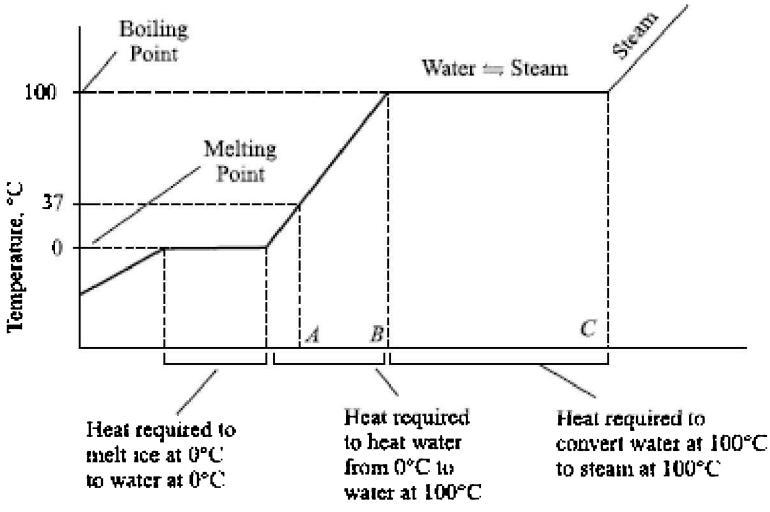


Fig. 14.9 *Heating curve of water*

Example 3 *Calculate the amount of energy in kJ necessary to convert 90 g of water from 0°C to water vapour at 110°C. Given specific heat of water = 4.184 J per gram per °C. Molar heat of vaporisation = 40.79 kJ mol*$^{-1}$.

Solution: The whole process can be divided into three steps:

Step 1 Conversion of water at 0°C to water at 100°C

$$\text{Heat required} = \text{Mass} \times \text{Specific heat} \times \text{Change of temperature}$$
$$= 90 \times 4.184 \times 100 \text{ J}$$
$$= 37656 \text{ J} = 37.66 \text{ kJ}$$

Step 2 Conversion of water at 100°C to steam at 100°C

$$\text{Number of moles} = \frac{90}{18} = 5$$

$$\text{Molar heat of vaporisation} = 40.79 \text{ kJ mol}^{-1}$$

$$\text{Heat required} = 5 \times 40.79 \text{ kJ} = 203.95 \text{ kJ}$$

Step 3 Conversion of steam at 100°C to steam at 110°

$$\text{Heat required} = \text{Mass} \times \text{Specific heat} \times \text{Change of temperature}$$
$$= 90 \times 4.184 \times 10 \text{ J}$$
$$= 3765.6 \text{ J} = 3.77 \text{ kJ}$$
$$\text{Total energy required} = 37.66 + 203.95 + 3.77$$
$$= 245.38 \text{ kJ}$$

Phase Change Could Threaten Life

People are sometimes stranded in the event of a sudden hailstorm or snowstorm or blizzard. In an effort to stay dehydrated, they tend to consume snow if water is not available. This could prove disastrous to them. Why? You may calculate the amount of heat energy that the human body will expend in consuming say 200 g of snow to quench the thirst (use Fig. 14.9 above). The quantity of heat expended by the body at 37°C will be large enough to put one's life in danger. Here are the calculations. Assume that the snow is at the temperature of −20°C.

Heat consumed by 200 g snow to heat from −20°C to 0°C

$$= 200 \times 1.184 \times 20 \text{ J}$$
$$= 4736 \text{ J} = 4.736 \text{ kJ}$$

Heat consumed by 200 g snow to heat from 0°C to water at 0°C

$$= \text{No. of moles of water} \times \text{Molar heat of fusion}$$
$$= \frac{200}{18} \times 6.01 \text{ kJ} = 66.778 \text{ kJ}$$

Total heat expended by the body to convert the snow to water at 0°C

$$= (4.736 + 66.778) \text{ kJ}$$
$$= 71.514 \text{ kJ}$$

This is a tremendous amount of energy. After losing this energy, the body temperature might fall drastically in further heating water at 0°C to a higher temperature. This could prove fatal. Hence, bikers are advised against doing this.



Fig. 14.10 *A scene of a blizzard*

Have you ever realised that steam is hotter than water at 100°C? People taking a steam bath could get steam burns if exposed to it for a longer period. Steam is more dangerous than just boiling water. For quantitative comparison of the damage done to the skin at body temperature of 37°C by boiling water at 100°C and steam respectively, you may again refer to Fig. 14.9.

The quantity of heat transferred by boiling water at 100°C to the skin at 37°C is given by the portion *AB* while the quantity of heat transferred by steam to the skin at 37°C is given by the portion (BC + AB). Evidently, heat transfer with steam is much more than that with boiling water.



Fig. 14.11 *Face burnt by steam*

14.9 PHASE DIAGRAM OF CARBON DIOXIDE SYSTEM

Phase diagram of the carbon dioxide system resembles that of the water system with some differences.

The phase diagram for the carbon dioxide system is shown in Fig. 14.12. It has three distinct areas in which carbon dioxide can exist either as ***solid, liquid*** or ***gas.***

1. Areas Area on the RHS of the curve *ABD* consists of vapour phase. Area above the curve *CBD* consists of the liquid phase while the area on the LHS of the curve *ABC* consists of the solid phase.

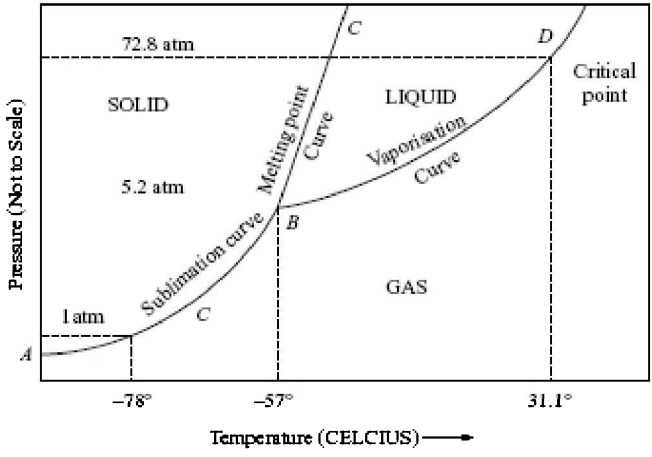


Fig. 14.12 *The phase diagram for carbon dioxide system*

2. Curves *AB* is the sublimation curve along which solid carbon dioxide is in equilibrium with the gas, *BD* is the vaporisation curve along which liquid carbon dioxide is in equilibrium with the gas. This curve ends at 31.1°C, the critical temperature of CO_2 and corresponding to a pressure of 72.8 atmospheres. The curve *BC* is the fusion curve along which solid and liquid carbon dioxide are in equilibrium with each other.

3. Point *B* is the triple point at which all the three phases of carbon dioxide co-exist in equilibrium with one another. The temperature of the system at this point is −57°C while the pressure is 5.2 atm. A slight variation in temperature or pressure at this point may result in the disappearance of one of the phases. For example, a slight increase in temperature will result in the disappearance of the solid phase and the equilibrium will shift along the curve BD. While the slight decrease in temperature will result in disappearance of liquid phase and the equilibrium will shift along the curve BA. Keeping the temperature constant, if the pressure is increased, the gaseous phase will disappear and the equilibrium will shift along the curve *BC*.

The phase diagram of carbon dioxide resembles that of water in showing three distinct areas for solid, liquid and gaseous phase. But it differs from the latter in several respects. In the first place, the melting point curve slopes away from the pressure axis. This indicates that increase of pressure raises the melting point of solid carbon dioxide.

The second difference is that solid carbon dioxide can exist in equilibrium with its liquid only at very high pressure equal to 5.2 atm. This is unlike the water system in which ice and water can exist in equilibrium even at a very low pressure equal to 4.58 mm of Hg (refer phase diagram of water).

The third difference is that the vapour pressure of solid carbon dioxide, even at extremely low temperature, is very high and many times higher than that of ice.

A significant feature of the carbon dioxide system is that even at atmospheric pressure, carbon dioxide gas can be directly solidified without the appearance of liquid phase merely on cooling to −78°C (Fig. 14.7). It is for this reason that solid carbon dioxide is commonly known as ***dry ice.***

Example 4 *Compare the phase diagrams of water and carbon dioxide.*

Solution: The phase diagram of water is unusual because the solid-liquid phase line has a negative slope, which means as the pressure increases, the melting point of ice decreases (refer to Fig. 14.13). As a result, ice can be liquefied within narrow temperature range by applying pressure.

In the phase diagram of carbon dioxide, the solid-liquid line has a positive slope. Thus, there is no liquid phase below 5.2 atm, only the solid and vapour phases exist under ordinary atmospheric condition. This is what makes dry ice "dry" at atmospheric conditions.

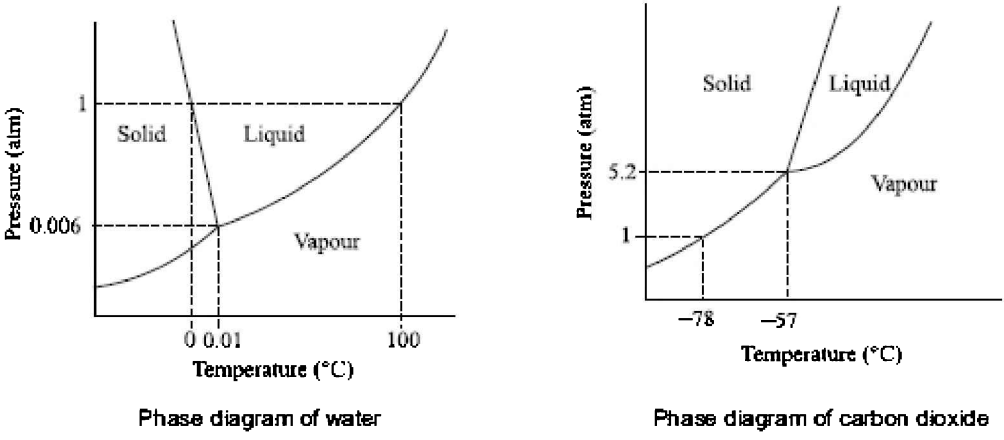


Fig. 14.13 *(a) Phase diagram of water (b) Phase diagram of carbon dioxide*

Example 5 *Explain with the help of phase diagram of carbon dioxide what happens when*

(a) We heat solid carbon dioxide initially at −100°C and 1 atm

(b) We increase the pressure of CO_2 at 25°C from 1 atm to 70 atm

Solution:

(a) On heating solid CO_2 initially at −100°C and 1 atm pressure, sublimation takes place when the temperature reaches −78°C (see Fig. 14.14).

(b) At 25°C, increasing the pressure from 1 atm to 70 atm condenses CO_2 to liquid state.

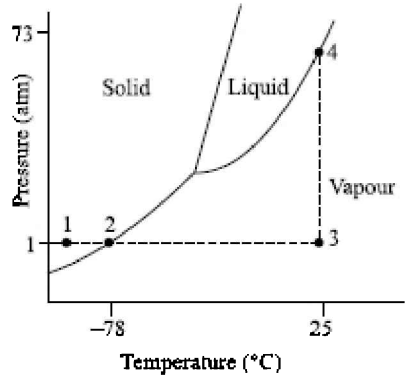


Fig. 14.14 *Phase diagram of carbon dioxide*

Example 6 *By using the following phase diagram (Fig. 14.15),*

(a) Determine the normal boiling point and melting point of the substance, and (b) determine the physical state of the substance at 2 atm pressure and 110°C.

Solution:

(a) In order to determine the normal boiling point and melting point, we shall draw a horizontal line corresponding to 1 atm pressure. The point where this line meets the solid-liquid curve is the melting point and the point where this line meets the liquid-vapour curve is the boiling point. We find that the normal melting and boiling points are 140°C and 205°C respectively (Fig. 14.16a).

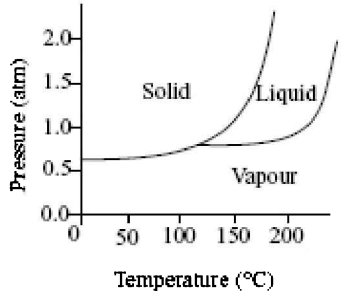


Fig. 14.15 *Phase diagram*

(b) In order to find the physical state of the substance at 2 atm pressure and 110°C, we draw a horizontal line at 2 atm and a vertical line at 110°C. The point where these horizontal and vertical lines meet lines in the region specified as solid. Therefore, physical state of the substance at 2 atm pressure and 110°C is solid (Fig. 14.16b)

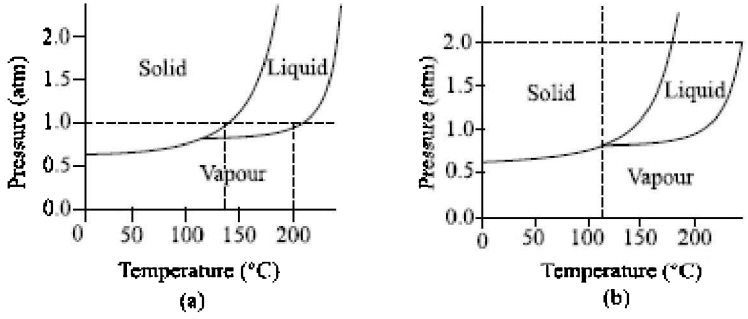


Fig. 14.16 *Phase diagram*

Example 7 *Sketch the phase diagram of a substance using the following data:*

Pressure	*Melting Point (°C)*	*Boiling Point (°C)*	*Sublimation Point (°C)*
0.5	-	-	*0*
1.0	*60*	*110*	-
1.5	*75*	*200*	-
2.0	*105*	*250*	-
2.5	*125*	*275*	-
3.0	*155*	*305*	-

The triple point is at 0.75 atm and 45°C.

Solution: A graph paper may be used to sketch the phase diagram. Take the pressure along *Y*-axis and temperature along *X*-axis. Mark the points corresponding to values of pressure and temperature. The following diagram (Fig. 14.17) is obtained.

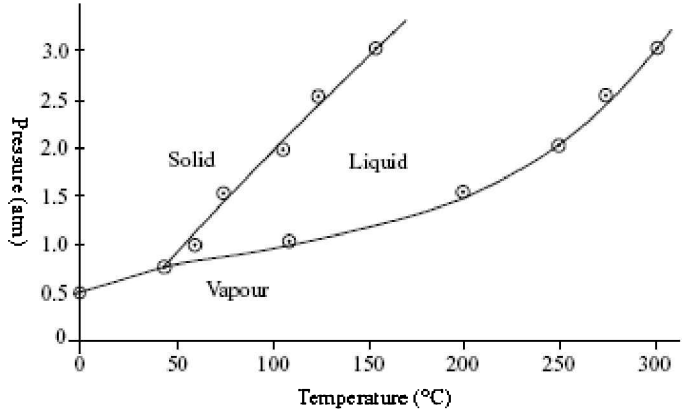


Fig. 14.17 *Phase diagram*

Polymorphism The existence of a given substance in more than one crystalline form with different physical properties is known as polymorphism. This phenomenon occurs in a number of elements and compounds. When it occurs in elements, it is referred to as allotropy.

Each polymorphic form constitutes a separate phase. The temperature at which one form changes into another, at a given pressure, is known as ***transition temperature.*** For example, rhombic sulphur when heated under a pressure of 1 atm, change into monoclinic sulphur at 95.6°C.

Similarly, monoclinic sulphur on cooling at a pressure of one atmosphere changes into rhombic sulphur at 95.6°C. Thus, 95.6°C is the transition temperature at which the two forms of sulphur (rhomic and monoclinic) change reversibly into each other.

14.10 PHASE DIAGRAM OF SULPHUR SYSTEM

It is a one-component system comprising ***four phases,*** viz. (a) rhomic sulphur, (b) monoclinic sulphur, (c) sulphur liquid, and (d) sulphur vapour. This is a typical example of a one-component system exhibiting solid-solid transformation.

Sulphur exists in two well-known crystalline forms, namely rhomic sulphur and monoclinic sulphur. The two forms are in equilibrium with each other at 95.5°C, which is called its ***transition temperature.*** It is defined as the ***"temperature at which one stable form of a solid is transformed into another stable solid form of it, without any change in temperature and pressure on the system being one atmosphere."***

Rhompic sulphur is stable below 95.5°C, whereas monoclinic sulphur is stable above this temperature.

According to phase-rule equation, all the four phases cannot co-exist in equilibrium. This is because on substituting $P = 4$, and $C = 1$ in the phase-rule equation, we get

$$F = C - P + 2$$
$$= 1 - 4 + 2 = -1$$

Thus, we get $F = -1$, which is meaningless. Hence, for a system of single component, it is not possible to have four phases together in equilibrium. However, three or fewer number of phases can exist together.

The phase diagram of the sulphur system is obtained experimentally by plotting pressure vs. temperature as shown in Fig. 14.18. The diagram consists of six stable curves (*BO*, *OA*, *AE*, *OC*, *AC* and *CF*) and four metastable curves (*OD*, *OG*, *AD* and *CD*). The curves divide the diagram into four areas, i.e. to the left of *BOCF*, below *BOAE*, to the right of *FCAE*and the one enclosed by *OCA*.

1. Areas The areas are bivariant, meaning that to locate any point in the areas, both temperature and pressure are to be specified. Each area represents the conditions for the stable existence of a single phase. In the areas, thus, there are two degrees of freedom, which also follows from the phase-rule equation, $F = C - P + 2$; putting the values $C = P = 1$, we get $F = 1 - 1 + 2 = 2$.

In the area to the left of *BOCF*, only S_R (rhomic sulphur) exists while in the area below *boae*, only S_V (sulphur vapour) exists; to the right of *fcae*, S_L (liquid sulphur) is present and in the region enclosed by *OCA*, S_M (monoclinic sulphur) exists.

2. Curves

(a) OB—Sublimation Curve of Rhombic Sulphur The phases present in equilibrium along this curve are S_R and S_V. The curve starts from the point *O*, the transition temperature of S_R to S_M and ends at *b* (50°C) below which vapour pressure of S_R cannot be measured. If heating is done rapidly, then it is possible to heat rhombic sulphur above the transition point along *OD*, the metastable curve. On slight disturbance it merges into the curve *OA*, which is the vapour-pressure curve of monoclinic sulphur.

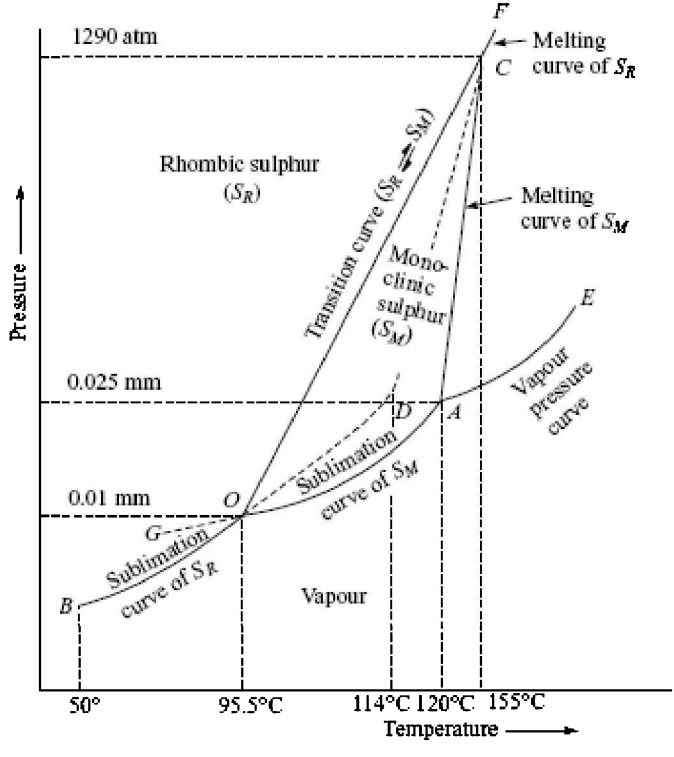


Fig. 14.18 *Phase diagram sulphur system*

(b) OA—Sublimation Curve of Monoclinic Sulphur The two phases present in equilibrium along the curve are S_M and S_V. The curve starts from the point *A*, melting point of S_M (120°C) and ends at *O*, the transition temperature of S_R (95.5°C).

Except at the point *O*, where three phases S_R, S_M and S_V are present in equilibrium, at any other point all along the curve only two phase S_V and S_M are in equilibrium. For a fixed value of temperature, pressure is automatically fixed. The degree of freedom, therefore, is one.

If the temperature of monoclinic sulphur is lowered then it would change into rhombic sulphur at 95.5°C, but it is possible to prevent this conversion by careful cooling. Then we will move along the curve *OG* which is a ***metastable vapour pressure curve of monoclinic sulphur.***

(c) AE—Vapour-Pressure Curve of Liquid Sulphur The two phases present in equilibrium along this curve are liquid sulphur, S_L, and vapour sulphur, S_V. The curve starts at A, the melting point of S_M, and ends at E, the critical point beyond which out of the two phases S_L and S_V only S_V (vapour sulphur phase) can exist. For any point on the curve, for a fixed value of pressure, the temperature has a fixed value. Therefore, the system also has one degree of freedom. The extended curve *AD* represents the metastable vaporisation curve of liquid sulphur.

(d) OC It is the transition curve and represents the equilibrium between rhombic and monoclinic sulphur and is obtained from the effect of pressure on the transition temperature of rhomic sulphur.

The slope of the curve *OC* is away from the vertical pressure axis, indicating that the transition point is raised by the rise of pressure. The curve ends at the point *C*, after which the monoclinic sulphur phase disappears.

(e) AC It is the ***transition curve*** and represents the equilibrium between monoclinic sulphur and liquid sulphur and results from the effect of pressure on the melting point of monoclinic sulphur. The curve is inclined away from the pressure axis showing that the melting point rises with the rise of pressure. The curve ends at the point *C*, after which monoclinic sulphur phase disappears.

(f) CD The curve represents the equilibrium between rhomic and liquid sulphur and the ***metastable melting point curve of rhombic sulphur.*** The curves *OC* and *AC* meet at *c*, at 155°C and 1290 atmospheres. It follows, therefore, that if liquid sulphur were cooled at a pressure higher than 1290 atmospheres then rhomic sulphur would crystallise at once, no monoclinic sulphur being formed. The curve passes through the point *C* and beyond this point, it becomes a stable melting point curve *CF* of rhomic sulphur.

3. Triple Points There are three stable triple points, viz *O*, *A* and *C*, in the phase diagram. At the point *O*, three phases in equilibrium are sulphur—rhombic, monoclinic and vapour. If one of the variables is changed, one of the three phases disappear. Similarly, *A* is also a triple point between mono-clinic, vapour and liquid sulphur. This point is again invariant. Further, lines *OC* and *AC* intersect at *C* to yield a three-phase equilibrium between rhombic, monoclinic and liquid sulphur. Since on changing one of the variables, either pressure or temperature, one of the phases disappears, therefore, the system at the triple point has no degree of freedom. We get the same result from phase rule equation:

$$F = C - P + 2$$
$$F = 1 - 3 + 2 = 0$$

D is a metastable triple point, the phases in equilibrium being S_R, S_L and S_V.

14.11 TWO-COMPONENT SYSTEMS

14.11.1 Applying Phase Rule To Two-Component Systems

A two-component system can be defined as one in which it is possible to express the composition of all the phases in terms of two substances. A two-component system may have as many as three degrees of freedom. This is because when $P = 1$ then

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

Thus, the system will have, besides temperature and pressure variables, ***one concentration variation for each phase present at the time of equilibrium.*** A three-dimensional model is required in which pressure, temperature and concentration could be plotted along the three axes at right angles to one another (Fig. 14.19). However, in actual practice, a simple plain diagram with two variables only is considered, the third variable is considered constant. In this way, use is made of the following three types of diagrams (Fig. 14.20)

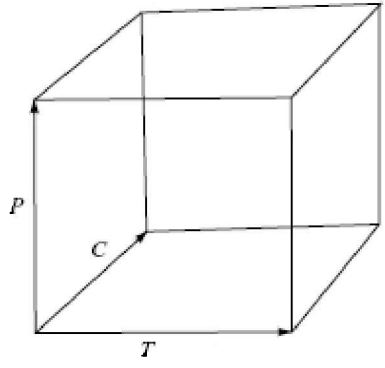


Fig. 14.19 *Space model for two-component system*

1. Pressure-temperature diagram
2. Composition-pressure diagram
3. Temperature-component diagram.

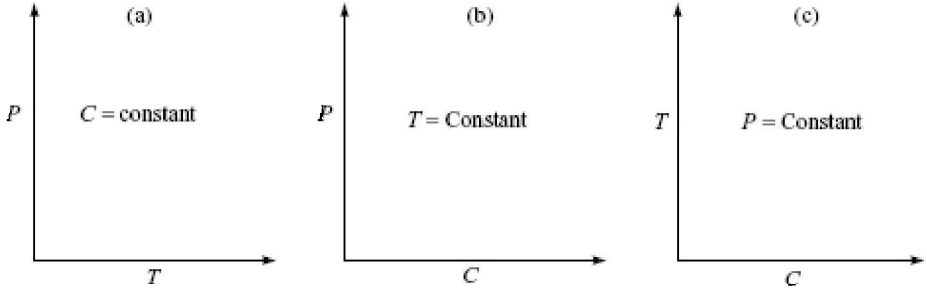


Fig. 14.20 *Two-dimensional diagram*

However, it is usually convenient to keep pressure constant at the atmospheric value and thus, a T–C diagram is often used. A diagram drawn for the constant value of temperature is called ***isothermal,*** while one obtained by keeping composition constant is called ***isoplethal*** diagram.

14.11.2 Reduced Phase Rule Equation

In case of systems consisting of only solid and liquid phases, small changes of pressure have very little effect on the systems. Such systems are called ***condensed systems.*** As the degree of freedom in such a case is reduced by one as pressure is taken as fixed at one atmosphere pressure, therefore, we can write a ***'reduced' phase-rule equation*** as

$$F = C - P + 1$$

'F' in the above equation represents the number of degrees of freedom which the system can possess in addition to the pressure.

14.12 TYPES OF TWO-COMPONENT SYSTEMS INVOLVING SOLID-LIQUID EQUILIBRIA

Broadly, there are three types of two-component systems involving solid-liquid equilibria:

Type I Those in which the two components do not react with each other but simply mix into each other in the molten state or in the solution. Examples of such systems are lead-silver system and KI–H_2O system.

Type II Those in which the components react to form a compound with congruent melting point. These are those systems in which the two pure components react to form a compound which is stable up to its melting point. At the melting point, it melts to give a liquid of the same composition as that of the solid compound. The compound formed is then said to have a congruent melting point.

For example, in the $FeCl_3$–H_2O system, each hydrate formed is stable up to the melting point and possesses a congruent melting point.

Type III Those in which the components react to form a compound with incongruent melting point. These are those two-component systems in which the compound formed does not remain stable up to the melting point. On heating, it starts decomposing before the melting point to give a new solid phase and a solution with composition different from that of the solid phase. When this happens, the compound is said to undergo a transition or peritectic reaction and is said to have an incongruent melting point. In general, a peritectic reaction may be represented by the equation,

$$C_2 \rightleftharpoons C_1 + \text{solution (or melt)},$$

C_2 represents the compound formed as a result of reaction between the two pure components and C_1 is the new compound (or a pure constituent) formed as a result of decomposition of the compound C_2 below its melting point. An example of this type of system is the Na_2SO_4–H_2O system in which the hydrates formed undergo peritectic reaction.

14.12.1 General Features of Phase Diagram of Two-Component System (Solids) Miscible in Liquid State

A number of mixtures of two components *A* and *B* of different compositions are prepared and their freezing points determined. We carry out the process in an open vessel in each case so that the pressure remains equal to the atmospheric pressure. These freezing points are then plotted against the compositions of the liquid mixtures. A phase diagram of the type shown in Fig. 14.21 is obtained.

The diagram consists of the curves *AC*, *BC*, the areas enclosed by *ADC*, *BCE*, areas above *ACB*, below *DCE* and the point *C*. Each of these is described below.

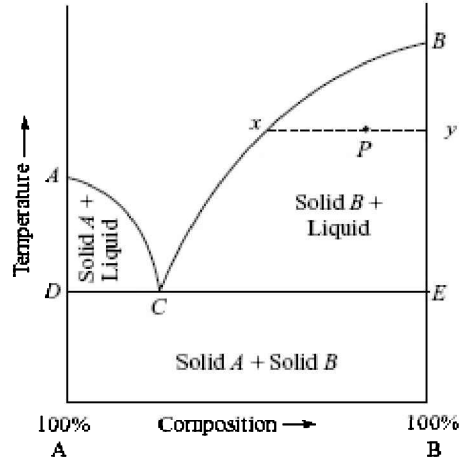


Fig. 14.21 *General shape of the phase diagram of two-component system miscible in liquid phase.*

1. Curves AC and BC The points *A* and *B* represent the freezing points of pure *A* and pure *B* respectively. The addition of *B* to *A* lowers the freezing point along the curve *AC*. Similarly, the addition of *A* to *B* lowers the freezing point along the curve *BC*. Thus, *AC* represents the freezing-point curve of *B* to which different amounts of *A* are being added. It is evident that if a liquid mixture rich in *A* (i.e. for any composition between *B* and *C*) is cooled, the solid *B* will separate out. Thus, the curves *AC* and *BC* represent the conditions of temperature at which the liquid mixture is in equilibrium with the solid *A* and the solid *B* respectively.

Ignoring the vapour phase, all along the curve *AC* or *BC* there are two phases in equilibrium (solid *A* + liquid along the curve *AC* and solid *B* + liquid along the curve *BC*), i.e. $P = 2$.

As $C = 2$

$\therefore$ $F = C - P + 1$ (reduced equation)

$= 2 - 2 + 1 = 1$

Thus, the condensed phase has one degree of freedom. This is otherwise also evident because the temperature or the composition of the liquid phase alone is sufficient to define the system completely.

2. Point C *C* is the meeting point for curves *AC* and *BC*. At this point, three phases are in equilibrium, viz. solid *A*, solid *B* and the liquid mixture, i.e. $P = 3$.

Hence, $F = C - P - 1 = 2 - 3 + 1 = 0$, i.e. the condensed system becomes invariant at the point C. Thus, there is only one temperature, at the atmospheric pressure, where the liquid phase can be in equilibrium with both the solids. The point C corresponds to a temperature below which any liquid mixture of A and B will freeze as a whole. The point C is, therefore, called ***eutectic point.*** The composition corresponding to C is called eutectic composition.

3. Areas

(a) Area above Curve ACB In this area, only liquid phase is present as the temperature is above the melting point of any mixture, i.e. $P = 1$. Hence,

$$F = C - P + 1 \text{ (reduced phase rule equation)}$$
$$= 2 - 1 + 1 = 2$$

Thus, there are two variables, i.e. the areas are bivariant. This means, to define the system completely, both temperature and composition need to be specified. Evidently, to define any point within the area, both the co-ordinates are required.

(b) Area Below DCE As DCE is passing through the eutectic point C, so in the area below DCE, only the solid phases, viz. pure A and pure B are present, i.e. $P = 2$. Hence,

$F = C - P + 1 = 2 - 2 + 1 = 1$, i.e. the condensed system is univariant. This is so because the composition of each phase is fixed (as each of them is a pure component), i.e. the composition is not variable. The only variable is the temperature.

(c) Areas Enclosed by ADC and BEC Each of these areas has two phases, being solid A + liquid in the area ADC and solid B + liquid in the area BEC. Thus, for each of these areas, the degree of freedom is one.

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

i.e. the condensed system is univariant.

The composition of the phases in the equilibrium at any point (say P) within these areas can be obtained by drawing a horizontal line passing through that particular point to find where it cuts AD or BE, to know the nature of solid and AC or BC to know the composition of the liquid. Any horizontal line like xy through the point P in these areas connects the compositions of the solid and the liquid phases in equilibrium and is called a ***tie line.*** (Fig. 14.21)

14.12.2 Cooling of Liquid Mixtures

Consider a system (Fig. 14.22) of composition represented by the line LS: L represents to system above its melting point so that it is the liquid phase, where S represents the same system completely in the solidified state. If the liquid L is cooled, no solid will separate out till the point P on the freezing-point curve BC is reached. At this temperature, the solid B will begin to separate out. The solidification results in the evolution of heat called heat of solidification. As a result, the rate of cooling will be slowed down up to the point Q. During cooling from P to Q, the composition of liquid phase will change from P to C along the curve PC. On reaching the eutectic point C, the second solid, viz., solid A will also begin to separate out and the temperature will remain constant till all the liquid has been solidified. According to phase rule, there is only one solid phase in a condensed system. Thus, eutectic point is indicated by complete break in the rate of cooling. The temperature will further fall, say from Q to S, only after the whole of the system has been solidified.

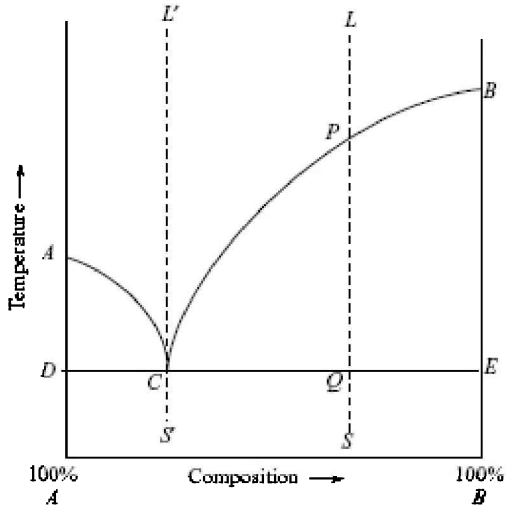


Fig. 14.22 *Cooling of liquid mixtures*

Starting from a liquid mixture (molten mixture) corresponding to the temperature and composition represented by the point L, if cooling is allowed to take place and temperature is plotted versus time, a curve of the type shown in Fig. 14.23 is obtained.

From *L* to *P*, the liquid cools rapidly. At *P*, the solid begins to separate out, heat is evolved and the rate of cooling becomes slow. Solid *B* keeps on separating out and the composition of the ***liquid phase keeps changing along the curve PQ.*** After reaching the point *Q'*, which corresponds to the eutectic point, the solid *A* also starts separating out and the temperature remains constant till the whole liquid solidifies at the point *Q*. Now further cooling results in the fall of temperature from *Q'* to *S*.

If the composition of the liquid mixture is exactly same as that of the eutectic, as shown by point *L'* in Fig. 14.24 then on cooling, the solid will separate only when the eutectic point is reached at *C*. The system will now solidify completely. The cooling curve will show only one break as shown in Fig. 14.24. The solid separates at the point *C* and is complete at the point *C"*. Further cooling results in the fall of temperature of the solid along *C" S"*.

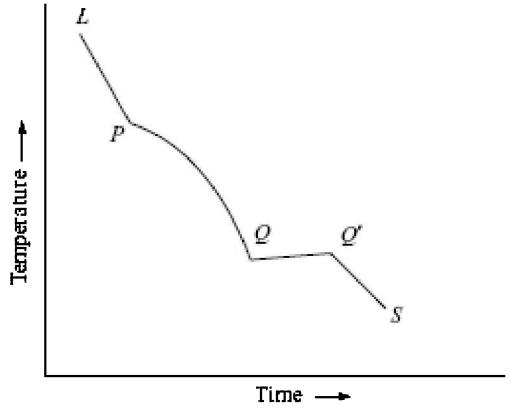


Fig. 14.23 *Cooling curve*

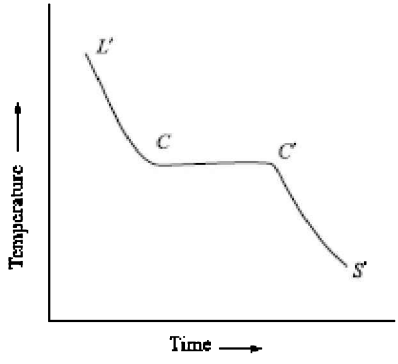


Fig. 14.24 *Cooling curve of eutectic mixtures*

14.13 EXPERIMENTAL DETERMINATION OF PHASE DIAGRAM OF TWO COMPONENT SYSTEMS

1. Cooling Curve Method (Thermal Analysis Method) This method is based on the principle illustrated in Fig. 14.22. A number of mixtures of the two components of different compositions are made. Each mixture is melted to form a homogeneous liquid and then allowed to cool. In this way, a cooling curve of the type shown in Fig. 14.23 is obtained for each of the mixtures. The point P corresponds to the freezing point and the point Q corresponds to the eutectic point for the composition taken. In this way, the freezing point and the eutectic points for the mixtures of different compositions are obtained. Freezing points are plotted versus composition to obtain the curves AC and BC, whereas plotting the eutectic temperatures versus composition, the line DCE is obtained. To complete the diagram, the freezing point of pure A and pure B are also determined by the cooling-curve method as a pure liquid solidifies at a constant temperature.

(a) Limitations of the Cooling Curve Method In case of some liquid mixtures, the separation of the solid does not occur readily and supercooling takes place. Thus, no break is observed at P. Instead, cooling continues beyond P along PP' and then the temperature rises suddenly and then follows the path RQ. The point P is then located by extrapolation of the curve QR as show in Fig. 14.25.

(b) Even if there is no Supercooling The temperature of arrest of the eutectic point is sometimes difficult to observe correctly as the mixture contains a large amount of the solid and the stirring becomes difficult.

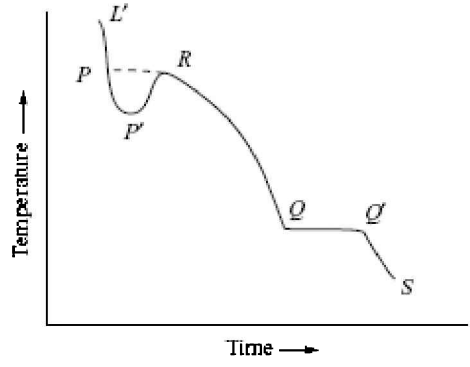


Fig. 14.25 Cooling curve with supercooling

2. Thaw-Melt Method This method employs heating the solid mixture of a known composition instead of cooling the liquid mixture. When a mixture of solids *A* and *B* corresponding to the composition *S* is heated slowly (Fig. 14.22), no change in composition takes place up to the eutectic point *Q*. On heating further, the liquid corresponding to the eutectic composition *C* begins to be formed. As the temperature is now raised from *Q* to *P*, the quantity of liquid increases and the composition changes from *C* to *P* (Fig. 14.22). At *P*, the last trace of the solid is about to disappear and above *P*, the system is completely liquid. The temperature corresponding to the point *Q* where the solid mixture just starts melting is called the thaw point and the temperature corresponding to the point *P* where the last trace of the solid melts is called the melting point.

Thus, the method requires preparing a number of solid mixtures of different compositions. To ensure mixing of the solids, the mixtures are prepared by melting, cooling and grinding. Each mixture is packed into a wide capillary tube and the thaw point and the melting point are determined by usual method. The plot of melting point versus compositions gives the curves *AC* and *BC* whereas the plots of thaw point versus compositions gives the line *DCE*.

14.14 STUDY OF SOME TWO-COMPONENT SYSTEMS

14.14.1 Phase Diagram Of Bismith-Cadmium System

This is an example of a two-component system which forms a simple eutectic. The various phases that may be present are (i) solid bismuth, (ii) solid cadmium, solution of bismuth in cadmium or vice versa in molten state, and (iv) vapour.

As small changes of pressure have negligible effect on this equilibrium, we can apply the reduced phase-rule equation,

$F' = C - P + 1$ when $F = 0$, $P = 3$ (as $C = 2$). Thus, The maximum number of phases (other than vapour) that can co-exist would be three.

Experimentally, a number mixtures of the two metals starting from 100% bismuth to 100% cadmium with intervals of 10% by mass are prepared in inert crucibles by heating them in an inert atmosphere in an electric furnace, and then studying their cooling curves. For each mixture, the temperature at which solidification starts and the temperature at which solidification is complete are recorded by inserting a thermocouple in a melt. These are then plotted on a temperature-composition diagram. The phase diagram thus obtained is shown in Fig. 14.26.

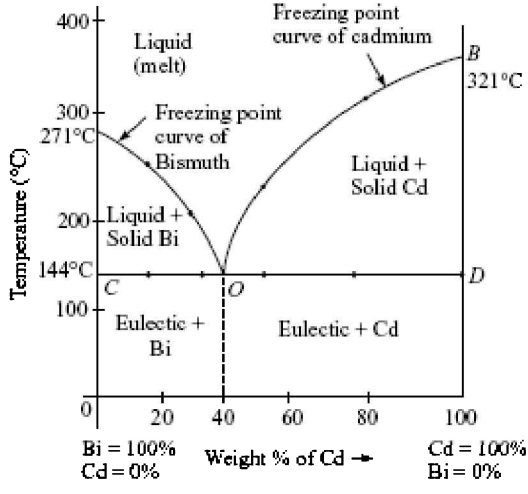


Fig. 14.26 *Phase diagram of Bi-Cd system*

The diagram consists of two curves *OA* and *OB* interacting at the point *O*. *O* is called the eutectic point. Significance of the curves and the point *O* is explained below.

(a) Curve AO It represents ***the freezing point curve of bismuth*** to which different amounts of cadmium are added. The point *A* represents the melting point or freezing point of pure bismuth (271°C). we find that the melting point (freezing point) of bismuth is lowered gradually by addition of cadmium into it. The added cadmium goes into the solution and the separation of bismuth occurs till the point *O* is reached. At this point, no more cadmium goes into solution as the solution becomes saturated with cadmium and hence, the melting point of bismuth does not fall further. Thus, the point *O* represents the composition with lowest melting point (144°C). Point *O* represents the eutectic point. Along the curve *AO*, two phases in equilibrium are solid bismuth and liquid melt (neglecting the vapour phase). Therefore, the system is univariant as shown below:

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

(b) Curve BO This is the ***freezing-point curve of cadmium*** to which different amounts of bismuth are added. The point *B* represents the melting point or freezing point of pure cadmium (321°C). We find that melting point of cadmium decreases as more and more of bismuth is added into it. The added bismuth goes into the solution and the separation of solid bismuth takes place. This continues till the point *O* is reached. At this point, no more bismuth goes into the solution and the solution is said to have become saturated with bismuth. Hence, the melting point does not fall any longer.

Along the curve, two phases, solid cadmium and liquid melt, are in equilibrium. Therefore,

$$F' = C - P + 1 = 2 - 2 + 1 = 1, \text{ i.e. the system is univariant.}$$

It may be noted that the points of curves *AO* and *BO* represent the initial freezing point while the points on the line *CD* represent the final freezing points. It may also be noted that the curve *AO* is not only the freezing point curve of bismuth but may also be considered as the ***solubility curve of cadmium.***

(c) Eutectic Point, O This is the point where the two curves *AO* and *BO* meet. At this point, solid bismuth and solid cadmium are in equilibrium with the melt, i.e. three phases are present.

Degree of freedom at the point O is zero.

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

The point O represents the lowest possible temperature (144°C) below which a liquid phase cannot exist and above which a liquid phase cannot be enriched in either component by freezing out the other component. Such a liquid mixture of two components which has the lowest freezing point compared to all other liquid mixtures is called ***eutectic mixture.*** This mixture freezes out completely at constant temperature and on freezing, gives the two components as solid phases in the same proportion in which they were present in the liquid phase. The temperature corresponding to the eutectic point O is called the ***eutectic temperature.*** This is always lower than the melting points of either component. In this system, eutectic mixture (containing about 40% Cd and 60% Bi by mass) melts at 144°C, which is lower than the melting point of bismuth (271°C) and that of cadmium (321°C).

Note: *Eutectic* means *melting readily* (Greek word).

14.14.2 PHASE DIAGRAM OF LEAD-SILVER SYSTEM

The various phases possible are (i) solid lead, (ii) solid silver, (iii) solution of lead and silver in molten state, and (iv) vapour.

Since small changes of pressure have negligible effect on the equilibrium existing between lead and silver in solid state or in molten state, we can use the ***reduced phase rule equation,*** $F' = C - P + 1$. According to this equation, when $F = 0$, P will be 3. Thus, the maximum number of phases (other than vapour) that can co-exist would be there.

The phase diagram of the lead-silver system is shown in Fig. 14.27. The diagram is drawn taking temperature and composition along the axes. The equilibrium diagram consists of two curves OA and OB, intersecting at the point O.

Various curves and points are described as under:

(a) Curve OA This is the ***freezing point curve of silver*** to which successive small quantities of lead are added. The point A indicates the melting point of pure silver (961°C). It is found that the melting point of silver is lowered gradually by the addition of lead into it. All along this curve, the added lead goes into the solution and the separation of silver occurs when the point O is reached. At this point, no more lead goes into the solution as the solution becomes saturated with respect to lead and hence, the melting point of silver does not fall any longer. Thus, the point O represents the lowest possible temperature (303°C) in the system that corresponds to fixed composition, viz. 2.4% Ag and 97.6% Pb. The point O is called the ***eutectic point.***

All along the curve AO, two phases, solid silver and liquid (melt), are present in equilibrium neglecting the vapour phase. Therefore, the system is univariant as shown by the following equation:

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

(b) Curve BO This is the ***freezing point curve of lead*** to which successive small amounts of silver are added. The point B represents the melting point of pure lead (327°C). It is seen that the addition of silver to lead lowers the melting point of lead. All along this curve, the silver which is added goes into the solution while the separation of lead takes place. This state of affairs continues till the point O is reached. At this point, no more silver goes into the solution and the solution becomes saturated with respect to silver. Hence, the melting point of lead does not fall any longer.

All along this curve, two phases, solid lead and liquid (melt), are present in equilibrium. Therefore, as before

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$ i.e., the system is univariant.

(c) Eutectic Point, O This is the point where two curves *AO* and *BO* meet. At this point, solid lead and solid silver are in equilibrium with the fused mass, i.e., three phases are present. Therefore, there are no degrees of freedom, as according to reduced phase rule equation.

$$F' = C - P + 1$$
$$= 2 - 3 + 1 = 0$$

The point *O* represents the lowest possible temperature (303°C) below which a liquid phase cannot exist and above which the liquid phase cannot be enriched in either component by freezing out the other component. ***Such a liquid mixture of two components—Ag and Pb—which has the lowest freezing point compared to all other liquid mixtures is called eutectic mixture*** (eutectic means melting easily). This mixture freezes out completely at a constant temperature and on freezing gives the two components as solid phases in the same proportions in which they are present in the liquid phase. The temperature corresponding to the eutectic point *O* is called the ***eutectic temperature.*** This is always lower than the melting points of the components constituting the eutectic mixture. For example, in the above system, we see that the alloy containing 2.6% of silver and 97.4% lead melts at 303°C, a temperature lower than the melting point of Ag (961°C) and that of Pb (327°C).

Pattinson's Process for Desilverisation of Lead Galena (PbS, an ore of lead) is usually associated with silver. When galena is processed for the extraction of lead, some traces of silver pass into it, because silver is soluble in lead to some extent. The lead thus obtained is known as argentiferous lead. The desilverisation of lead is carried out which can be easily understood from the phase diagram of lead-silver system, shown in Fig. 14.27.

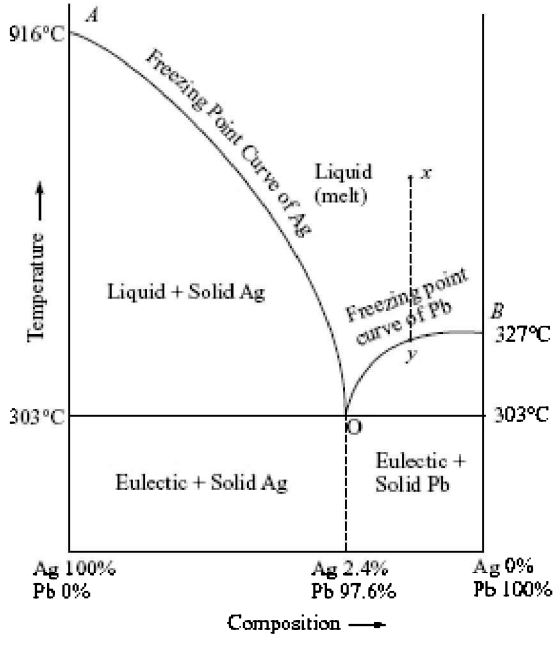


Fig. 14.27 *Lead-silver system.*

The argentiferous lead containing a small percentage of silver is first of all heated to a temperature well above its melting point so that the system consists only of liquid phase represented by the point *x* in Fig. 14.27. It is then allowed to cool gradually along the line *xy*

without any change in concentration till the point *y* is reached. When this point is reached, lead starts separating and the solution will contain progressively increasing amounts of silver. Further cooling shifts the system along the line *y O*. Lead continues to separate out (which can be removed with the help of ladles/perforated spoons) and the melt continues to be richer and richer in silver, till the point *O* is reached where an alloy containing about 2.4% of silver is obtained.

The above principle is employed in Pattinson's process which is used for increasing the relative proportions of silver in the alloy. The relative increase in the amount of solid lead that separates out and in the increase in the proportion of silver in the melt on cooling is shown in Fig. 14.28.

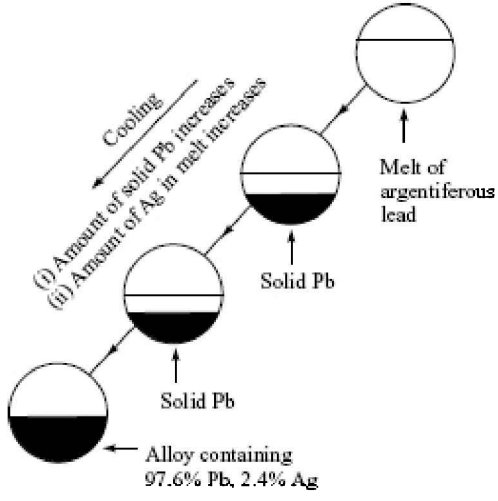


Fig. 14.28 *Cooling the melt of argentiferous lead.*

14.14.3 PHASE DIAGRAM OF KI-H_2O SYSTEM

The phase diagram of KI-H_2O system in shown in Fig. 14.29. Since, KI does not form hydrates, the only phases that are possible are (i) solid KI, (ii) ice, (iii) solution of KI in water, and (iv) vapour.

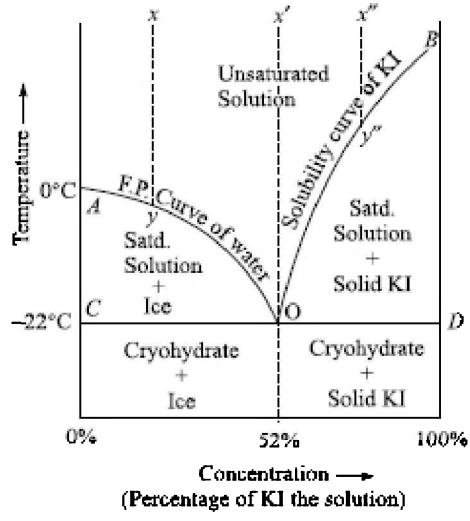


Fig. 14.29 *KI-$H_2$0 system*

The diagram (Fig. 14.29) consists of the curves *AO*, *BO*, the point *O* and the various areas above and below the curves *AO* and BO, as described below:

1. Curve

(a) Curve AO This curve represents ***the freezing point curve of water to which successive quantities of potassium iodide are added*** or in other words, the curve *AO* shows the effect of the addition of potassium iodide on the freezing point of water (or m. pt. of ice) under normal conditions. At this point, three phases—ice, water liquid and vapours—are in equilibrium. It is observed that by gradual addition of potassium iodide to it, the freezing point of water is lowered and the curve *AO* bends downwards. This however does not go indefinitely. As soon as the solution is saturated with respect to potassium iodide, the lowest temperature is reached at the point *O*, then further addition of KI will not produce further lowering in the freezing point of water.

The point '*O*' corresponding to concentration of 52% potassium iodide represents the lowest temperature that can be attained in this system. This eutectic temperature in this case is called ***cryohydric point*** and the eutectic itself is called a *cryohydrate*.

All along the curve *OA*, two phases, namely solution and ice, are in equilibrium (neglecting the vapour phase). Therefore, the system is univariant as shown by reduced phase-rule equation:

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

(b) Curve OB This curve is the ***solubility curve of potassium iodide in water at different temperatures.*** It represents the effect of temperature on the solubility of solid potassium iodide. It is observed that solubility of potassium iodide increases with the rise of temperature and is maximum at the point B, the boiling point of the saturated solution. However, the curve comes to an end before it can touch the 100% potassium iodide axis. Conversely, if the standard solution of potassium iodide in water is cooled, potassium iodide separates out and the solution becomes dilute and the curve *BO* is followed till the point *O* is reached. Here, the solution freezes as a whole with a fixed composition.

All along the curve *OB*, there are two phases, solid KI and solution, in equilibrium and being

a two-component system, the number of degrees of freedom according to reduced phase-rule equation would be

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

2. Cryohydric Point, O It is the point where the two curves *AO* and *BO* intersect. Here, three phases—ice, solid salt, and solution—are in equilibrium. If the vapour phase is not neglected then the fourth phase is also present. Point *O* is, therefore, called a quadruple point. It we apply the original phase rule equation, we find that the system is invariant, i.e.

$$F' = C - P + 2 = 2 - 4 + 2 = 0$$

Therefore, any change in temperature or composition will cause one of the phases to disappear. The point *O* corresponds to a definite temperature (−22°C) and composition (52% KI and 48% ice).

Effect of Cooling Potassium Iodide Solution The solution phase exists in the area above *AOB* (Fig. 14.29. Let the solution represented by the point *x* be allowed to cool gradually along the line *XY* without any change in composition till the point *Y* is reached. As soon as this point is reached, ice starts separating and on further cooling, the solution continues becoming more and more concentrated till the cryohydric point *O* is reached where the solid KI also appears. Similarly, if a solution of composition *x"* lying on the right hand of point *O* is cooled then KI will begin to separate as soon as the point *Y"* is reached. The composition will change with temperature along *y"O* and more and more of KI will continue to separate out until the point *O* is reached. Ultimately, as before, the whole of the mixture will freeze to give a eutectic mixture.

Now consider a solution of composition represented by the point *x'* lying vertically above the cryohyric point *O*. When such a solution is allowed to cool gradually along the line *x'O* without any change in composition, the solution will solidify as a whole, i.e., on reaching the point O, both ice and KI start separating out simultaneously.

Hence, we conclude that all solutions on cooling show no further change in temperature at the eutectic point *O*. Moreover, on cooling a solution of eutectic composition, the solution freezes at the eutectic temperature without any change in composition.

14.15 FREEZING MIXTURES

A good freezing mixture is the one which satisfies the following conditions:

1. ***It should have low cryohydric temperature.*** This condition is fulfilled by having a salt which is highly soluble.
2. The ***heat of solution of the salt should be high.*** This condition is satisfied by salts whose solubility rapidly increases on increasing the temperature.
3. ***The components should be such that an intimate mixture can be obtained from them.***
4. ***The material should be cheap.***

In actual practice, the common freezing mixture is made from ice and common salt (sodium chloride). Although the common salt is very cheap, it is not a good salt to use because the heat of solution of this salt is very low and heat absorbed is almost due to the heat of fusion of ice. Calcium chloride hexa-hydrate and ice form a good freezing mixture because this has a low cryohydric point and high heat of solution.

For attaining very low temperatures (−50 to −70°C), ***acetone-dry ice mixture*** is quite often used. Acetone is taken in a Dewar or insulated flask and dry ice is added to it till the lowest temperature is attained.

14.16 PHASE DIAGRAM OF MAGNESIUM-ZINC SYSTEM

This is a two-component system in which the compound formation takes place with a congruent melting point. This system involves the formation of an intermetallic compound $MgZn_2$. It has four phases—solid magnesium, solid zinc, solid $MgZn_2$ and the liquid solution of Mg and Zn.

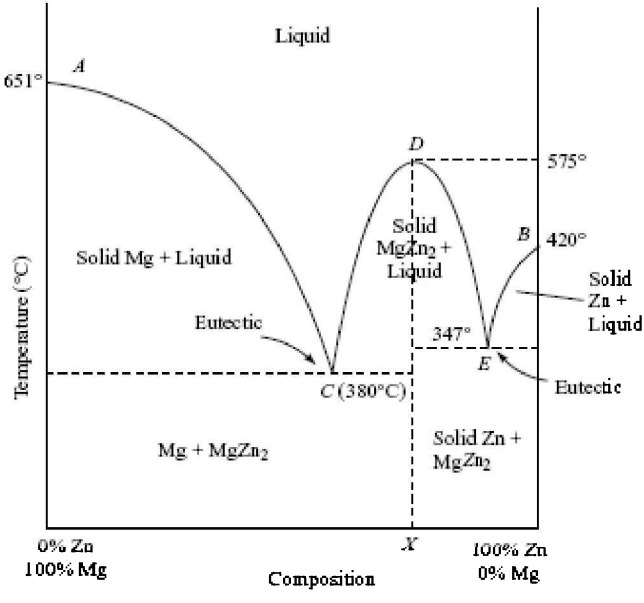


Fig. 14.30 *Phase diagram of magnesium-zinc system*

The complete phase for the magnesium-zinc system is shown in Fig. 14.30. It appears to be made of two simple eutectic diagrams. The one toward the left represents the eutectic system Mg-$MgZn_2$, while the one to the right is the system Zn-$MgZn_2$.

1. Curves AC, CDE and BE *AC* is the freezing-point curve of magnesium, *BE* is the freezing-point curve of zinc, and *CDE* is that of the compound $MgZn_2$.

The curve *AC* shows that the melting point of magnesium is 651°C. It is lowered on the addition of zinc. This continues until the point *C* is reached. Here, a new phase, solid $MgZn_2$, appears.

The curve *CD* shows the increase of concentration of zinc in the melt with rise of the same, i.e., $MgZn_2$. The point D, therefore represents the melting point of $MgZn_2$ (575°C). The curve *DE* now shows the lowering of the melting point with the addition of zinc until the lowest point is attained. Here, solid zinc appears.

The curve *BE* exhibits that the melting point of zinc (420°C) falls with the addition of magnesium until the point *E* is reached.

Along the freezing point curve *AC*, *CDE* and BE, there are two phases in equilibrium, viz., one solid phase (Mg, Zn, or $MgZn_2$) and the other liquid phase. Applying the reduced phase-rule equation, and substituting values, we get the value of *F* as 1.

$$F' = C - P + 1 = 2 - 2 + 1 = 1$$

This shows that the systems Mg/liquid, Zn/liquid, and $MgZn_2$/liquid are all monovariant having degree of freedom as one.

2. Eutectic Points C and E There are two eutectic points in the phase diagram. The systems at the points *C* and *E* have two components and three phases in equilibrium.

Point	*Phase Present*
C	Solid Mg, solid $MgZn_2$, Liquid
E	Solid Zn, solid $MgZn_2$, Liquid

These systems are, therefore, non-variant.

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

3. Congruent Melting Point The composition of the compound $MgZn_2$ and the melt at *D* is identical. The corresponding temperature is the congruent melting point of the compound. Here, the system has two phases, viz., the solid compound and the melt. Both these can be represented by one component ($MgZn_2$). Therefore, the system *D* is non-variant, as per the reduced phase-rule equation.

$$F = C - P + 1 = 1 - 2 + 1 = 0$$

4. The Areas The area above the curves *AC*, *CDE* and *BE* represents the solution of magnesium and zinc (the melt). The single-phase system at any point in this area is bivariant. The phases present in the other regions of the phase diagram have been labelled in Fig. 14.30.

14.17 PHASE DIAGRAM OF FERRIC CHLORIDE-WATER SYSTEMS

This is a two-component system with congruent melting points. In this system, the two components, namely ferric chloride and water react to form four stable hydrates, represented by the formulae $Fe_2Cl_6 \cdot 12H_2O$, $Fe_2Cl_6 \cdot 7H_2O$, $Fe_2Cl_6 \cdot 5H_2O$ and $Fe_2Cl_6 \cdot 4H_2O$. The double formula is used for ferric chloride in order to avoid writing of factional number of water molecules of crystallisation. Each hydrate possesses a congruent melting point, i.e. is stable up to the melting point and melts at the melting point to give liquid of the same composition as that of the solid compound or in other words, at this temperature, the saturated solution of hydrate has the same composition as the solid phase. Besides the above four phases, there are two more solid phases, namely anhydrous Fe_2Cl_6 and ice, one liquid phase, viz. solution, and one gaseous phase, viz. vapour. Thus, in all, there are ***eight*** possible phases. The different phases existing in equilibrium under different conditions of temperatures and compositions are shown in the phase diagram given in Fig. 14.31 corresponding to the congruent melting point of each hydrate, a maximum is obtained in curve, as shown in figure.

The various curves and points in the above diagram are explained as under:

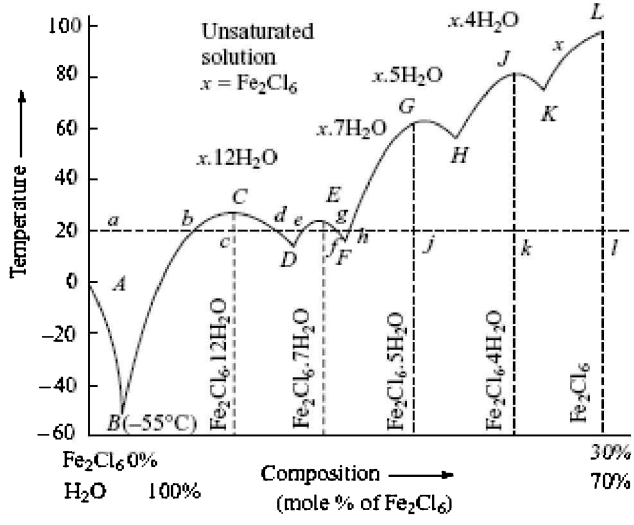


Fig. 14.31 *$FeCl_3$ – H_2O system*

Note: The points corresponding to capital letters *A, B, C,…* lie on the curve while the points corresponding to small letters lie on the dotted horizontal line.

(a) Curve AB and Point B Point *A* represents the freezing point of water. ***Curve AB represents the freezing curve of water to which increasing amounts of $FeCl_3$ have been added.*** When the point *B* is reached, the solution is saturated with the hydrate $Fe_2Cl_6 \cdot 12H_2O$ which then starts separating along with the ice. Thus, *B* is a ***cryohydric point*** where the phases in equilibrium are ice, solid $Fe_2Cl_6 \cdot 12H_2O$, saturated solution and vapour, i.e. there are 4 phases in equilibrium. Hence, the point *B* is a ***quadruple point.*** The degree of freedom can be calculated as $F = C - P + 2 = 2 - 4 + 2 = 0$, i.e. the system is ***invariant.*** Point *B* is a ***eutectic point.***

(b) Curve BC and Point C On adding more of $FeCl_3$, the ice phase disappears and now three phases in equilibrium, viz. solid $Fe_2Cl_6 \cdot 12H_2O$, saturated solution and vapour. Hence, $F = C-P + 2 = 2-3 + 2 = 1$, i.e. the system becomes univariant. The equilibrium is represented by the curve BC. Thus, the curve *bc* represents the solubility curve of $Fe_2Cl_6 \cdot 12H_2O$. At the point *C* (corresponding to 37°C), the saturated solution has the same composition as that of the solid $Fe_2Cl_6 \cdot 12H_2O$. The point *C* thus represents a ***congruent melting point.***

(c) Curve CD and Point D Further addition of $FeCl_3$, depresses the melting point of $Fe_2Cl_6 \cdot 12H_2O$ and the curve *CD* is followed. Thus, the curve *CD* represents the ***melting curve of*** $Fe_2Cl_6 \cdot 12H_2O$. At the point D, a new solid phase, viz. $Fe_2Cl_6 \cdot 7H_2O$, starts separating out. Hence, at the point D, again there are four phases in equilibrium, namely $Fe_2Cl_6 \cdot 12H_2O$, $Fe_2Cl_6 \cdot 7H_2O$, saturated solution and vapour, i.e., the point *d* is a ***quadruple point*** and is ***invariant.*** Point *d* is in fact a ***eutectic point*** or a ***transition point*** representing the transition.

$$Fe_2Cl_6 \cdot 12H_2O \rightleftharpoons Fe_2Cl_6 \cdot 7H_2O$$

(d) Curve DE and Point E Like the curve *BC*, the curve *DE* is the solubility curve of $Fe_2Cl_6 \cdot 7H_2O$ and point *E* is the congruent melting point of $Fe_2Cl_6 \cdot 7H_2O$.

(e) Curve EF and Point F Like the curve *CD*, the curve *EF* is the melting curve of $Fe_2Cl_6 \cdot 7H_2O$. At the point *F*, a new solid, viz. $Fe_2Cl_6 \cdot 5H_2O$, appears. The point *F* thus, a ***quadruple point,*** the four phases in equilibrium being $Fe_2Cl_6 \cdot 7H_2O$, $FeCl_6 \cdot 5H_2O$, saturated solution and vapour. Point *F* is another ***transition point,*** representing the change.

$$Fe_2Cl_6 \cdot 7H_2O \rightleftharpoons Fe_2Cl_6 \cdot 5H_2O$$

(f) Curve FG and Point G Curve *FG* is obviously the solubility curve of $Fe_2Cl_6 \cdot 5H_2O$ and the point *G* is the congruent melting point of $Fe_2Cl_6 \cdot 5H_2O$

(g) Curve GH and Point H Curve *GH* is the melting curve of $Fe_2Cl_6 \cdot 5H_2O$ and *H* is a transition point (quadruple point) where the new solid phase making appearance is $Fe_2Cl_6 \cdot 4H_2O$ and *H* is a transition point.

(h) Curve HJ and Point J Curve *HJ* is the solubility curve of $Fe_2Cl_6 \cdot 4H_2O$ and *J* is the ***congruent melting point*** of $FeCl_6 \cdot 4H_2O$.

(i) Curve JK and Point K Curve *JK* is the melting curve of $Fe_2Cl_6 \cdot 4H_2O$ and at point *K*, the anhydrous Fe_2Cl_6 starts separating, so that point *k* is also a ***quadruple point*** as well as the ***transition point.***

(j) Curve KL It is simply the ***solubility curve of anhydrous*** Fe_2Cl_6.

Isothermal Evaporation of an Unsaturated Solution of Ferric Chloride

Using the phase diagram of $FeCl_3$–H_2O system Fig. 14.31, the behaviour on evaporation of an unsaturated ferric chloride solution at constant temperature can be explained. Suppose an unsaturated solution at temperature between the temperature of points *E* and *F* (say at 31°C) is evaporated at constant temperature. Suppose such a solution is represented initially by the point a. As the solution is heated, water evaporates off and the horizontal path ***al*** is followed. The various changes occurring on the way are as follows:

1. The concentration of the solution increases till the point *b*, where the solid $Fe_2Cl_6 \cdot 12H_2O$ begins to separate out.
2. Heating beyond the point *b*, causes more and more water to evaporate off and more and more of the hydrate $Fe_2Cl_6 \cdot 12H_2O$ separates out till point *C* where there is only solid $Fe_2Cl_6 \cdot 12H_2O$ and no water at all.
3. Heating beyond the point *C*, causes the water to come out of the hydrate $Fe_2Cl_6 \cdot 7H_2O$. The latter keeps on dissolving into the former till a solution of composition corresponding to point *d* is obtained.
4. Continued evaporation leads to the point *e* where solid $Fe_2Cl_6 \cdot 7H_2O$ starts separating out then to the point *F* where there is only solid $Fe_2Cl_6 \cdot 7H_2O$ which then begins to lose water and form solution till a solution having composition corresponding to point *g* is obtained.
5. At *h*, solid $Fe_2Cl_6 \cdot 5H_2O$ starts separating out till the point J, where there is only solid

$Fe_2Cl_6 \cdot 5H_2O$.

6. Beyond the point *j*, no solution is obtained because the point *j* lies at a temperature below that of the unsaturated solution. Evaporation beyond the point *j* results in the formation of next lower hydrate, viz. $Fe_2Cl_6 \cdot 4H_2O$. Thus, all along the path *jk* there are $Fe_2Cl_6 \cdot 5H_2O$ and $Fe_2Cl_6 \cdot 4H_2O$ in equilibrium. At the point *k*, there is only $Fe_2Cl_6 \cdot 4H_2O$.
7. Heating beyond the point *k* leads to a gradual formation of anhydrous salt which will ultimately be the only residue.

14.18 PHASE DIAGRAM OF NA_2SO_4 – H_2O SYSTEM

This is an example of a two-component system with incongruent melting point. Various phases present in the system are (i) solid $Na_2SO_4 \cdot 10H_2O$, (ii) solid $Na_2SO_4 \cdot 7H_2O$, (iii) solid Na_2SO_4 (rhombic), (iv) solid Na_2SO_4 (monoclinic), (v) ice, (vi) solution in water, and (vii) water vapour. The equilibrium diagram obtained between composition and temperature is shown in Fig. 14.32.

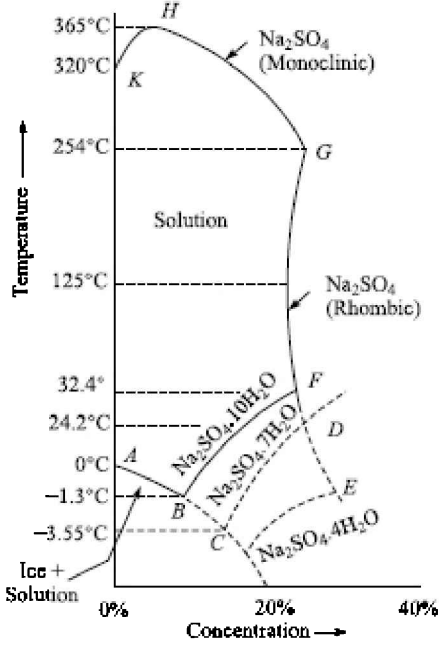


Fig. 14.32 *Na_2SO_4–H_2O system*

The diagram consists of the curves *AB, BC, BF, CD, FD, FG* and *GH:* triple point *A* and quadruple points *B, C, D, F* and *G*. However, in the discussion of these curves and points given below, the vapour phase has been taken into consideration.

I. Curve AB and Point B It is the freezing-point curve or the curve showing the composition of solutions in equilibrium with ice at different temperatures. At the point *A*, ice is in equilibrium with water and vapour at 0°C. *A* is, therefore, a triple point. On adding anhydrous sodium

sulphate, the temperature falls as shown by the freezing-point curve *AB*. All along the curve *AB*, we have three phases, namely ice, solution and vapour in equilibrium. Hence, the curve *AB* represents a univariant system.

$$F = C - P + 2$$
$$= 2 - 3 + 2 = 1$$

At the point *B* (−1.3°C), the fourth phase, namely sodium sulphate decahydrate, also appears, so that the system is now invariant:

$$F = C - P + 2 = 2 - 4 + 2 = 0$$

The point *B* is, therefore, a stable quadruple point.

2. Curve BC and Point C Under certain careful conditions, it is possible to travel along the curve *BC* in which case decahydrate fails to appear at *B*. At the point *C*, sodium sulphate heptahydrate separates out. The curve *BC* is, therefore, a metastable curve and the point *C* is a metastable quadruple point, the four phases co-existing in metastable equilibrium at this point *C* are ice, heptahydrate, solution and vapour.

3. Curve CD and Point D If the temperature is raised and more of anhydrous sodium sulphate is added, ice phase disappears as we travel along the curve *CD*. The curve *CD* represents the metastable solubility curve of sodium sulphate heptahydrate. All along this curve, three phases, viz., heptahydrate, solution and vapour are present in equilibrium. Hence, the curve *CD* represents a univariant system as per phase rule equation.

$$F = C - P + 2$$
$$= 2 - 3 + 2 = 1$$

At the point *D*, the fourth phase (anhydrous sodium sulphate) makes its appearance. ***Point D,*** therefore, represents a ***second metastable quadruple point.*** By lowering the temperature, it is theoretically possible to reach point *E*, at which sodium sulphate tetrahydrate would separate out. Practically, this has not been possible.

4. Curve BF and Point F It is the stable solubility curve of sodium sulphate decahydrate. All along this curve, three phases, namely sodium sulphate decahydrate, solution and vapour co-exist. This represents a stable univariant system, however only up to the point *F* (32.4°C). At the point *F*, rhombic form of the salt appears as one of the solid phases. At this point, all the four phases—decahydrate anhydrous salt, solution and vapour are in equilibrium. Point *F* is thus a stable quadruple point.

Point *F* is also called ***transition point*** because decahydrate changes into a solid anhydrous salt (rhomic). The water lost by the decahydrate is taken up by the solution and as a result, at this point the composition of solid phase and liquid phase becomes different. The point *F* is, therefore, also said to represent incongruent melting point.

5. Curve FG and Point G It is the solubility curve for anhydrous rhombic sodium sulphate. This curve is obtained by warming decahydrate. Shape of the curve shows that the solubility of rhombic sodium sulphate decreases up to 125°C, after which it again rises up to the quadruple point *G* (254°), the pressure at this point being 27.5 atmospheres. At this point transition of rhombic to monoclinic sodium sulphate takes place. So, point *G* is another stable quadruple point, the four phases co-existing in equilibrium at this point are rhombic sodium sulphate, monoclinic sodium sulphate, solution and vapour. This point is different from the previous quadruple points in the sense that there are no water molecules present in the two solid phases. It is also a transition point.

6. Curve GH It is the solubility curve of monoclinic sodium sulphate. It is clear from the graph

that its solubility steadily falls with the rise of temperature and finally the curve ends at *H*, the critical temperature (365°C) at which the solution and vapour phase merge into each other, the solubility there by reducing to zero.

7. Curve HK It shows the solubility of anhydrous sodium sulphate in water vapour, the two curves *GH* and *HK* being continuous.

14.19 SODIUM CHLORIDE-WATER SYSTEM

This is a system with an incongruent melting point. Sodium chloride reacts with water to form the dihydrate $NaCl \cdot 2H_2O$ which is not stable up to the melting point and starts decomposing above 0.15°C, according to the equation,

$$NaCl \cdot 2H_2O \rightleftharpoons NaCl + \text{Saturated solution}$$

Hence, this temperature (viz. 0.15°C) is called the incongruent melting point and represents the transition point for the above decomposition (See Fig. 14.33)

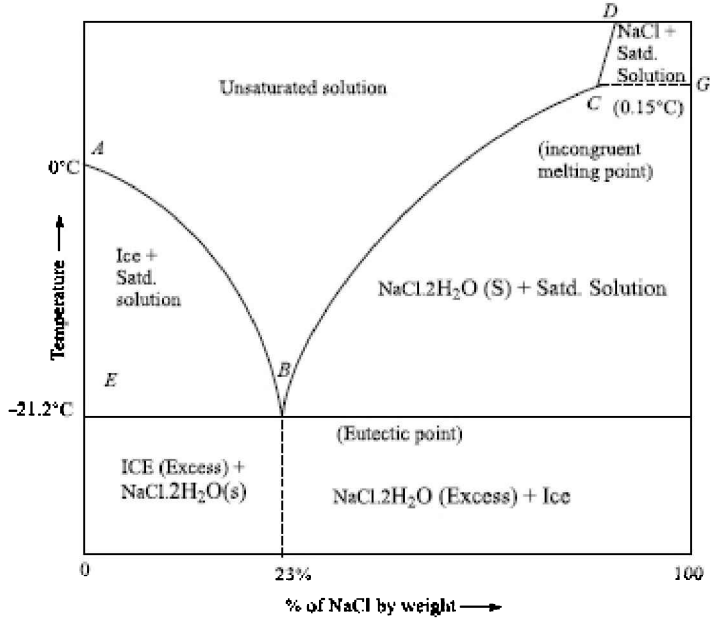


Fig. 14.33 *Phase diagram of NaCl-H_2O system*

The different possible phases which exist in this system are NaCl(s), $NaCl \cdot 2H_2O$(s), ice(s) and solution. The phase diagram showing the phases that exist under different conditions are shown in Fig. 14.33. Vapour phase has not been taken into consideration here.

The different curves, points and areas of this phase diagram are briefly explained below.

1. Curve AB and Point B The point *A* represents the freezing point of water, i.e. 0°C at one atmospheric pressure. The curve *AB* represents the freezing-point curve of water to which

increasing amounts of NaCl have been added. On adding more and more of NaCl to water, freezing point decreases along the curve *AB*. The NaCl added goes into the solution and ice keeps on separating till the point *B* is reached. Along the curve *AB*, the two phases in equilibrium are ice and solution. Applying reduced phase-rule equation, we get,

$$F' = C - P + 1 = 2 - 2 + 1 = 1 \text{ i.e., it is univariant.}$$

The point *B* corresponds to a temperature of −21.2°C and has 23% NaCl by weight. Here, the solution becomes saturated and NaCl · $2H_2O$ starts separating out as a solid phase. Below this point, ice and NaCl · $2H_2O$(s) separate out together as a whole. Hence, the point *B* is the eutectic point. The three phases in equilibrium at this point are ice, NaCl · $2H_2O$(s) and solution. Hence, applying reduced phase-rule equation.

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

2. Curve BC and Point C The curve *BC* represents the solubility curve of NaCl · $2H_2O$(s). From the curve, it is obvious that the solubility of NaCl · $2H_2O$(s) increases with increase of temperature. Along the curve *BC*, the two phases in equilibrium are NaCl · $2H_2O$(s) and solution. Hence, it is univariant.

The point *C* corresponds to a temperature of 0.15°C. Here, NaCl · $2H_2O$(s) starts decomposing and gives anhydrous NaCl and saturated solution. This point *C* is transition temperature and also a incongruent melting point. Curve CG is the metastable solubility curve of NaCl·$2H_2O$.

3. Curve CD It represents the solubility curve of anhydrous NaCl. It is very steep showing that the increase in the solubility of anhydrous NaCl is very very slow with increase of temperature. All along the curve *CD*, the two phases in equilibrium are anhydrous NaCl and solution.

14.20 PHASE DIAGRAM OF COPPER SULPHATE–WATER SYSTEM

This is a two-component system with incongruent melting points. Copper sulphate and water combine to form hydrates such as $CuSO_4 \cdot 5H_2O$, $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot H_2O$. These salts start dissociating to form the lower hydrate and the anhydrous salt below their melting points which are also the transition temperatures. Starting with $CuSO_4 \cdot 5H_2O$, the following equilibria are set up:

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g) \quad \ldots(14.1)$$

$$CuSO_4 \cdot 3H_2O(s) \rightleftharpoons CuSO_4 \cdot H_2O(s) + 2H_2O(g) \quad \ldots(14.2)$$

$$CuSO_4 \cdot H_2O(s) \rightleftharpoons CuSO_4(s) + H_2O(g) \quad \ldots(14.3)$$

Applying the law of chemical equilibrium to each of these heterogeneous equilibria taking $p_{solid} = 1$, we get

$$\text{For equilibrium (14.1), } (K_p)_1 = p_{H_2O}^2 \text{ or } p_{H_2O} = \sqrt{(K_p)_1} = \text{constant}$$

$$\text{For equilibrium (14.2), } (K_p)_2 = p_{H_2O}^2 \text{ or } p_{H_2O} = \sqrt{(K_p)_2} = \text{constant}$$

$$\text{For equilibrium (14.3), } (K_p)_3 = p_{H_2O} \text{ or } p_{H_2O} = (K_p)_3 = \text{constant}$$

Thus, for each of the above equilibria, vapour pressure of water vapours would become constant at constant temperature. Study of the above equilibria is based on the above observation. ***In constrast with the study of other salt hydrates, temperature is kept constant and the pressure over the salt is continuously decreased,*** till the dehydration of the salts and the dissociation equilibrium is set up. The experiment may be carried out taking the crystals of $CuSO_4 \cdot 5H_2O$ in a flask connected to a vacuum pump and a manometer and placing a flask in the thermostat at a fixed temperature (say 25°C) as shown in Fig. 14.34. The dissociation pressure is noted from time to time, from the manometer till a constant value is obtained. It is observed that as the suction is applied (i.e. water vapour is sucked out), the pressure inside the flask decreases till 7.8 mm of mercury and becomes constant at 25°C. It remains constant at this level till the whole of $CuSO_4 \cdot 5H_2O$ changes into $CuSO_4 \cdot 3H_2O$. On applying the suction further, the pressure falls abruptly till at 5.6 mm and again becomes constant. It remains constant till the whole of $CuSO_4 \cdot 3H_2O$ is converted into $CuSO_4 \cdot H_2O$. On continuing suction further, an abrupt decrease in pressure is observed till again at 0.8 mm, it becomes constant. It remains constant till the whole of $CuSO_4 \cdot H_2O$ is converted into the anhydrous $CuSO_4$ and the vapour pressure of water falls to zero.

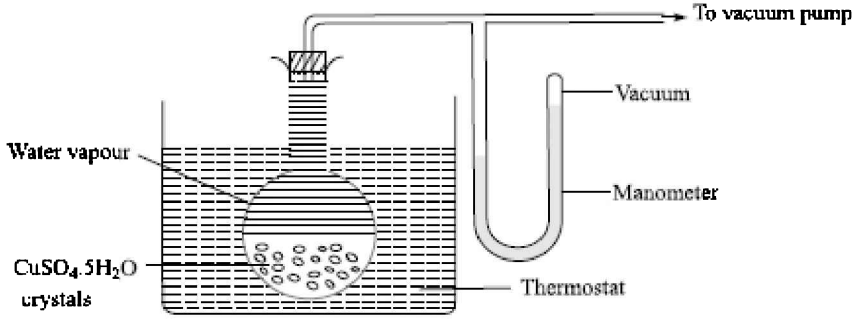


Fig. 14.34 *A set up for the study of dissociation equilibrium of $CuSO_4$ $5H_2O$*

Thus at 25°C.

For equilibria (14.1), p_{H_2O} = 7.8 mm

For equilibria (14.2), p_{H_2O} = 5.6 mm

For equilibria (14.3), p_{H_2O} = 0.8 mm

The various changes taking place are represented graphically as shown in Fig. 14.30

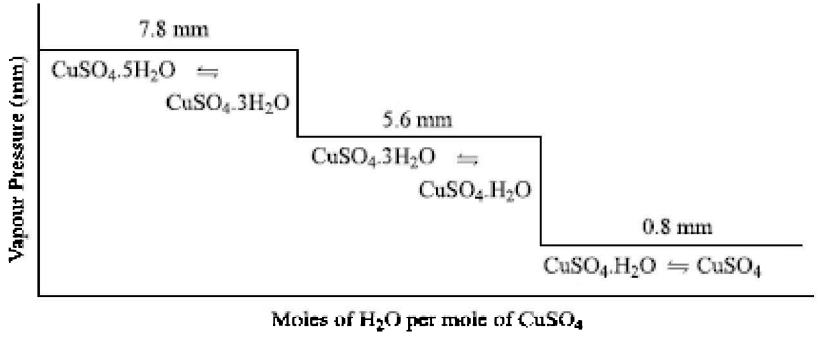


Fig. 14.35 *Dehydration of $CuSO_4 \cdot 5H_2O$ at 25°C*

Each of the three equilibria occurring here involves two solids and one gas, i.e. no of phases = 3. Hence, applying phase-rule equation,

$$F = C - P + 2 = 2 - 3 + 2 = 1$$

The following points about equilibria involving salt hydrates may be noted:

1. Higher the temperature, higher is the vapour pressure. For example, if dehydration of $CuSO_4 \cdot 5H_2O$ is carried out at 50°C, the vapour pressure for equilibria (14.1) to (14.3) are found to be 45.4, 30.9 and 4.5 mm respectively.
2. Above 102°C, pentahydrate is not stable. Hence, $CuSO_4 \cdot 3H_2O$ is the first stable hydrate and only two horizontal portions would be found in the vapour pressure-dehydration diagram.
3. For a definite vapour pressure to exist, there must be two solid phases in equilibrium in addition to the water vapour. Hence, it is wrong to speak of "vapour pressure of a salt hydrate" because a hydrated salt has no vapour pressure of its own.

Example 8 *List the three criteria for the phase equilibrium of a multi-component system.*

Solution:

(a) Thermal equilibrium (temperature is same in every phase)

(b) Mechanical equilibrium (pressure is same in every phase)

(c) Chemical equilibrium (chemical potential of a component is same in every phase)

Example 9 *Calculate the degrees of freedom of sulphur at the transition point.*

Solution: At the transition point ($S_L \rightleftharpoons S_M$), $P = 2$, As $C = 1$,
Hence, $F = C - P + 2 = 1 - 2 + 2 = 1$

Example 10 *The melting-point curve of the water system has a negative slope whereas the melting-point curve of sulphur has a positive slope. Explain.*

Solution: Negative slope of melting-point curve of ice means that it slopes towards the pressure axis. In this case, as the pressure is increased, melting point of the ice decreases. Positive slope of melting-point curve of sulphur (monoclinic) means that it slopes away from the pressure axis. In this case, the melting point increases with increase of pressure.

Example 11 *What type of systems are represented by curves (lines), points and areas in one-component systems?*

Solution: Areas represent bivariant systems, lines represent invariant systems and points represent non-variant systems.

Example 12 *What will be the number of degrees of freedom for a system consisting of saturated aqueous solution of sodium chloride in contact with solid salt and vapour?*

Solution: $P = 3$ (solid, liquid and vapour), $C = 2$ (NaCl and H_2O), $F = C - P + 2 = 2 - 3 + 2 = 1$

Example 13 *What is meant by triple point of water? Why is it different from the normal melting*

point of ice?

Solution: Triple point of water represents a point in the phase diagram at which all the three phases i.e., solid ice, liquid water and water vapour exist together (at 0.0098°C and 4.58 mm pressure). At normal melting point of ice (0°C, 1 atmospheric pressure), only ice and water exist together.

Example 14 *Suggest the possible maximum number of phases that can co-exist in the following systems:*

(a) Sulphur system

(b) Lead and silver alloy system

(c) Potassium iodide-water system

Solution:

(a) As $C = 1$ and minimum, $F = 0$. Hence, maximum $P = C - F + 2 = 3$ (triple point).

(b) $C = 2$, $F = 0$ Hence, $P = C - F + 2 = 2 - 0 + 2 = 4$ (quadruple point)

(c) $C = 2$, $F = 0$ Hence, $P = C - F + 2 = 2 - 0 + 2 = 4$ (quadruple point).

Example 15 *What is the criteria for two phase equilibria for one-component system?*

Solution: At a given temperature and pressure, free energy is the same in each phase.

Example 16 *Calculate the degrees of freedom of Pb-Ag system at the eutectic point.*

Solution: At the eutectic point, $P = 3$ (solid Pb, solid Ag and melts). As $C = 2$, applying condensed phase-rule equation, viz., $F = C - P + 1$, we get, $F = 2 - 3 + 1 = 0$. We neglect vapour phase here.

Example 17 *How many phases and components are present in the following system?*

(a) Mixture of molten lead, tin and bismuth

(b) Two ice cubes floating on water in a closed container in the presence of water vapour

Solution:

(a) $P = 1$ (liquid phase only), $C = 3$ (Pb, Sn, Bi)

(b) Ice $\rightleftharpoons$ water $\rightleftharpoons$ vapour, $P = 3$, $C = 1$ (H_2O only)

Example 18 *Is it possible to have a quadruple point in the phase diagram for a one-component system?*

Solution: Quadruple point is a point where four different phases meet. Thus, $P = 4$, substituting the values in phase-rule equation,

$$F = C - P + 2 \text{ or } F = 1 - 4 + 2 \text{ or } F = -1$$

This is absurd. Therefore, a one-component system cannot have a quadruple point in the phase diagram.

Example 19 *Calculate the number of phases, components and degrees of freedom in the*

following systems:

Solution:

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

No. of phases = 1 (gases mix uniformly to give one phase)

No. of components = 1

Degrees of freedom

$$F = C - P + 2$$
$$= 1 - 1 + 2$$

or $$F = 2$$

(b) Solid carbon with gaseous CO, CO_2 and O_2

No. of phases = 2 (1 for solid carbon and 1 for gases)

No. of components = 2

Degrees of freedom $F = C - P + 2 = 2 - 2 + 2 = 2$

Example 20 *Calculate the number of phases and degrees of freedom for the following systems:*

(a) A gas in equilibrium with its solution in a liquid

(b) A solution of one solid in one liquid in equilibrium with solvent vapour

(c) Two partially miscible liquids in absence of vapour

Solution:

(a) $P = 2$ (one gaseous, one liquid), $C = 2$ (gas and solvent)

(b) $P = 3$ (one solid, one liquid, one gaseous), $C = 2$ (one solid component, one liquid component)

(c) $P = 2$ (both liquid phases), $C = 2$ (both liquid components)

Example 21 *Calculate the degrees of freedom for the following:*

(a) A mixture of nitrogen and oxygen gases contained in a vessel

(b) Rhombic sulphur in equilibrium with monoclinic sulphur

Solution:

(a) Mixture of nitrogen and oxygen

No. of phases = 1 (Gases form a single phase)

No. of components = 2

Degrees of freedom are given by,

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

(b) Rhombic sulphur in equilibrium with monoclinic sulphur.

No. of phases = 2

No. of components = 1

Degrees of freedom are obtained as follows:

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

Example 22 *Write down the number of components, the number of phases and number of degrees of freedom (in addition of those already fixed) in the following examples:*

(a) Solid carbon in equilibrium with gaseous CO, CO_2, and O_2 at 100°C.

(b) A 2 molar aqueous solution of sulphuric acid (partly dissociated into hydrogen, bisulphate and sulphate ions) at 1 atm.

Solution:

(a) $C = S - E - R$ (in a chemically reactive system)

$S = 4$ (C, CO, CO_2, O_2) $E = 1$, $R = 0$ so that $C = 3$

Degrees of freedom, $F = C - P + 2 = 3 - 2 + 2 = 3$

(b) $2H_2SO_4(aq) \rightleftharpoons 3H^+ + HSO_4 + SO_4{}^{2-}{}_4$

Phases: Only one liquid phase (solution), i.e. $P = 1$

Components $C = 1$

Degrees of freedom $F = C - P + 2 = 1 - 1 + 2 = 2$

Example 23 *Find out the number of components present in the following systems:*

(a) Silver(s) $\rightleftharpoons$ Solution of silver and lead (l) + Lead (s) + Vapours of silver and lead (g)

(b) Water (l) $\rightleftharpoons$ water vapours (g)

(c) $NH_4Cl_{(s)} \rightleftharpoons NH_3(g) + HCl_{(g)}$

(d) $CaCO_{3(s)} \rightleftharpoons CaO(s) + CO_{2(g)}$

Solution:

(a) $C = 2$ (Pb and Ag)

(b) $C = 1$ (H_2O only)

(c) $C = 1$ (NH_4Cl only)

(d) $C = 2$ (any two out of $CaCO_3$, CaO and CO_2 can describe the composition of any phase)

SUMMARY

1. A *phase* is a homogeneous part of a system that is separated from the rest of the system by a well-defined boundary.
2. The number of components of a system at equilibrium is defined as the number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation, –ve and zero signs being permitted.
3. Degree of freedom of a system is the smallest number of variable factors, i.e. temperature, pressure and concentration of the components, which must be arbitrarily fixed in order that the conditions of the system may be completely defined.
4. Gibbs phase rule equation is

$$F = C - P + 2$$

where F = degree of freedom

C = Number of components

P = Number of phases

5. A system is said to be in *equilibrium* if the properties like temperature, composition, etc., of various phases do not undergo any change with time. A system is said to be in a state of ***true*** equilibrium if the same state can be achieved from either direction.
6. If the state of the system can be achieved only from one direction and that too by very careful change of conditions, it is said to be in **metastable** equilibrium.
7. For a multiphase equilibrium containing a number of components distributed among them, the chemical potential of any component is the same in all the phases.
8. Transition point can be determined by colour change, density change, solubility change or cooling curve method.
9. Triple point of a system is the point where all the three phases are in equilibrium.
10. It is not possible to liquefy CO_2 by cooling below 5.2 atm pressure.
11. A two-component system can be defined as one in which it is possible to express the composition of all the phases in terms of two substances.
12. A good freezing mixture is one which satisfies the following conditions. (i) It should have a low cryohydric temperature. (ii) Heat of solution of the salt should be high. (iii) The components should be such that an intimate mixture can be obtained from them. (iv) The material should be cheap.

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. In terms of number of phases (P), components (C) and degrees of freedom (F), the phase rule is expressed as

   (a) $P + C = F + 2$

   (b) $F = P + C - 2$

   (c) $P + F = C + 2$

   (d) $P - F = C + 2$

2. The number of degrees of freedom for the system $NH_4Cl(s) \rightleftharpoons NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g)$ is

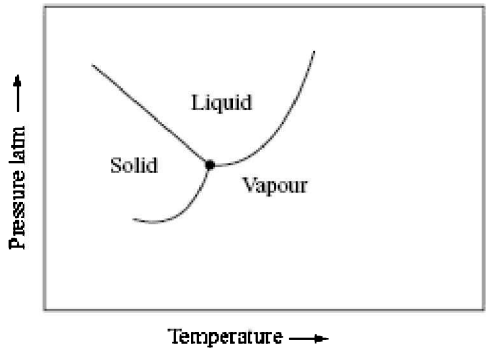
   (a) 1

   (b) 3

   (c) 0

   (d) 2

3. In the phase diagram of a one-component system, which of the following statements is correct?



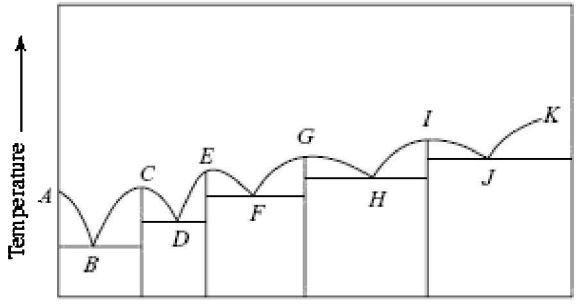
(a) The melting point of the solid increases with increases of pressure.

(b) The solid can be in equilibrium with the vapour only at a temperature on or below the triple point.

(c) The solid, if heated at 1 atm, will sublime.

(d) The three lines meet at the critical point.

4. In the phase diagram of a one-component system, which of the following statements is correct?



Phase diagram of $FeCl_3$ – water system

(a) eutectic point

(b) congruent point

(c) triple point

(d) critical point

5. The number of phases of a mixture of four gases enclosed in a container are

(a) 4

(b) 3

(c) 1

(d) 0

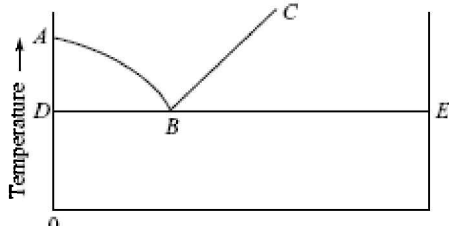
6. The phase diagram for $FeCl_3$–water system is shown alongside.

The diagram shows the formation of

(a) three hydrates
(b) four hydrates
(c) six hydrates
(d) five hydrates

7. The phase diagram of KI–water system is given alongside.
The cryohydric point in the curve is
(a) *AB*
(b) *DB*
(c) *BC*
(d) *BE*

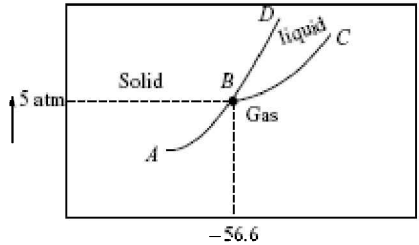
8. The phase diagram of KI–water system is given alongside.
The cryohydric point in the curve is



Phase diagram of KI – water system

(a) *A*
(b) *B*
(c) *C*
(d) *D* and *E*

9. Lowest temperature is reached by using

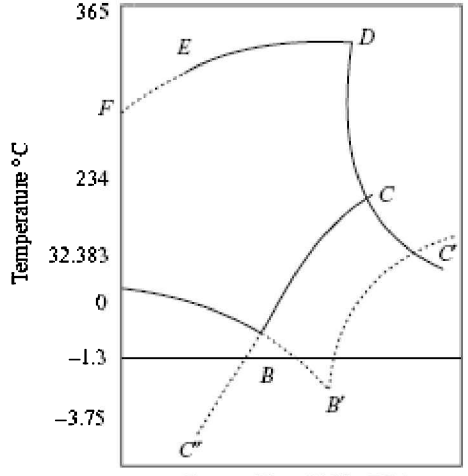


Phase diagram of CO_2 system

(a) $CaCl_2 \cdot 2H_2O$
(b) Acetone + dry ice
(c) NH_4Cl

(d) Ether + dry ice

10. In the phase diagram of CO_2, the system is bivariant
    (a) at the point *B*
    (b) at the critical point
    (c) in the region *ABD*
    (d) along *BD*
11. A compound with an incongruent melting point decomposes on heating into
    (a) a liquid of the same composition as solid
    (b) a new solid phase and a solution with a composition different from that of the solid phase
    (c) a new solid phase and a solution with the same composition as that of the solid phase
    (d) a solution of fixed composition.
12. In the phase diagram of Na_2SO_4–water, the point *D* is the



Phase diagram of Na_2SO_4– water system

    (a) transition temperature at which rhombic Na_2SO_4 is converted into monoclinic Na_2SO_4
    (b) transition temperature at which Glauber's salt change into monoclinic sodium sulphate
    (c) point at which $Na_2SO_4 \cdot 10H_2O$ change into $Na_2SO_4 \cdot 7H_2O$
    (d) temperature at which Na_2SO_4 becomes completely soluble in water
13. In the phase diagram for CO_2 (as shown in Q. 10), which of the following statements is not correct regarding this system?
    (a) The curves *AB* and *BC* represent equilibria between solid CO_2 and gas, and liquid CO_2 and gas respectively.
    (b) At 5 atm pressure and −56.6°C temperature, the system has zero degrees of freedom.
    (c) At all pressures below 5 atm, heating of solid CO_2 will result in sublimation.

(d) The melting point of CO_2 decreases with increase in pressure.

14. The number of eutectics in the phase diagram of the Fe_2Cl_6–water system is

(a) 6

(b) 5

(c) 4

(d) 3

15. In the phase diagram of CO_2 (as shown in Q. 10), the curve *BD* represents equilibrium between

(a) Solid and gas

(b) Solid and liquid

(c) gas and liquid

(d) Solid, liquid and gas.

16. In the phase diagram of the Fe_2Cl_6–water system, the point *g* corresponds to the compound

(a) $Fe_2Cl_6 \cdot 12H_2O$

(b) $Fe_2Cl_6 \cdot 7H_2O$

(c) $Fe_2Cl_6 \cdot 6H_2O$

(d) $Fe_2Cl_6 \cdot 5H_2O$

17. The phase diagram of Na_2SO_4–water (Q. 12), the curve *EF* represents the

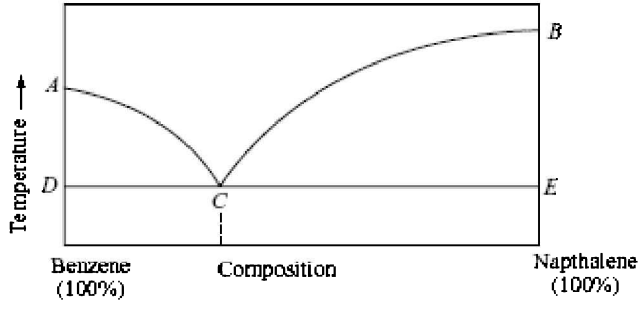
(a) solubility curve of $Na_2SO_4 \cdot 7H_2O$

(b) metastable solubility curve of monoclinic Na_2SO_4

(c) transition curve of monoclinic Na_2SO_4 to rhombic Na_2SO_4

(d) solubility curve of monoclinic Na_2SO_4

18. The phase diagram for the benzene-naphthalene system is shown below. Which of the following statements is not correct?



(a) Along curve *AC*, solid benzene is in equilibrium with liquid solution.

(b) Above curve *AC* and *BC*, the two components are present only as a homogeneous liquid solution.

(c) The intensive properties of the system at *C* are entirely fixed under all conditions of pressure.

(d) At a given pressure, the system is monovariant along *BC*.

Answers

1. (c)
2. (a)
3. (b)
4. (a)
5. (c)
6. (b)
7. (c)
8. (b)
9. (d)
10. (c)
11. (b)
12. (c)
13. (d)
14. (b)
15. (b)
16. (d)
17. (b)
18. (c)

SHORT-ANSWER QUESTIONS

1. With the help of a diagram, explain the application of phase rule in the extraction of silver from an are of lead.
2. Calculate the number of components present in the following systems.
   (a) A solution of common salt
   (b) $NH_3(g)$
   (c) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
   (d) $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$
   (e) $H_2O(l) \rightleftharpoons H_2O(l)$
3. Draw well-labelled phase diagram of the KI–H_2O system. Discuss how the cooling will proceed if the solution contains (a) more than 52% KI, (b) less than 52% KI, and (c) 52% KI?
4. How does phase diagram of KI–H_2O system differ from that of the Pb-Ag system and why? Why do you understand by 'cryohydric point'?
5. Calculate the number of phases in the following systems:
   (a) $NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

(b) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H2(g)$

(c) I_2 dissolved in CCI_4

(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(e) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$

6. Discuss the principle for the preparation of freezing point.
7. Sketch the cooling curve for the following alloys of Pb-Ag system and explain what happens as their melts are cooled:
   (a) An alloy of eutectic composition.
   (b) An alloy of any other composition.
8. Draw the composition-temperature phase diagram of sodium sulphate-water system and label it properly.
9. Explain how the NaCl–H_2O system is considered to be a system with incongruent melting point. Draw the labelled diagram for this system.
10. Using the $FeCl_3$–H_2O system phase diagram, explain how the isothermal evaporation of an unsaturated $FeCl_3$ solution proceeds.
11. Draw a labelled phase diagram of the Mg–Zn system. Indicate clearly the eutectic points and congruent melting points on the diagram.
12. Draw a labelled diagram of the $FeCl_3$–H_2O system. Where do the congruent melting points and eutectic points (transition points) lie? Write the equilibria existing at different transition points.
13. Draw a well-labelled phase diagram of the water system. What do you interpret from the slope of the melting-point curve?
14. Draw a well-labelled phase diagram of the sulphur system. What do you interpret from the slopes of transition curve of *SR* and melting curve of S_M?
15. Why are three-dimensional diagrams required for studying a two-component system? How is the problem simplified?
16. Explain the term 'degree of freedom' with suitable examples as used in phase rule.
17. Derive the criteria for phase equilibria for a multi-component and multi-phase system.
18. Give two examples each of two-component system in which
   (i) the components do not react with each other.
   (ii) the components react to form a compound with congruent melting point
   (iii) the components react to form a compound with incongruent melting point
19. Calculate the total number of variables of a system of C components and P phases.
20. Calculate the number of variables of a system of C components and P phases, because of its being in equilibrium.
21. What are the main points of difference in the phase diagram of the CO_2 and H_2O systems?
22. Draw a well-labelled phase diagram of the water system. Discuss the effect of change of temperature at constant pressure on this system.
23. How is the $CuSO_4$–H_2O system studied? Explain briefly.
24. How are the number of components of a chemically reactive system calculated? Explain with two examples.

25. What do you understand by phase diagram? How are bivariant, univariant and non-variant systems represented in a phase diagram?

GENERAL QUESTIONS

1. Draw a labelled phase diagram of the sulphur system and discuss its salient features.
2. Briefly describe the cooling-curve method and thaw-melt method for construction of a phase diagram of a two-component system miscible in the liquid phase (molten state).
3. (a) Lead (m.p. 327°C) and silver (m.p. 961°C) form a eutectic mixture at 303°C with 2.6% by weight of silver.

   (i) Draw a phase diagram (temperature-composition) for the system.

   (ii) Label each region and discuss it fully.

   (iii) Sketch and explain the type of cooling curve expected for 80% by weight of silver and 2.6% by weight of silver.

   (b) Discuss the desilversation of lead on the basis of this phase diagram.
4. Define 'Gibbs phase rule'. How can you derive it thermodynamically?
5. Build the complete phase diagram for sulphur considering two solid phases, one liquid phase and one gas phase. Can all the phases co-exist?
6. Draw a phase diagram of the water system. Label it and discuss the importance of various points, lines and areas at equilibrium. Discuss the effect of change of temperature at constant pressure.
7. State the phase rule. Explain the terms used. Apply this rule to the lead-silver system.
8. Draw the complete phase diagram of sulphur system and prove that the conclusions in regard to the degrees of freedom as derived from this diagram are the same as the deduction from phase rule.
9. Draw a well-labelled diagram of carbon dioxide system. Discuss its main features. How does it differ from phase diagram of the water system?
10. How is phase diagram of a two-component system comprising of two solid components miscible in the liquid phase constructed? What are its main features?
11. Briefly describe a two-component system which involves compound formation with congruent melting point.
12. Draw and explain the phase diagram of a one-component system compairing more than one solid phase.
13. Draw a labelled temperature-pressure phase diagram of sulphur system. Describe two ways in which the triple point of the system in the metastable equilibrium can be obtained.
14. Draw a schematic diagram of the KI–H_2O system explaining the main points of information about the equilibria presented in various areas along different lines and at various points in the diagram.
15. Explain, with a suitable example, the following terms used in the phase-rule study of heterogeneous equilibria:

   (a) Triple point

   (b) Transition point

   (c) Invariant system

(d) Eutectic point

(e) Cryohydric point

(f) Metastable equilibrium.

16. Draw a labelled phase diagram of the water system and discuss its salient features.

17. How is the phase diagram of the Bi–Cd system constructed? Discuss the main features of this diagram.

18. Discuss the salient features of the phase diagram of the lead-silver system.

19. Draw a schematic phase diagram for the water-sodium sulphate system. Clearly explain the main points of information about the equilibria represented in various areas, along different curves and at various points of the diagram.

20. Draw a schematic phase diagram of the sulphur system. Explain clearly the main points of information about the equilibria represented in various areas, along different lines, and at various points of the diagram.

21. Define a condensed system from the phase rule point of view and say how much a system can be dealt with the help of a simple phase diagram. Draw the lead-silver phase diagram and explain how argentiferous lead containing a very low percentage of silver can be concentrated by cooling. State the maximum limit of concentration thus obtained.

22. (a) Draw the phase diagram of ferric chloride-water system. Briefly describe its important features.

(b) Briefly explain how the isothermal evaporation of an unstatured solution of ferric chloride proceeds.

23. Using the above diagram, briefly explain how the phase rule is applied in the preparation of 'freezing mixtures.'

24. Describe the main features of $NaCl–H_2O$ system after drawing a well-labelled diagram.

25. Draw a lead-silver phase diagram and illustrate the principle of 'Pattinson's process' for enrichment of silver.

26. Draw a well-labelled phase diagram of Mg–Zn system. Discuss the main features of this diagram.

27. Discuss how the equilibria involving salt hydrates are studied taking the example of $CuSO_4–H_2O$ system.



Distribution Law

15

LEARNING OBJECTIVES

- Define Nernst distribution law
- Appreciate limitations of distribution law
- Derive Nernst distribution law from thermodynamic considerations
- Apply modifications in distribution law in case of change in molecular state
- Study the applications of distribution law to
  (a) determine solubility of a solute in a solvent
  (b) determine the extent of association or dissociation of a solute in a solvent
- Study chemical equilibrium involving formation of complex compounds
- Appreciate the utility of distribution law in the process of extraction
- Derive the formula for the amount of substance left unextracted and the volume of extracting liquid used each time
- Understand the principle behind Parke's process for desilverisation of lead
- Learn the determination of degree of hydrolysis from distribution law
- Understand the principle of liquid-liquid chromatography

15.1 NERNST DISTRIBUTION LAW—INTRODUCTION

It has long been observed that when a substance is added to a mixture of two immiscible liquids, the substance distributes itself between the two liquids in such a manner that the concentration ratio of the substances in the two liquids is constant at constant temperature.

In 1872, Berthelot and Jungfleish found that when solutions of iodine in carbon disulphide of different concentrations were shaken with distilled water, the iodine distributed itself between the two solvents in such a way that at a given temperature, the ratio of its concentration in the two layers was constant. Nernst, however, showed that the ratio of concentration was constant only when the solute had the same molecular state in the two solvents.

The Nernst distribution law is stated as follows:

A solute distributes itself between two immiscible solvents in such a way that the ratio of concentrations of the solute in the two solvents is constant at constant temperature, independent of any other molecular species present, provide that the solute has the same molecular state in both the solvents.

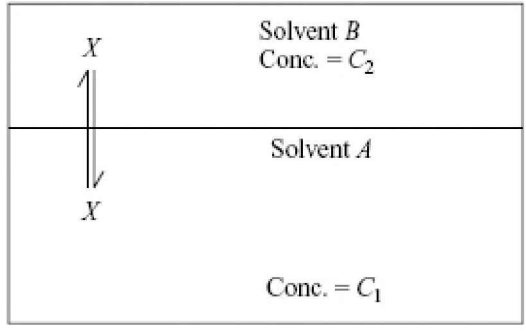


Fig. 15.1 *Distribution of solute X between immiscible solvents A and B*



Fig. 15.2 *Walther Nernst was awarded the Nobel Prize in Chemistry in 1920 in recognition of his work on theories behind the calculation of chemical affinity.*

If a solute X distributes itself between the two immiscible solvents A and B (Fig. 15.1), then we have

$$\frac{\text{Concentration of } X \text{ in Solvent } A}{\text{Concentration of } X \text{ in Solvent } B} = \frac{C_1}{C_2} = K \quad \text{(constant)}$$

Provided 'X' remains in the same molecular species in both the solvents. The constant K is called ***distribution coefficient*** or ***partition coefficient.***

15.1.1 Limitations of Distribution Law

The distribution law is applicable only if the following conditions are fulfilled:

1. The temperature remains constant throughout the experiment.
2. The two liquids (solvents) should be mutually immiscible.
3. The amount of the solute added should be small, i.e. the solution should be dilute. It is observed that in some cases, the solute added affects the mutual solubility of the solvents.

4. The solute must have the same molecular state in both the solvents. That is, it should not undergo association or dissociation in any of the solvents. Thus, the law is not valid for distribution of benzoic acid between water and benzene, because in benzene, benzoic acid undergoes association to form dimers, i.e. it exists as $(C_6H_5COOH)_2$. Similarly, the law is also not valid for the distribution of an electrolyte between water and a nonpolar solvent, because the electrolytes undergo dissociation in water.

Organic compounds are soluble in organic solvents like $CHCl_3$, CCl_4, ether, CH_2Cl_2, etc., and ionic compounds are soluble in water. Again, the organic solvents as mentioned above and water are immiscible with each other. This provides us an opportunity to purify organic compounds or inorganic compounds. If it is an organic compound, on adding it to the mixture of the organic solvent and water and shaking, the organic compound will go to the organic solvent and inorganic impurity, if any will be absorbed by water. On evaporating the organic layer, the pure organic compound can be retrieved.



Fig. 15.3 *Separating funnel*

Example 1 *When varying amounts of iodine were shaken with CCl_4-water mixture, the following concentrations of iodine (in g/100 cm^3) were obtained:*

CCl_4 layer	*5.1*	*10.2*	*15.2*	*20.3*
Water layer	*0.06*	*0.119*	*0.178*	*0.236*

Show that these results illustrate the distribution law:

Solution:

Conc. in CCl_4 layer (C_1)	Conc. in H_2O layer (C_2)	$C_1/C_2 = K$
5.1	0.06	5.1/0.06 = 85.0
10.2	0.119	10.2/0.119 = 85.7

15.2	0.178	15.2/0.178 = 85.4
20.3	0.236	20.3/0.236 = 86.0

Since the value of K comes out to be almost constant, the given data illustrates the distribution law.

Example 2 *If the distribution coefficient of benzoic acid between water and benzene is 0.304 at 20°C, calculate the number of moles of benzoic acid which may be extracted from 100 cm^3 of 0.2 molar aqueous solution by 10 cm^3 of benzene.*

Solution: 1000 cm^3 of aqueous solution contains benzoic acid = 0.2 mole.

$\therefore$ 100 cm^3 of aqueous solution contains benzoic acid = 0.02 mole

Suppose the amount of benzoic acid extracted into benzene = x mole

$\therefore$ Amount of benzoic acid left in aqueous solution = $(0.02 - x)$mole

$\therefore$ Conc. of benzoic acid in aqueous layer = $\dfrac{(0.02-x)}{100}$ mole /cm^3

and conc. of benzoic acid benzene layer = $\dfrac{x}{10}$ mole/cm^3.

Hence, $\dfrac{(0.02-x)/100}{x/10} = 0.34$ which gives $x = 0.005$

Example 3 *Succinic acid was shaken with a mixture of water and ether. The concentrations of the acid in the two layers are as follows (per 10 cm^3 of solution). Find out the partition coefficient.*

In water layer:	*0.0244*	*0.071*	*0.121*
In ether layer:	*0.0046*	*0.013*	*0.022*

If succinic acid has normal molecular mass of 118 in water, find its molecular mass in ether.

Solution: Partition coefficient (distribution coefficient) of succinic acid between water and ether is given by the ratio:

$$K = \frac{\text{Conc. in water } (C_1)}{\text{Conc. in ether } (C_2)}$$

From first set: $K = \dfrac{0.0244}{0.0046} = 5.30$

From second set: $K = \dfrac{0.071}{0.013} = 5.47$

From third set: $K = \dfrac{0.121}{0.022} = 5.50$

$\therefore$ mean value of partition coefficient, $K = \dfrac{5.30 + 5.47 + 5.50}{3} = 5.42$

Since the value of $K = C_1/C_2$ is almost constant, succinic acid must have the same molecular mass in both the solvents.

As mol. mass of succinic acid in water is equal to 118, therefore, mol. mass of succinic acid in ether is also equal to 118.

Example 4 *An aqueous solution of succinic acid at 15°C containing 0.07g in 10 cm^3 is in equilibrium with an ethereal solution containing 0.013 g in 10 cm^3. Succinic acid has its normal molecular mass in both the solvents. What will be the concentration of an ethereal solution which is in equilibrium with an aqueous solution containing 0.024 g in 10 cm^3?*

Solution: *First experiment*

$$\text{Conc. of succinic acid in water} \quad (C_1) = 0.07 \text{ g in } 10 \text{ cm}^3 = \frac{0.07}{10} \text{ g/cm}^3$$

$$\text{Conc. of succinic acid in ether} \quad (C_2) = 0.013 \text{ g in } 10 \text{ cm}^3 = \frac{0.013}{10} \text{ g/cm}^3$$

Succinic acid has the same molecular mass in both the solvents; therefore, distribution law is applicable.

$$K = \frac{C_1}{C_2} = \frac{0.07/10}{0.013/10} = 5.38$$

Second experiment

$$\text{Conc. of succinic acid in water:} \quad (C_1) = 0.024 \text{ g in } 10 \text{ cm}^3 = \frac{0.024}{10} \text{ g/cm}^3$$

We want to calculate concentration of succinic acid in ether, i.e. C_2 according to the distribution law,

$$\frac{C_1}{C_2} = K$$

Substituting the values we get,

$$\frac{0.024/10}{C_2} = 5.35 \qquad (K \text{ will have the same value as in the first experiment})$$

or $$C_2 = \frac{0.024}{10} \times \frac{1}{5.38} = 0.00045$$

Thus, concentration of succinic acid in ether layer,

$$= 0.00045 \text{ g/cm}^3$$

PROBLEMS FOR PRACTICE

1. Calculate how much compound would be extracted from 100ml of an aqueous solution containing 5 g of the compound if extracted with 50 ml of ether. The partition coefficient of the compound between ether and water is 4.

[Ans. 3.33 g]

2. The distribution coefficient of an organic acid between water and ether is 0.30 at 25°C. Calculate the number of moles of an acid which may be extracted from 100ml of 0.025 molar aqueous solution by 10 ml of ether, provided the acid has normal molecular mass in both the solvents.

[Ans. 0.000625 mole]

3. Succinic acid has the same molecular mass in water and ether. When varying amounts of the acid were shaken with ether-water mixture, the following results were obtained:

Conc. in water layer (C_1): 25.4 33.2 42.6

Conc. in ether layer (C_2): 4.2 5.5 7.1

Calculate the partition coefficient and show that these figures illustrate the distribution law.

[Ans. 6.03]

4. The following data show the concentrations of solutions of iodine in water and CS_2 in equilibrium at 18°C.

Grams of I_2/10 ml of CS_2:	1.64	1.29	0.63	0.40
Grams of I_2/10 ml of H_2O:	0.0041	0.0041	0.0016	0.0010

Show that these results are in arrangement with the distribution law:

5. In the distribution of succinic acid between ether and water at 20°C, 25 ml of the ethereal layer contained 0.08 g of the acid. Find the weight of the acid present in 50 ml of the aqueous solution in equilibrium with it if the value of K for succinic acid between water and ether is 5.3.

[Ans. 0.848 g]

15.2 THERMODYNAMIC DERIVATION OF DISTRIBUTION LAW

The derivation is based upon the principle that ***if there are two phases in equilibrium (in this case two immiscible solvents containing the same solute dissolved in them), the chemical potential of a substance must be same in both the phases.***

From thermodynamics, we know that the chemical potential (μ) of a substance in a solution given by,

$$\mu = \mu^\circ + RT \ln a$$

where μ° is the standard chemical potential and 'a' is the activity of the substance (solute) in the solution.

For the solute in liquid A, we have

$$\mu_A = \mu_A^\circ + RT \ln a_A \qquad \ldots(15.1)$$

For the solute in liquid B we have,

$$\mu_B = \mu_B^\circ + RT \ln a_B \qquad \ldots(15.2)$$

Since the liquids A and B are in equilibrium,

$$\mu_A = \mu_B \qquad \ldots(15.3)$$

or $$\mu_A^\circ + RT \ln a_A = \mu_B^\circ + RT \ln a_B$$

or $$RT \ln a_A - RT \ln a_B = \mu_B^\circ - \mu_A^\circ$$

or $$\ln \frac{a_A}{a_B} = \frac{\mu_B^\circ - \mu_A^\circ}{RT} \qquad \ldots(15.4)$$

At a given temperature, μ°_A and μ°_B are constant for given substance in a particular solvents. Hence, at constant temperature, we have

$$\ln \frac{a_A}{a_B} = \text{constant [from Eq. (15.4)]} \quad \ldots(15.5)$$

or $$\frac{a_A}{a_B} = \text{constant}$$

This is the exact expression for the distribution law. However, if the solutions are dilute, the activities may be replaced by concentrations so that the expression (15.5) is modified to

$$\frac{C_A}{C_B} = \text{constant}$$

which is the original form of the distribution law.

15.3 MODIFICATION IN DISTRIBUTION LAW IN CASE OF CHANGE IN MOLECULAR STATE

Case I the solute undergoes dissociation in one of the solvents Suppose, the solvent *X* dissolves in Phase I without any change in the molecular state but undergoes dissociation into *Y*, *Z*, etc., in Phase II. Then, the following two equilibria will be set up as shown in Fig. 15.4.

(i) $X \rightleftharpoons X$

Phase I Phase II

(ii) $X \rightleftharpoons Y + Z$ in the same Phase II

Let us suppose, total concentration of Solute *X* in Phase I = C_1 and total concentration of Solute *X* in Phase II = C_2

Also, suppose the degree of dissociation if the solute in Phase II is α

Then, concentration of undissociated (simple) molecules in Phase II = $(1 - \alpha) C_2$

Applying the distribution law to the equilibrium (i), we get

$$\frac{C_1}{(1-\alpha)C_2} = K \text{ (Partition coefficient)}$$

It is understandable that if the solute undergoes dissociation in Phase I (with degree of dissociation = α) but remains normal in Phase II then the formula obtained will be

$$\frac{C_1(1-\alpha)}{C_2} = K$$

From the above expression, the degree of dissociation α can be obtained.

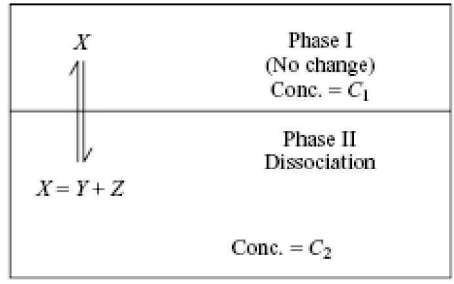


Fig. 15.4 *Dissociation in Phase II*

Case 2 The solute undergoes association in one of the solvents

Suppose the Solute X remains in the normal molecular state in Phase I but n molecules of it associate to form complex molecules X_n in Phase II. Then, the following two equilibria will exist simultaneously, as shown in Fig. 15.5.

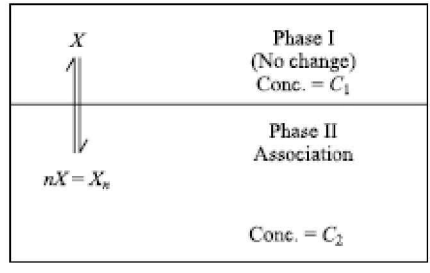


Fig. 15.5 *Association in Phase II*

(i) $X \rightleftharpoons X$

Phase I Phase II

(ii) $nX \rightleftharpoons X_n$ in the same Phase II.

$C_2(1-\alpha)$ $\frac{1}{2}C_2\alpha$

Suppose the total conc. of Solute X in Phase I = C_1 and total conc. of Solute X in Phase II = C_2

Suppose α is the degree of association of the solute in Phase II.

The concentration of the associated molecules in Phase II, i.e. $[X_n] = \frac{1}{n}C_2\alpha$ and concentration of the associated molecules in Phase II = $(1 - \alpha)\, C_2$

Applying the distribution law to the equilibrium (i), we get

$$\frac{\text{Conc. of Solute } X \text{ in Phase I}}{\text{Conc. of normal moles of } X \text{ in Phase II}} = \text{constant}$$

We have to take into account concentrations of identical molecular species in the two phases.

i.e., $$\frac{C_1}{(1-\alpha)C_2} = \text{constant} \qquad \ldots(15.6)$$

Now applying the law of chemical equilibrium to the equation (ii), we get

$$\frac{\text{Conc. of associated molecules in Phase II}}{(\text{Conc. of normal molecules in Phase II})^n} = \text{constant}$$

i.e.
$$\frac{\frac{1}{n}C_2\alpha}{[(1-\alpha)C_2]^n} = \text{constant}$$

or
$$\frac{C_2\alpha}{[(1-\alpha)C_2]^n} = \text{constant} \qquad (\because n = \text{constant})$$

Taking the *n*th root, we get

$$\frac{\sqrt[n]{C_2\alpha}}{(1-\alpha)C_2} = \text{constant} \qquad \ldots(15.7)$$

Dividing Eq. (15.6) by Eq. (15.7), we get

$$\frac{C_1}{\sqrt[n]{C_2 \cdot \alpha}} = \text{constant} \qquad \ldots(\text{Exact formula})$$

When the molecules in Phase II are almost completely associated, $\alpha = 1$ and, therefore,

$$\frac{C_1}{\sqrt[n]{C_2}} = \text{constant} \qquad \ldots(\text{Approx. formula})$$

Thus, when the solute undergoes dissociation in one of the solvents, the constant value for the partition co-efficient is obtained not for the ratio C_1/C_2 but for the ratio $C_1/\sqrt[n]{C_2}$.

The formula, $C_1/\sqrt[n]{C_2} = K$, is commonly used for finding the value of *n*, i.e., the extent of association of the solute molecules in one of the solvents. This is done by finding out the concentrations C_1 and C_2 of the solute in the two solvents in a number of experiments. The value of *n* is then calculated.

Case 3 When the solute combines with one of the solvents Suppose, the solute *X* remains in the normal molecular state in Phase I but one molecule of it combines with *n* molecules of the solvent *S* to form the compound molecule. $X \cdot nS$ in Phase II. Then, the following two equilibria will be established as shown in Fig. 15.6.

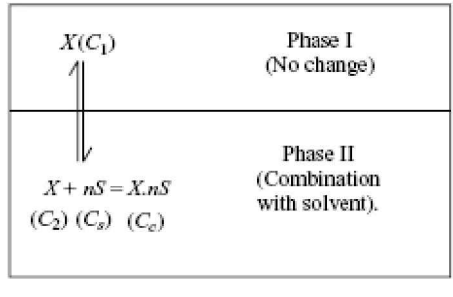


Fig. 15.6 *Combination with solvent in Phase II*

(i) $X \rightleftharpoons X$

Phase I Phase II

(ii) $X + nS \rightleftharpoons X \cdot nS$ in the same Phase II.

Let us suppose, concentration of Solute X (normal molecules) in phase = C_1

Concentration of normal molecules in Phase II = C_2

Concentration of solvent molecules in Phase II = C_S

and Concentration of the compound molecules in phase II = C_C

Applying the distribution law to the equilibrium (i), we get

$$\frac{C_1}{C_2} = K, \text{ the distribution coefficient} \qquad \ldots(15.8)$$

Now, applying the law of chemical equilibrium to the equilibrium (ii), we get

$$\frac{C_C}{C_2 \times (C_S)^n} = K_1, \text{ equilibrium constant} \qquad \ldots(15.9)$$

Since the solvent in Phase II is present in excess, its concentration (C_S) remains almost constant despite of combination with the solute X, particularly if the solute is added in small quantity, i.e., the solution is dilute. Thus, $(C_S)^n$ is constant.

Equation (15.9) thus, becomes, $\frac{C_C}{C_2} = K_1(C_S)^n$, K_2, another constant

Adding 1 to both the sides, we get

$$1 + \frac{C_C}{C_2} = 1 + K_2$$

or

$$\frac{C_2 + C_C}{C_2} = 1 + K_2$$

Dividing Eq. (15.8) by Eq. (15.9), we get

$$\frac{C_1}{C_2} \times \frac{C_2}{C_2 + C_C} = \frac{K}{1 + K_2}$$

or

$$\frac{C_1}{C_2 + C_C} = \frac{K}{1 + K_2} = K_3, \text{ another constant}$$

But $C_2 + C_C$ is the total concentration of the normal as well as the solvated molecules of the solute X in Phase II. Thus, the above equation, signifies that

$$\frac{\text{Total conc. of the solute } X \text{ in Phase I}}{\text{Total conc. of the solute } X \text{ in Phase II}} = \text{constant}$$

Thus, we conclude that ***when the solute enters into chemical combination with one of the solvents, there is no modification of the distribution law equation except that the numerical value of the partition constant is changed.***

15.4 APPLICATIONS OF DISTRIBUTION LAW

1. Determination of Solubility of a Solute in a Solvent

When two immiscible solvents are in contact with each other and the solute is added in such a large excess that saturated solutions are formed then the concentrations of the solutions at this stage will be equal to their solubilities. Assuming that the distribution law is applicable for such concentration, we have

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K$$

where, conc. $C_1 = S_1$ is the solubility of the solute in Solvent 1
and conc. $C_2 = S_2$ is the solubility of the solute in Solvent 2

Knowing the distribution coefficient K and the solubility of the solute in one of the solvents, that in the other can be calculated.

Example 5 *At 15°C, an aqueous solution of oxalic acid contains 5.0 g of oxalic acid per 100 cm^3 of water in equilibrium with an ethereal solution containing 0.50 g per 100 cm^3. The solubility of oxalic acid in water at 15°C is 10 g per 100 cm^3. Calculate the solubility in water.*

Solution: Conc. of oxalic acid in water (C_1) = 5.0 g in 100 cm^3 = 50.0 g/litre

Conc. of oxalic acid in ether (C_2) = 0.50 g in 100 cm^3 = 5.0 g/litre

$\therefore$ distribution coefficient of oxalic acid between water and ether is given by

$$K = \frac{C_1}{C_2} = \frac{50}{5.0} = 10.0$$

In saturated solutions, the ratio of concentrations is equal to the ratio of solubilities

i.e. $$K = \frac{\text{Solubility in water } (S_1)}{\text{Solubility in ether } (S_2)}$$

But $$S_1 = 10 \text{ g/100 cm}^3 \text{ (given)}$$

$$10 = \frac{10}{S_2} \quad \text{or} \quad S_2 = 1.0 \text{ g}$$

i.e. solubility of oxalic acid in ether = 1.0 g/100 cm^3

PROBLEMS FOR PRACTICE

1. The solubility of iodine in carbon tetrachloride at 25°C is 29.1 g/litre. If a solution of iodine in water containing 0.103 g/litre is in equilibrium with a solution of carbon tetrachloride containing 8.2 g of iodine/ litre, calculate the solubility of iodine in water at 25°C.

[Ans. 0.366 g/litre]

2. At 25°C, an aqueous solution of iodine containing 0.0576 per litre is in equilibrium with CCl_4 solution containing 4.412 g of iodine per litre. If the solubility of iodine in water is 0.340 g/litre, what will be its solubility in CCl_4?

[Ans. 26.04 g/litre]

3. Find the solubility of iodine in CCl_4 at a temperature when water becomes saturated with 0.350 g of iodine per litre and the distribution coefficient is 88 in favour of CCl_4.

[Ans. 30.80 g/litre]

2. To Determine the Extent of Association or Dissociation of a Solute in a Solvent Using Distribution Law When a solute undergoes association in one of the solvents ($nX \rightleftharpoons X_n$) in which its total concentration is C_2 and has the normal molecular state in the second solvent in which its total concentration is C_1 then distribution law formula is modified to

$$\frac{C_1}{\sqrt[n]{C_2}} = K, \text{ the distribution coefficient}$$

From this formula, the value of n can be calculated by either of the two methods given below.

(a) Hit and Trial-Method The value of C_1 and C_2 obtained from different experiments are put in the equation.

$$\frac{C_1}{\sqrt[n]{C_2}} = K$$

By putting n = 2, 3, 4, etc. … one by one, the values of K are calculated in each case. The number which gives a constant value for K is the correct value for n.

(b) Logarithmic Method Writing again the distribution law equation when association in one liquid takes place,

$$\frac{C_1}{\sqrt[n]{C_2}} = K \quad \text{or} \quad \frac{C_1}{C_2^{1/n}} = K$$

or
$$C_1 = (C_2)^{1/n} \cdot K$$

Taking logarithms of both sides, we get

$$\log C_1 = \frac{1}{n} \log C_2 + \log K$$

For two sets of values, C_1, C_2 and C'_1, C'_2, we can write the equations

$$\log C_1 = \frac{1}{n} \log C_2 + \log K \qquad \ldots(15.10)$$

and
$$\log C'_1 = \frac{1}{n} \log C'_2 + \log K \qquad \ldots(15.11)$$

Subtracting Eq. (15.11) from Eq. (15.10), we get

$$\log C_1 - \log C'_1 = \frac{1}{n}(\log C_2 - \log C'_2)$$

$$n = \frac{\log C_2 - \log C'_2}{\log C_1 - \log C'_1}$$

Hence, n can be calculated.

Similarly, when the solute undergoes dissociation in one of the solvents ($X \rightleftharpoons Y + Z$) in which its total concentration is C_2 and has the same normal molecular state in the other solvent, in which its concentration is C_1 then we have

$$\frac{C_1}{C_2(1-a)} = K, \text{ the distribution coefficient}$$

Example 6 *In the distribution of solute between water (C_1) and chloroform (C_2), the following results were obtained:*

C_1	C_2
0.163	0.761
0.436	5.43

What information do you gather regarding the molecular state of the solute in chloroform?

Solution: If the solute exists as simple (normal) molecules in water as well as in chloroform, the ratio $C_1/C_2 = K$ should be constant.

For first set: $$\frac{C_1}{C_2} = \frac{0.163}{0.761} = 0.212$$

For second set: $$\frac{C_1}{C_2} = \frac{0.436}{5.43} = 0.080$$

We observe that the ratio C_1/C_2 is not constant and hence the distribution law in its simple from is not applicable. In other words, the molecular state of the solute is not the same in the two solvents.

Suppose the solute is associated as double molecules in chloroform. Then the ratio $C_1/\sqrt{C_2}$ should be constant.

For first set: $$K = \frac{C_1}{\sqrt{C_2}} = \frac{0.163}{\sqrt{0.761}} = 0.1869$$

For second set: $$K = \frac{C_1}{\sqrt{C_2}} = \frac{0.436}{\sqrt{5.43}} = 0.1871$$

As the ratio $C_1/\sqrt{C_2}$ comes out to be constant, this proves that the solute exists as double molecules in chloroform.

Example 7 *In the distribution of benzoic acid between water and benzene, the following results are obtained:*

C_1 *(in water)*	1.50	1.95	2.97
C_2 *(in benzene)*	24.20	41.2	97.0

Assuming that benzoic acid exists as single molecules in water, show that it exists as double molecules in benzene.

Solution: If benzoic acid exists as normal (single) molecules in water and as dimer (double molecules) in benzene, the ratio $C_1/\sqrt{C_2}$ should be constant. This can be seen as follows:

C_1 (in water)	C_2 (in benzene)	$\frac{C_1}{\sqrt{C_2}} = K$
1.5	24.20	$\frac{1.5}{\sqrt{24.20}} = 0.305$
1.95	41.2	$\frac{1.95}{\sqrt{41.2}} = 0.304$
2.97	97.0	$\frac{2.97}{\sqrt{97.0}} = 0.302$

As the ratio $C_1/\sqrt{C_2}$ comes out to be almost constant, this proves that benzoic acid exists as double molecules in benzene.

Example 8 *Succinic acid shows normal molecular mass in water and is associated in benzene. The following data was obtained on the distribution of succinic acid between water and benzene.*

C_1 in water (g/litre)	*1.50*	*1.95*	*2.89*
C_2 in benzene (g/litre)	*24.20*	*41.20*	*96.50*

Calculate the molecular mass of succinic acid in benzene.

Solution: By hit-and-trial method. Suppose succinic acid exists as double molecules (dimer) in benzene. Then the ratio $C_1/\sqrt{C_2}$ should be constant. Let us find it out

C_1 (in water)	C_2 (in benzene)	$C_1/\sqrt{C_2} = K$
1.50	24.20	$\frac{1.5}{\sqrt{24.20}} = 0.305$
1.95	41.20	$\frac{1.95}{\sqrt{41.20}} = 0.304$
2.97	97.0	$\frac{2.89}{\sqrt{96.50}} = 0.303$

As $C_1/\sqrt{C_2} = K$ comes out to be almost constant, this proves that $n = 2$.

Molecular mass of succinic acid in benzene = 2 × 11.8 = 236

By logarithmic method. According to this method, the value of n is given by

$$n = \frac{\log C_2 - \log C_2'}{\log C_1 - \log C_1'}$$

This given data is tabulated as under:

S.No.	C_1	log C_1	C_2	log C_2
1.	1.50	0.176	24.2	1.384
2.	1.95	0.290	41.2	1.616
3.	2.89	0.461	96.3	1.985

From (1) and (2),

$$n = \frac{1.616 - 1.384}{0.290 - 0.176} = 2.04$$

From (2) and (3),

$$n = \frac{1.985 - 1.616}{0.416 - 0.290} = 2.16$$

From (3) and (1),

$$n = \frac{1.985 - 1.384}{0.461 - 0.176} = 2.11$$

The whole-number value of $n = 2$,

i.e. succinic acid exists as $\left[\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}\right]_2$ in benzene.

Hence, molecular mass of succinic acid in benzene = 2 × 118 = 236

PROBLEMS FOR PRACTICE

1. Acetic acid was shaken with water and CCl_4 and the following concentrations in moles per litre are found in two layers:

Aqueous layer	5.02	7.8	10.70
CCl_4 layer	0.292	0.725	1.410

Assuming that acetic acid has single molecules in water, show that it has double molecules in CCl_4 solution.

2. In the distribution of a solute between water (C_1) and chloroform (C_2), the following results were obtained (in which C_1 and C_2 have been expressed in the same units):

C_1	0.0160	0.0237
C_2	0.338	0.753

What information do you get regarding the molecular state of the solute in chloroform?

[Ans. Double molecules]

3. An experiment on the distribution of phenol between water and CCl_4 gave the following results:

Conc. in aqueous soln. (C_1):	0.094	0.163	0.274	0.436
Conc. in $CHCl_3$ soln. (C_2):	0.254	0.761	1.85	5.53

What conclusion can be drawn from these results concerning the molecular condition of phenol in chloroform solution?

[Ans. Exists as double molecules]

15.5 STUDYING CHEMICAL EQUILIBRIUM INVOLVING FORMATION OF COMPLEX COMPOUNDS

Some typical reactions involving complex ions are

$$KI + I_2 \rightleftharpoons KI_3$$
$$CuSO_4 + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]SO_4$$

Consider the reaction,

$$KI + I_2 \rightleftharpoons KI_3 \quad \text{or} \quad I^- + I_2 \rightleftharpoons I_3^-$$

The Distribution law helps us determine the equilibrium constant for such equilibrium reactions and to establish the formula for complex ions on the basis of the constancy in the value of the equilibrium constant. The study of this equilibrium involves the following steps:

1. A solution of iodine in CS_2 is shaken with water to find out the distribution coefficient of iodine between water and CS_2.
2. A solution of iodine in CS_2, of known concentration, is shaken with KI solution, also of known concentration (see Fig. 15.7).
3. After the distribution of iodine is complete between the two layers, the concentration of iodine left in the CS_2 layer is determined by titration against standard sodium thiosulphate solution.

Calculations

Suppose,

Initial concentration of iodine in CS_2 = a moles/litre

Initial conc. of KI solution = b moles/litre

Conc. of I_2 left in CS_2 layer after distribution = C moles/litre

Distribution coefficient of I_2 between water and CS_2 = K

Since, iodine reacts with KI, the total concentration of iodine (free + combined) in the aqueous layer is much higher (than if no KI were present).

Thus, total conc. of I_2 (free + combined) in aqueous layer

$$= \text{Initial conc. of } I_2 \text{ in } CS_2 - \text{Conc. of } I_2 \text{ left in } CS_2 \text{ layer}$$
$$= a - c \text{ moles/litre}$$

Concentration of free I_2 in aqueous layer can be obtained from distribution law equation.

$$\frac{\text{Conc. of free } I_2 \text{ in aqueous layer}}{\text{Conc. of } I_2 \text{ in } CS_2 \text{ layer}} = K, \text{ i.e. distribution coefficient}$$

But conc. of I_2 in CS_2 layer = c moles/litre

$\therefore$ conc. of free I_2 in aqueous layer = $K \times C$ moles/litre

= d moles/litre (say)

According to the reaction,

$$KI + I_2 \rightleftharpoons KI_3$$

No. of moles I_2 combined = No. of moles of KI combined = No. of moles of KI_3 formed

$\therefore$ conc. of KI_3 in aqueous layer = d moles/litre

$\therefore$ conc. of KI in aqueous layer = $(b - d)$ moles/litre

$\therefore$ conc. of I_2 in the aqueous layer = $K \times C$ moles/litre

Substituting these values in the equilibrium law expression, viz. the equilibrium constant, K' can be calculated.

$$K' = \frac{[KI_3]}{[KI][I_2]}$$

Starting with different initial concentrations of iodine and KI solutions, the value of K' is determined in each case. If we obtain nearly constant values of K' it confirms the formula of the complex (KI_3).

Example 9 *The partition coefficient of iodine between CS_2 and H_2O is 410. A solution of KI containing 8 g of the salt per litre was taken with CS_2 until equilibrium was attained. It was found that at equilibrium, the aqueous layer contained 2.15 g of iodine per litre and the CS_2 layer, 35.42 g iodine per litre. Calculate the equilibrium constant for the reaction.*

$$KI + I_2 \rightleftharpoons KI_3$$

Given that the concentration of iodine in the aqueous layer is the sum offree and combined iodine.

Solution: The equilibrium constant for the reaction is given by,

$$K = \frac{[KI_3]}{[KI][I_2]} \qquad \text{(i)}$$

In the CS_2 layer, all the iodine is present as free iodine. Concentration of ***free iodine*** in the aqueous layer can be calculated by using the equation for partition coefficient.

$$\frac{\text{Conc. of free iodine in } CS_2 \text{ layer } (C_1)}{\text{Conc. of free iodine in aqueous layer } (C_2)} = K \text{ (partition coefficient)}$$

Substituting the values, we have

$$\frac{35.42}{C_2} = 410$$

or
$$C_2 = \frac{35.42}{410} \text{ g/litre} = \frac{35.42}{410 \times 254} \text{ moles/litre}$$

$$= 0.0003401 \text{ moles/litre}$$

or
$$[I_2] = 0.0003401 \text{ M}$$

Total iodine in aqueous layer = 2.15 g/litre = $\frac{2.15}{254}$ moles/litre = 0.008465 moles/litre

$\therefore$ Combined iodine in the aqueous layer = $0.008465 - 0.0003401$

$= 0.008125$ moles/litre

But

$$[KI_3] = [\text{combined } I_2] \text{ (As per the chemical equation)}$$
$$[KI_3] = 0.008125 \text{ M}$$

Molar conc. of

$$KI = \frac{8}{166} \text{ moles/litre} = 0.04819 \text{ moles/litre}$$

KI used in forming KI_3 = 0.008125 moles/litre

$\therefore$ conc. of free KI, i.e. $[KI] = 0.04819 - 0.008125$

$= 0.04007$ moles/litre

Substituting the values in Eq. (i), we get,

$$K = \frac{[KI_3]}{[KI][I_2]} = \frac{0.008125}{0.04007 \times 0.0003401} = 596.2$$

15.6 UTILITY OF DISTRIBUTION LAW IN THE PROCESS OF EXTRACTION

The distribution law is of great practical utility in extraction and purification of substances. However, the following conditions must be satisfied to achieve efficient extraction.

1. The Value of Distribution Coefficient of the Substance Between Water and the Extracting Solvent Should be Greater in Favour of the Extracting Substance
Distribution coefficient of a substance in water can be varied. If it is desired to lower the distribution coefficient in water, i.e. to make it less soluble in water, this is very much possible. Let us say the substance under question is an organic acid. Its solubility in water can be decreased by adding a small quantity of a mineral acid, which will release H^+ ions. The solubility of the organic acid will be depressed because of common-ion effect.

2. The Extracting Liquid Should not be Used in One Lot but in a Number of Smaller Lots *The following example will establish the truth of this requirement.*

Suppose *X*g of the substance are present in 1 litre of the aqueous solution. Also suppose 1 litre of ether is available as the extracting solvent and that the distribution coefficient of the substance between ether and water is 2. If whole of the extracting liquid is used in one lot and xg be the amount of the substance extracted into ether then we will have

$$\frac{\text{Conc. in ether}}{\text{Conc. in } H_2O} = \frac{x/1000}{(X-x)/1000} = 2$$

or $$x = \frac{2}{3}X = 0.67X$$

Thus, only 67% of the total amount will be extracted in this case.

Instead, suppose the whole of the ether is used in two instalments, each of 500 cm^3. After shaking with the first instalment of 500 cm^3, suppose x_1 *g* of the substance passes into the ether layer.

Then clearly,

$$\frac{x_1/500}{(X-x_1)/1000} = 2 \quad \text{or} \quad x_1 = \frac{1}{2}X = 0.5X$$

Thus, 50% of the total amount is extracted out in this operation. Therefore, the amount of the substance left unextracted = $X - \frac{1}{2}X = \frac{1}{2}X$. Now, one litre of the aqueous solution containing $\frac{1}{2}$ *X*g of the substance is shaken with the remaining 500 cm^3 of ether. Suppose the amount extracted into ether by this operation is x_2 g. It is calculated as under:

$$\frac{x_2/500}{\left(\frac{X}{2}-x_2\right)/1000} = 2 \quad \text{or} \quad x_2 = \frac{1}{4}X = 0.25X$$

i.e. 25% of the total substance passes into the ether layer in this operation. Therefore, the total amount of the substance extracted = 50 + 25 = 75%.

Thus, when 1 litre of ether is used in two equal instalments, the % extraction increases from 67 to 75. Similarly, it can be seen that if one litre of ether is used in four equal instalments, the extraction can be increased to 93.75%. Thus, keeping the total quantity of extracting solvent as constant, we can extract more by using smaller lots of the solvent at a time.

15.7 GENERAL FORMULA FOR AMOUNT OF SUBSTANCE LEFT UNEXTRACTED AND VOLUME OF EXTRACTING LIQUID USED EACH TIME

Suppose *W* g of the substance is present in *V* ml of the solution made in Solvent *A*. Also, suppose that *V* ml of the extracting solvent *B* is used each time and *K* is the distribution coefficient of the substance between the solvents *A* and *B*.

If w_1 g is the amount of the substance is left unextracted in solvent *A* after the first operation then

we have,

$$\frac{\text{Conc. in } A}{\text{Conc. in } B} = K$$

i.e. $$\frac{w_1/V}{(W-w_1)/v} = K \quad \text{or} \quad K\frac{(W-w_1)}{v} = \frac{w_1}{V}$$

or $$KV(W-w_1) = w_1 v$$

or $$w_1(v+KV) = KVW$$

$$w_1 = \frac{KV}{(v+KV)}W \qquad \ldots(15.12)$$

After the second operation, if w_2 g be the amount of the substance left unextracted in Solvent A so that the amount extracted is $(w_1 - w_2)$ g then we have the relation

$$\frac{w_2/V}{(w_1-w_2)/v} = K \quad \text{or} \quad w_2 = \left(\frac{KV}{v+KV}\right)w_1 \qquad \ldots(15.13)$$

Substituting the value of w_1 from Eq. (15.12), we get,

$$w_2 = \left(\frac{KV}{v+KV}\right)\left(\frac{KV}{v+KV}\right)W = \left(\frac{KV}{v+KV}\right)^2 W$$

In general, after the nth operation, the amount of the substance that will be left unextracted is given by

$$\boxed{w_n = \left(\frac{KV}{v+KV}\right)^n W} \qquad (15.14)$$

In order that the extraction may be most efficient, clearly w_n should have the smallest possible value, i.e., smaller lots of the solvent. This can be so only if the factor $\left[\frac{KV}{v+KV}\right]^n$ is as small as possible. In this factor, the denominator $v + KV$ is greater than the numerator KV. Therefore, $KV/(v + KV)$ is less than 1. Hence, the above factor will be smallest possible when n has the largest possible value. It proves that ***multi-step extraction is more economical than single-step extraction.***

Caution

For solving numerical problems, it may be mentioned here that K is the distribution coefficient of the substance between the solvent A already present and the extracting solvent B. If K is given for the distribution of the substance between solvents B and A (i.e. reverse order), the reciprocal of this value should be used in Eq. (15.14).

Parke's Process for Desilverisation of Lead

Silver is more soluble than zinc than in lead. Zinc is immiscible with molten lead. Thus, when zinc is added to argentiferous lead, a large quantity of silver goes into the molten zinc layer leaving little silver in the molten lead layer, because the distribution coefficient of silver between zinc and lead is 300 at 880°C. Zinc containing silver forms the upper layer. Thus, by repeating the process, almost

total quantity of silver can be extracted from lead.

Example 10 *The distribution coefficient of a substance between chloroform and water is 5. Show that the amount of substance extracted from 100 ml of an aqueous solution is more by using 50 ml chloroform at a time in two instalments rather than using 100 ml in one lot.*

Solution: Given that,

$$K = \frac{\text{Conc. in chloroform } (C_1)}{\text{Conc. in water } (C_2)} = \frac{5}{1}$$

Suppose the total amount of the substance to be extracted is W g, present in 100 ml of aqueous solution.

(a) When 100 ml of chloroform is used in one lot

Suppose the amount of substance extracted into chloroform = w g

$\therefore$ amount of the substance left unextracted in water = $(W - w)$g

i.e. the conc. of the substance in chloroform = $\frac{w}{100}$ g per ml

and conc. of the substance in water = $\frac{(W-w)}{100}$ g per ml

$\therefore$ by distribution law,

$$\frac{w/100}{(W-w)/100} = 5 \quad \text{or} \quad w = 5(W-w)$$

or
$$w = \frac{5}{6}W = 0.833\ W\text{g}$$

i.e. the amount extracted will be 0.833 Wg.

(b) **When 50 ml of chloroform is used at a time**

(i) In the first extraction,

suppose, the amount of the substance extracted into chloroform = w_1 g

$\therefore$ amount of the substance left unextracted in water = $(W - w_1)$ g

i.e. conc. of the substance in chloroform layer = $\frac{(W-w_1)}{100}$ g/ml

$\therefore$ by distribution law,

$$\frac{w_1/50}{(W-w_1)/100} = 5 \quad \text{or} \quad \frac{w_1}{50} \times \frac{100}{W-w_1} = 5$$

or
$$2w_1 = 5(W-w_1) \quad \text{or} \quad w_1 = \frac{5}{7}W = 0.714\ W\text{g}.$$

Amount of the substance left unextracted in 100 ml of the aqueous solution

$$= W - 0.714\,W = 0.286\ W\text{g}.$$

(ii) In the second extraction,

Suppose the amount of substance extracted into chloroform = w_2 g

Then amount of substance left unextracted in water = $(0.286\ W - w_2)$g

i.e. conc. of substance in chloroform = $w_2/50$ per ml

and conc. of substance in water = $(0.286\ W - w_2)/100$ g per ml

Applying distribution law, we get

$$\frac{w_2/50}{(0.286W - w_2)/100} = 5$$

or
$$\frac{w_2}{50} \times \frac{100}{0.286W - w_2} = 5$$

or
$$2w_2 = 5(0.286\ W - w_2) \quad \text{or} \quad w_2 = 0.204\ W \text{ g.}$$

$\therefore$ total amount of the substance extracted = $0.714\ W + 0.204\ W = 0.918\ W$

Since $0.918\ W$ g is more than $0.833\ W$ g, the given statement is correct.

Example 11 *At 25°C, the distribution ratio of H_2S between water (G) and benzene (C_2) is 0.17.*

(a) What is the minimum volume of C_6H_6 necessary at 25°C to extract in one step 90% of H_2S present in one litre of 0.1 molar aqueous solution?

(b) What total volume of benzene will be required if the 90% extraction were to be completed in three steps of equal volumes of benzene?

(c) Using 100 ml of benzene every time, how many extractions will be required to complete 90% extraction?

Solution: (a) Suppose volume of benzene required = V litres

As extraction is 90%, amount left unextracted = 10%

$$\frac{w_n}{W} = \frac{10}{100} = 0.1$$

$$n = 1 \qquad V = 1 \text{ litre} \qquad K = 0.17$$

Substituting these values in the general formula for extraction,

$$\frac{w_n}{W} = \left(\frac{KV}{v + KV}\right)^n$$

or
$$0.1 = \left(\frac{0.17 \times 1}{v + 0.17 \times 1}\right)^1 \text{ or } v = 1.53 \text{ litres}$$

(b) Suppose the total volume of benzene required = $3v$ litre (v litre in each step) Then clearly,

$$v = v \text{ litre}, n = 3$$

Further, as the extraction = 90%, amount left unextracted = 10%

i.e.
$$\frac{w_n}{W} = \frac{10}{100} = 0.1$$

Also, V = litre and $K = 0.17$

Putting these values in the formula,

$$\frac{w_n}{W} = \left(\frac{KV}{v + KV}\right)^n, \text{ we get } 0.1 = \left(\frac{0.17 \times 1}{v + 0.17 \times 1}\right)^3$$

or $$(v + 0.17 \times 1)^3 = \frac{(0.17)^3}{0.1} \quad \text{or} \quad (v + 0.17)^3 = 10 \times (0.17)^3$$

Taking cube roots of both the sides, we get

$$v + 0.17 = (10)^{1/3} \times 0.17$$

Taking logarithm of both the sides, we get

$$\log(v + 0.17) = \frac{1}{3}\log 10 + \log 0.17 = \frac{1}{3} + \bar{1}.2304 = 0.3333 + \bar{1}.2304 = \bar{1}.5637$$

$$v + 0.17 = \text{antilog}(\bar{1}.5637) = 0.3662$$

$$v = 0.3662 - 0.17 = 0.1962 \text{ litres}$$

Total volume required = $3v = 3 \times 0.9162$ litres = 0.5886 litre

(c) Here, $\frac{w_n}{W} = \frac{1}{10} = 0.1$

$$v = 100 \text{ ml} = 0.1 \text{ litre}, V = 1 \text{ litre}, K = 0.17, n = ?$$

Substituting these value in the formula,

$$\frac{w_n}{W} = \left(\frac{KV}{v + KV}\right)^n, \text{ we get } 0.1 = \left(\frac{0.17 \times 1}{0.1 + 0.17 \times 1}\right)^n \text{ or } 0.1 = \left(\frac{0.17}{0.27}\right)^n$$

Taking logarithm of both the sides, we get,

$$n \log \frac{0.17}{0.27} = \log 0.1 \text{ or } n(\log 17 - \log 27) = \log 1/10 \text{ or } n(0.2304 - 0.4314) = -1$$

or $$n(-0.2010) = -1 \text{ or } n = \frac{1}{0.201} = 5$$

Thus, 5 extractions are needed to accomplish the work.

PROBLEMS FOR PRACTICE

1. 1000 ml of an aqueous solution containing 30 g of an organic acid is extracted with 300 ml of ether using 100 ml in each operation. Calculate the amount of the organic acid left in aqueous. The partition coefficient of organic acid between ether and water is 3.

[Ans. 13.65 g]

2. When one litre of an aqueous solution containing 5 g of a solute is shaken with 50 ml of ether, it is found that 0.85 g of the solute passes into ether layer. How much of the solute will be left unextracted when the same aqueous solution is shaken with a second instalment of 50 ml of ether? What would be the difference if there were one extraction only with 100 ml of ether? The solute may be supposed have the same molecular weight in both water and ether.

[Ans. (a) 3.46 g (b) 0.J0J more will be left unextracted]

3. An aqueous solution contains 10 g of solute per litre. When 1 litre of the solution is treated with 100 ml of ether, 6 g of the solute are extracted. How much of the solute would be extracted from the aqueous solution by a further 100 ml ether? Assume that the molecular state of solute is the

same in ether and water.

[Ans. 2.4 g]

4. 100 ml of an aqueous solution of iodine containing 0.008 g of iodine was extracted with 20 ml of carbon tetrachloride. If iodine is 15 times more soluble in carbon tetrachloride than in water, find out the amount of iodine remaining in the aqueous layer. If iodine is extracted a second time with 20 ml of carbon tetrachloride, how much of it will remain unextracted in the aqueous layer?

[Ans. 0.002 g, 0.0005 g]

15.8 DETERMINATION OF DEGREE OF HYDROLYSIS FROM DISTRIBUTION LAW

Let us consider the case of aniline hydrochloride. Determination of degree of hydrolysis of this salt involves the following steps:

1. Determination of the Hydrolysis Constant* Aniline hydrochloride is hydrolysed as

$$C_6H_5NH_3Cl + H_2O \rightleftharpoons C_6H_5N^+H_3OH^- + HCl$$
$$\downarrow$$
$$C_6H_5NH_2 + H_2O$$

The hydrolysis constant is given by

$$K_h = \frac{[\text{Free aniline}][\text{Free HCl acid}]}{[\text{Unhydrolysed salt}]}$$

To get the value of K_h, we need to find the molar concentrations of free aniline, free HCl acid and the unhydrolysed salt in an aqueous solution of aniline hydrochloride. This is done by shaking an aqueous solution of aniline hydrochloride of known concentration with benzene. As a result, the free aniline distributes itself between the two solvents, i.e. water and benzene, whereas HCl acid and the unhydrolysed salt remain in the aqueous layer only as shown in Fig. 15.7.

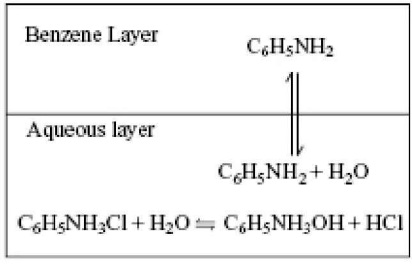


Fig. 15.7 *Shaking an aqueous solution of aniline hydrochloride with benzene*

(a) Calculation of Concentration of Free Aniline in Aqueous Layer The concentration of aniline present in the benzene layer is found by taking a known volume of this layer, evaporating off the benzene and finding the weight of aniline left. Knowing the concentration of aniline in the benzene layer, that in the aqueous layer can be calculated if the partition coefficient of aniline between water and benzene is known.

(b) Calculation of Concentrations of Free HCl Produced

From the hydrolysis equation,

Number of moles of HCl produced = Total number of moles of aniline produced.

But total amount of aniline produced = Amount of aniline present in the benzene layer + Amount of aniline present in the aqueous layer.

These quantities have been calculated in Step (a) above. Hence, the total number of moles of aniline produced and the free HCl produced can be calculated. Knowing the volume of the aqueous layer, the concentration of free HCl in the aqueous layer can be calculated.

(c) Calculation of the Concentration of the Unhydrolysed Salt From the hydrolysis equation, we can say that the number of moles of the salt hydrolysed is equal to total number of moles of the aniline produced or free HCl produced, which has already been shown in Step (b) above. Knowing the initial number of moles of the salt taken, the number of moles of the salt left unhydrolysed can be calculated. Knowing the volume of the aqueous layer, the concentration of the unhydrolysed salt can be calculated.

2. Calculation of Degree of Hydrolysis Knowing the hydrolysis constant K_h, the degree of a solution of aniline hydrochloride having a concentration of C moles/litre can be calculated directly from the expression.

$$h = \sqrt{\frac{K_h}{C}}$$

To understand terms like hydrolysis constant and degree of hydrolysis, refer chapter on Electrochemistry II.

This was a case of salt of weak base and strong acid. When other salts are being considered, viz. salts of strong base and weak acid or weak base and weak acid, the relevant equation between hydrolysis constant and degree of hydrolysis may be used.

Relation between K_h and C

(a) For salts of weak acid and strong base, (or for salts of strong acid and weak base), $h = \sqrt{\frac{K_h}{C}}$

(b) For salts of weak acid and weak base, $h = \sqrt{K_h}$ assuming h is very small as compared to J.

Example 12 *In an experiment to determine the hydrolysis constant of aniline hydrochloride at 20°C, 15 g of salt were shaken with 1000 cm^3 of water and 100 cm^3 of benzene until equilibrium was established. 50 cm^3 of benzene layer was then found to contain 0.2360 g of aniline. The partition coefficient of aniline between benzene and water at 20°C is found to be 11.3. Calculate the hydrolysis constant and the degree of hydrolysis of aniline hydrochloride.*

Solution: Aniline hydrochloride is hydrolysed as,

$$C_6H_5NH_3Cl + H_2O \rightleftharpoons C_6H_5NH_3OH + HCl$$
$$\downarrow$$
$$C_6H_5NH_2 + H_2O$$

Hence,

$$K_h = \frac{[\text{Free aniline}][\text{Free HCl acid}]}{[\text{Unhydrolysed salt}]}$$

Thus, to find K_h, we need to find the molar concentrations of free aniline, free HCl and hydrolysed salt in aqueous solution.

To Calculate the Concentration of Free Aniline in the Aqueous Layer It is given that 50 cm^3 of benzene layer contains 0.2360 g of aniline, i.e. concentration of aniline present in the benzene layer

$$= 0.2360 \text{ g of aniline in } 50 \text{ cm}^3 \text{ of benzene}$$
$$= \frac{0.2360}{93} \times \frac{1000}{50} \text{ moles/litre}$$
$$= 0.05075 \text{ moles/litre} \qquad (\because \text{Mol. mass of aniline, } C_6H_5NH_2 = 93)$$

As partition coefficient of aniline between benzene and water is given to be 11.3, this means

$$\frac{\text{Conc. in benzene layer}}{\text{Conc. in aqueous layer}} = 11.3$$

But conc. in benzene layer = 0.05075 moles/litre

$\therefore$ Conc. in aqueous layer = $\frac{0.05075}{11.3}$ moles/litre = 0.00449 moles/litre

$\therefore$ Amount of aniline present in 1000 cm^3 of aqueous layer = 0.00449 moles

As the volume of aqueous layer is 1000 cm^3 therefore, concentration of free aniline is given by

[Free aniline] = 0.00449 moles/litre

To Calculate the Concentration of Free HCl Acid Produced We understand from the hydrolysis equation that,

No. of moles of HCl produced = No. of moles of aniline produce

But total amount of aniline produced = Amount of aniline present in the benzene layer + Amount of aniline present in the aqueous layer

Conc. of aniline in the benzene layer = 0.05075 moles/litre

$\therefore$ Amount of aniline present in 100 cm^3 of benzene layer = 0.005075 moles

Also, conc. of aniline in aqueous layer = 0.00449 moles/litre

$\therefore$ Amount of aniline present in 1000 cm^3 of aqueous layer = 0.00449 moles

$\therefore$ Total amount of aniline produced = 0.005075 + 0.00449 = 0.009565 moles

Thus, no. of moles of HCl produced = 0.009565 moles

As volume of the aqueous layer is 1000 cm^3, [Free HCl] = 0.009565 moles/litre

To Calculate the Concentration of the Unhydrolysed Salt From the hydrolysis equation, we can say,

$$\text{No. of moles of aniline hydrochloride hydrolysed} = \text{No. of moles of aniline or HCl produced} = 0.009565 \text{ moles}$$

As aniline hydrochloride taken was 15 g and molecular mass of aniline hydrochloride ($C_6H_5NH_3Cl$) is 129.5, therefore

$$\text{No. of moles of aniline hydrochloride taken} = \frac{15}{129.5} \text{ moles} = 0.11583 \text{ moles}$$

$\therefore$ No. of moles of salt left unhydrolysed = 0.11583 − 0.009565 = 0.10625 moles

As the volume of the aqueous layer is 1000 cm^3,

[Unhydrolysed salt] = 0.10626 moles/litre

Hence,

$$K_h = \frac{[\text{Free aniline}][\text{Free HCl acid}]}{[\text{Unhydrolysed salt}]}$$

$$= \frac{0.0049 \times 0.009565}{0.10626} = 4.04 \times 10^{-4}$$

As aniline is a salt of weak base and strong acid, the degree of hydrolysis will be,

$$h = \sqrt{\frac{K_h}{C}}$$

where, C is the original concentration of the salt.

But, $C = 0.11583$ moles/litre (calculated above)

$$h = \sqrt{\frac{4.04 \times 10^{-4}}{0.11583}} = 5.9 \times 10^{-2}$$

3. Separation of a Mixture of Small Amounts of Organic Substances Using Liquid-liquid Chromatography

This is versatile technique for separation of a mixture of small amounts of organic substances. The separation is carried in a glass tube packed with an inert solid material (silica) soaked in Solvent 1. The mixture solution is dropped at the column top. Then another immiscible Solvent 2 is allowed to flow down the column (Fig. 15.8). A film of Solvent 1 held by the silica forms the stationary liquid phase, while the running Solvent 2, the mobile liquid phase.

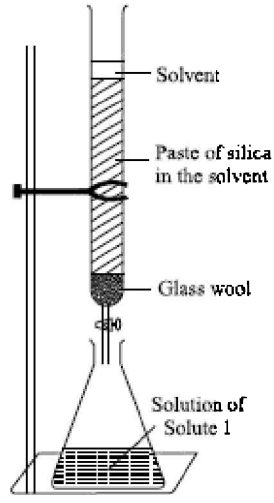


Fig. 15.8 *Set-up of the apparatus for liquid-liquid chromatography*

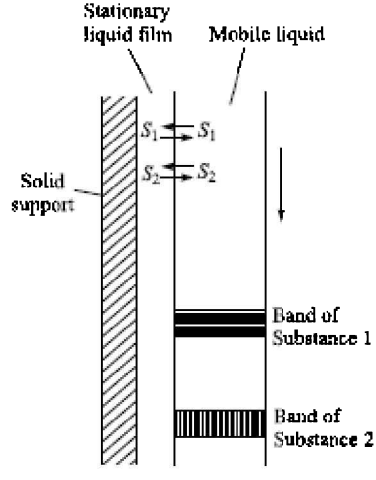


Fig. 15.9 *Separation of substances 1 and 2 (S_1 and S_2) in the form of bands*

The liquid film on the solid support acts as the ***stationary*** state while the second liquid which is immiscible with the first liquid forms the mobile liquid phase. The solute which is more soluble in Solvent 2 comes down in the column first (distribution coefficient of the substance 2 in the liquids 2 and 1 is more than unity).

Thus, $$\frac{C_S}{C_M} = K_D$$

where, C_S = Concentration in stationary liquid phase

C_M = Concentration in the mobile liquid phase

K_D = Distribution coefficient.

Different components in the mixture have different distribution coefficients. They pass into the mobile phase in order of their distribution coefficients. ***The component (say S_2) with higher distribution coefficient is extracted first and is the first to move down the column. The location of the components is easy if they are coloured.*** Otherwise, they are visualised with the help of a locating agent (Fig. 15.9). The portion of the solvent (or band) containing each component is received in a separate vessel and the solute recovered from its distillation.

SOLVED EXAMPLES

Example 13 *A solute distributes in the ratio of 10 : 1 between ether and water. If 5 g of the solute is added to a liquid mixture containing 100 cm^3 each of ether and water, what is the mass of solute dissolved in aqueous layer?*

Solution: Let the mass of the solute in aqueous layer be = x g

Then the mass of the solute in ether layer = $(5 - x)$ g

Conc. of solute in ether layer = $(5 - x)$ g per 100 cm^3

Conc. of solute in aqueous layer = 5 g per 100 cm^3

According to distribution law,

$$\frac{5-x}{x} = \frac{10}{1} \quad \text{or} \quad 5 - x = 10x \quad \text{or} \quad x = 0.45 \text{ g}$$

Example 14 *In an experiment 1, w_1 g of a solute are added to two immiscible solvent. Its concentrations are found to be C_1 and C_2. In another experiment, w_2 g of the solute are added to the pair of same solvents. Its concentration is found to be C'_1 and C'_2. In Solvent 2, solute undergoes association as $nA \rightleftharpoons A_n$. Formulate an equation to calculate n.*

Solution:

$$\frac{C_1}{\sqrt[n]{C_2}} = K \text{ i.e., } \frac{C_1}{(C_2)^{1/n}} = K. \qquad \ldots(1)$$

$$\frac{C'_1}{\sqrt[n]{C'_2}} = K \text{ i.e } \frac{C'_1}{(C'_2)^{1/n}} = K \qquad \ldots(ii)$$

From (i) and (ii)

$$n = \frac{\log C_2 - \log C'_2}{\log C_1 - \log C'_1}$$

Example 15 *In the expression for distribution law, is the value of partition coefficient affected on changing the units of concentrations?*

Solution: No. As $K = C_1/C_2$, there is no effect on changing the units of concentrations C_1 and C_2 as long as they are in the same units.

Example 16 *Can we find the distribution coefficient of iodine between water and ethyl alcohol?*

Solution: No, because ethyl alcohol and water are miscible. The two layers cannot be separated.

Example 17 *Why is the constant value of partition coefficient according to the expression $K = C_1/C_2$ not obtained even at constant temperature in the following experiments?*

(a) HCl is added to water and CCl_4.

(b) CH_3COOH is added to water and benzene.

(c) NH_3 is added to water and CS_2.

Solution: This is because a change in molecular state takes place.

(a) HCl undergoes dissociation in water ($HCl + aq \rightarrow H^+ + Cl^-$).

(b) CH_3COOH undergoes association in benzene, i.e.

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

(c) NH_3 combines with water ($NH_3 + H_2O \rightleftharpoons NH_4OH$).

Example 18 *On shaking a solute with two immiscible liquids, it is observed that 10% of the solute in Solvent 2 undergoes dimerization. Derive an expression for constant value of K.*

Solution:

$$K = \frac{C_1}{\sqrt[n]{C_2 \alpha}}$$

α = 10% = 0.10 and n = 2, substituting the values of α and n, we get

$$K = \frac{C_1}{\sqrt{0.1 C_2}}$$

Example 19 *Why is zinc used in Parke 's process for desilverisation of lead?*

Solution: This is because silver is more soluble in zinc than in lead. Also, zinc is immiscible with molten lead.

Example 20 *Why is 100% extraction not possible howsoever large number of instalments of the extracting solvent may be used?*

Solution: Amount left unextracted after n instalments each of volume v ml from a solution containing W g of the solute in V ml of the solution is given by the equation,

$$w_n = \left[\frac{KV}{v + KV}\right]^n W$$

where, K = Partition coefficient of solute between the original solvent and the extracting solvent.

As $KV/(V + KV) < 1$, therefore, w_n will become smaller and smaller if n is larger. It can be seen from the equation that w_n can never be equal to zero however large value n we may have.

SUMMARY

1. *Nernst distribution law states:* A solute distributes itself between two immiscible liquid solvents in such a way that the ratio of concentrations of the solute in the two solvents is constant at constant temperature, independent of any other molecular species present, provided that the solute

has the same molecular state in both the solvents.

2. The distribution law is applicable only if
   (a) the temperature remains constant throughout the experiment
   (b) the two liquids should be mutually immiscible
   (c) the amount of solute added should be small
3. Thermodynamic derivation of distribution law is based upon the principle that if there are two phases in equilibrium, the chemical potential of a substance must be same in both the phases.
4. When the solute combines with one of the solvents, there is no modification in the distribution law equation except that the numerical value of the partition constant is changed.
5. Distribution law can be used to determine the solubility of a solute in a solvent and to determine the extent of association or dissociation of a solute in a solvent.
6. Parke's process for desilverisation of lead is based on the principle of distribution law. Silver is more soluble than zinc in lead.

KEY RELATIONS

1. $\dfrac{\text{Conc. of } X \text{ in solvent } A}{\text{Conc. of } X \text{ in solvent } B} = \dfrac{C_1}{C_2} = K$

2. Modification in distribution law equation

Dissociation $\qquad \dfrac{C_1(1-\alpha)}{C_2} = K$

Association $\qquad \dfrac{C_1}{\sqrt[n]{C_2}} = K$

3. $\dfrac{C_1}{C_2} = \dfrac{\text{Solubility of solute in solvent 1 } (S_1)}{\text{Solubility of the solute in solvent 2 } (S_2)}$

4. $K' = \dfrac{[KI_3]}{[KI][I_2]}$ (For the reaction $KI + I_2 \rightleftharpoons KI_3$)

5. $w_n = \left(\dfrac{KV}{v + KV}\right)^n W$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. When a bottle of soda water is opened, the partial pressure of CO_2_____.
   (a) decreases
   (b) increases
   (c) remains the same
   (d) none of these
2. Benzoic acid when shaken with mixtures of benzene and water undergoes dimerisation in benzene. The distribution law applicable here is

(a) $\frac{C_1}{C_2} = K_D$

(b) $\frac{C_1}{\sqrt[3]{C_2}} = K_D$

(c) $\frac{C_1}{\sqrt[2]{C_2}} = K_D$

(d) none of these

3. The Nernst distribution law $K_D = C_1/C_2$ is not applicable if the solute undergoes

   (a) association in one of the solvents

   (b) dissociation in one of the solvents

   (c) association and dissociation in one of the solvents

   (d) none of the above

4. With the help of distribution law, we can

   (a) determine the association or dissociation of the solute in one of the solvents

   (b) determine the solubility of the solute in various solvents

   (c) deduce the formula of complex ions

   (d) all of the above

5. When succinic acid or oxalic acid is shaken with ether and water, it____in water.

   (a) associates to form dimer

   (b) dissociates into ions

   (c) remains the same

   (d) none of these

6. The Nernst distribution law equation $C_1/C_2 = K$ applies when

   (a) the molecular state of the solute is the same in both the solvents

   (b) the molecular state of the solute is different in both the solute

   (c) the molecular state of the solute is different in both the solute

   (d) none of these

7. In the first extraction, the amount of the substance left unextracted is given by the formula (K is distribution coefficient, V ml of the aqueous solution contain A grams of an organic substance)

   (a) $x_1 = A\frac{KV}{KV+v}$

   (b) $x_1 = A\frac{KV}{KV+v^2}$

   (c) $x_1 = A^2\frac{KV}{KV+v}$

   (d) $x_1 = A\frac{K^2V}{KV+v}$

8. The greater the distribution ratio in favour of the organic solvent, the _____ will be the amount extracted in any one operation.

(a) greater

(b) lesser

(c) equal

(d) none of these

9. The distribution law is applied in the

   (a) Haber's process for the manufacture of NH_3

   (b) Parke's process for the extraction of Ag

   (c) Contact process for the manufacture of H_2SO_4

   (d) None of the above

Answers

1. (a)
2. (c)
3. (c)
4. (d)
5. (b)
6. (a)
7. (a)
8. (a)
9. (b)

SHORT-ANSWER QUESTIONS

1. Explain the application of distribution law in the determination of degree of hydrolysis of aniline hydrochloride.
2. How can distribution law be used to study the formation of complex ions I_3^-?
3. Define distribution law. How is the law modified if the solute forms dimers in one of the solvents?
4. Define 'chemical potential'. Applying the concept of 'chemical potential', how can 'Nernst distribution law' be derived?
5. Define distribution law. Derive the expression showing how the law is modified if the solute undergoes association in one of the solvents with degree of association equal to α.
6. State the Nernst distribution law. Derive the modified expression if the solute undergoes dissociation in one of the solvents with degree of dissociation equal to α.
7. A solute has normal molecular state in Solvent 1 but one mole of it combines with n moles of Solvent 2 to form a compound. Derive the modified expression for distribution law and comment on the result obtained.
8. How do we use distribution law in desilverisation of lead?
9. A solute undergoes association in a solvent according to the equation $nX \rightleftharpoons X_n$. How can you determine the value of n by applying distribution law?

GENERAL QUESTIONS

1. Define 'hydrolysis constant' and 'degree of hydrolysis'. Applying distribution law, how can the degree of hydrolysis of aniline chloride at a particular concentration be determined?
2. Define distribution law. discuss its application to establish the formation of complex ion I_3^- according to the following equilibrium:

$$I^- + I_2 \rightleftharpoons I_3^- \text{ (or } KI + I_2 \rightleftharpoons KI_3\text{)}$$

3. State and explain Nernst distribution law. How can it be applied to determine
   (a) the solubility of a solute in a particular solvent?
   (b) the extent of association or dissociation of the solute in a solvent?
4. In order to extract a solute *A* from its solution in a solvent *Y* by means of solvent *X* when both *X* and *Y* are immiscible, explain as to why it is always advised to use small lots of the solvent *X* at a time. Derive the necessary relation.
5. Derive the expression for the amount of solute left unextracted after *n* instalments of υ ml each from a solution containing *W* g solute in *V* ml the solution.
6. Discuss the statement: "Multi-step extraction is more economical than a single-step extraction"
7. State and explain 'Nernst distribution law'. What are the conditions under which the law is applicable? Derive the law thermodynamically.
8. Define distribution law. How is the law modified if the solute undergoes
   (a) association in one of the solvents
   (b) dissociation in one of the solvents
9. State 'Nernst distribution law'. Prove that the law does not undergo modification if the solute combines with one of the solvents except that the numerical value of the partition coefficient changes.



Electrochemistry-I 16

LEARNING OBJECTIVES

- Classify electrical conductors into different types
- Differentiate between strong and weak electrolytes
- Learn factors affecting electrolytic conductors
- Differentiate between metallic and electrolytic conductors
- Define conductance, resistance, specific resistance (resistivity), specific conductivity and interrelate them
- Differentiate between equivalent conductance and molar conductance
- Derive a relationship between molar conductivity and specific conductivity
- Learn the measurement of different types of conductivities
- Study the effect of dilution on specific conductance and equivalent conductance
- Learn the postulates of Arrhenius' theory of ionisation
- Study Ostwald dilution law
- Study variation of conductivity with concentration of strong electrolytes and Debye-Huckel-Onsagar equation
- Learn Kohlrasch law and its applications
- Study migration of ions and transport number
- Determination of transport number by Hittorf method and moving boundary method
- Derive a relation between ionic conductance and transport number
- Understand applications of conductance measurement

16.1 INTRODUCTION

We can broadly classify substances into two types as far as conduction of electricity through them is concerned. These are conductors and insulators.

Substances that allow the passage of electricity through them are called ***conductors*** while those which do not allow electricity to pass through them are called ***insulators.***

Conductors can be further classified into two types as stated below:

1. Electronic Conductors These substances conduct electricity without undergoing any decomposition. Electricity is conducted by the flow of electrons in this type of conductors which are mostly metals with the exception of graphite and certain minerals.

2. Electrolytic Conductors (Electrolytes) These substances undergo decomposition when electricity is passed through them. Acids, bases, and salt solutions in water and fused salts come under this category. Electricity is conducted by ions in this case.

Electrolytes can be subclassified into two types:

(a) Strong Electrolytes Substances like strong acids (H_2SO_4, HNO_3, HCl, etc.), strong bases (NaOH, KOH, etc.) and salts in solution or molten state are completely ionised and conduct electricity to a large extent. Such electrolytes are called strong electrolytes.

(b) Weak Electrolytes Substances such as weak acids (like CH_3COOH) and weak bases (like NH_4OH) are not completely ionised in solution and hence do not conduct electricity to a great extent and are called weak electrolytes.

Non-ionic substances like sugar, urea, etc., do not conduct electricity at all and are called non-electrolytes.

16.1.1 Factors Affecting Electrolytic Conductance

Factors affecting electrical conductivity of solutions are described below:

1. Interionic Attraction Interaction between the ions of the solute determine the conductivity. Greater the attractive forces between the ions of the solute, smaller will be the conductivity. Such interactions are called solute-solute interactions.

2. Solvation of Ions These are the interactions between the ions of the solute and the solvent known as solute-solvent interactions. Greater the extent of solute-solvent interactions (solvation of ions), smaller the electrical conductance.

3. Viscosity of the Solvent This factor involves solvent-solvent interactions. Greater the viscosity of the solvent, greater will be the hindrance to the movement of the solute ions and hence, smaller will be the conductance.

4. Temperature The two types of conductors show different behaviours with increase of temperature. While the conductance of electrolytic conductors increases, that of metallic conductors decreases with the rise of temperature. In the case of electrolytic conductors, the inter-ionic attractions and viscosity decrease with increase of temperature. This results into increase of conductance. However, we observe a decrease in conductance of metallic conductors with temperature due to increase in the vibrations of kernels of metal atoms, which impede the flow of electrons resulting in decrease of conductance.

16.1.2 Main Points of Difference Between Metallic and Electrolytic Conductors

The main points of difference between the two types of conductors are given in Table 16.1.

Table 16.1 *Metallic and electrolytic conductors*

Metallic Conductor	Electrolytic Conductor
1. In metallic conductors, the electricity is conducted by the flow of electrons from a negative potential to a positive (or less negative) potential.	1. In electrolytic conductors, the electric current is carried out by the charged ions moving towards the oppositely charged electrodes.
2. No chemical change takes place when a metallic (or electronic) conductor is conducting electricity No new products are formed.	2. Conduction of electricity by electrolytic conductors is accompanied by some definite chemical process with the evolution of some gases or deposition of some metals at the

	electrodes.
3. In metallic conduction, temperature has the effect of decreasing the conductance, i.e., conductance of a metallic conductor decreases with increase of temperature. Metallic conductance becomes pronounced at low temperature. This is because at low temperature, the kernels of the atoms have the least vibrations and offer the least resistance to the flow of electrons.	3. In electrolytic conductors, the conductance In electrolytic conductors, the conductance increases with the rise of temperature. This is due to increase in the mobility of the ions and increase in the degree of ionisation of the electrolytes.

16.2 ELECTRICAL RESISTANCE AND ELECTRICAL CONDUCTANCE

1. Resistance The law that gives the exact relationship between resistance, current and voltage is called Ohm's law. It states:

If to the ends of a conductor, a voltage 'E' is applied and a current 'I' flows through it then the resistance 'R' of the conductor is given by E/I.

Current is generally measured in amperes, whereas voltage is measured in volts. If one ampere of current flows through a conductor when a voltage of one volt is applied to it, the resistance of the conductor is taken as 1 ohm (written as Ω).

Mathematically, the law can be put as

$$R = \frac{E}{I}$$

All electrolytic solutions as well as metallic conductors obey Ohm's law.

2. Conductance The reciprocal of the electrical resistance is called the conductance. It is usually represented by C. Thus,

$$C = \frac{1}{R}$$

It is more common practice to speak of the conductance of a solution rather than its resistance.

Units The units of conductance are siemen (S) or ohm^{-1} or mho ($1\ S = 1\ \Omega^{-1}$).

3. Specific Conductance (k) Resistance (R) of a conductor is

(a) directly proportional to its length (l), and

(b) inversely proportional to its area of cross section (a)

i.e. $$R \propto \frac{l}{a}$$

or $$R = \rho \frac{l}{a} \qquad \ldots(16.1)$$

where ρ is the constant of proportionality, called ***specific resistance*** or ***resistivity.*** Its value depends upon the material of the conductor.

"The reciprocal of resistivity is known as ***specific conductivity*** or simply ***conductivity."*** It is denoted by K.

Thus, if K is the specific conductivity and C is the conductance of the solution then

$$R = \frac{1}{C} \quad \text{or} \quad \rho = \frac{1}{K}$$

Substituting the values of R and P in Eq. (16.1) above

$$\frac{1}{C} = \frac{1}{K} \times \frac{l}{a} \text{ or } K = C \times \frac{l}{a}$$

Now, if l = 1 cm and a = 1 sq. cm then

$$K = C$$

Hence, specific conductivity of a solution is defined as the ***conductance of a solution of 1 cm length and having 1 sq cm as the area of cross section.*** Alternatively, it may be defined as the ***conductance of one centimetre cube of the solution of the electrolyte.*** This is illustrated in Fig. 16.1.

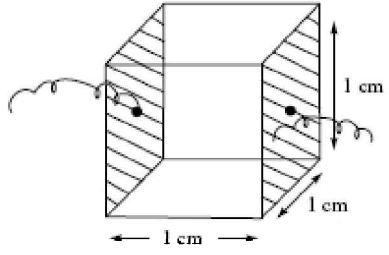


Fig. 16.1 *Specific conductivty.*

If the volume of the solution is V cm^3, the specific conductivity of such a solution at this dilution ***V*** is written as K_V.

Units Resistivity or specific resistance (ρ)

$$= R\frac{a}{l} = \text{ohms}\,\frac{(\text{cm})^2}{\text{cm}} = \text{ohm cm or ohm m in SI units.}$$

$$\text{Specific conductivity } (K) = \frac{1}{\rho} = \frac{1}{\text{ohm cm}}$$

$$= \text{ohm}^{-1}\ \text{cm}^{-1} \text{ or } \Omega^{-1}, \text{cm}^{-1}, \text{or S cm}^{-1}, \text{or S m}^{-1} \text{ in SI units}$$

Note IUPAC recommends the use of the term ***resistivity*** over ***specific resistance*** and the term ***conductivity*** over ***specific conductance*** or ***specific conductivity.***

4. Equivalent Conductance (Equivalent Conductivity) ***Equivalent conductivity*** of a solution at a dilution V is defined as the ***conductance of all the ions produced from one gram equivalent of the electrolyte dissolved in V cm^3 of the solution when the distance between the electrodes is so large that whole of the solution is*** contained between them. It is represented by λ_{eq}.

(a) Relationship between Equivalent Conductivity and Specific Conductivity The relationship between equivalent conductivity and specific conductivity may be obtained as follows:

Consider a rectangular vessel with its two opposite walls one cm apart and made of some metal sheets so that they act as the electrodes.

Case I: Suppose 1 cm^3 of the solution containing 1 g eq. of the electrolyte is taken in the vessel (Fig. 16.2). The conductance of this solution will be its specific conductivity. Further, 1 cm^3 of the solution

taken contains one gram equivalent of the electrolyte, the conductance of the solution will be its equivalent conductivity (by definition). Thus, when 1 cm^3 of the solution containing one gram equivalent of the electrolyte is considered, the equivalent conductivity becomes equal to its specific conductivity.

Case II Suppose 4 cm^3 of the solution containing one gram equivalent of the electrolyte is taken in the vessel. The conductance of the solution will be still equal to its equivalent conductivity at this dilution but now there will be 4 cubes, each of volume 1 cm^3 as shown in Fig. 16.2. The conductance of each 1 cm^3 of the solution is equal to its specific conductivity so that the total conductance of the solution, i.e., equivalent conductivity is four times the specific conductivity.

$$\text{Equivalent conductivity} = \text{Specific conductivity} \times V$$

where, V is the volume in cm^3 containing one gram equivalent of the electrolyte.

If the solution has a concentration of 'C' gram equivalents per litre, i.e. C gram equivalents are present in 1000 cm^3 of the solution then the volume of the solution containing one gram equivalent will be $\frac{1000}{C}$. Hence, the above expression may be written as

$$\Lambda_{eq} = K \times \frac{1000}{C_{aq}} = K \times \frac{1000}{\text{Normality}}$$

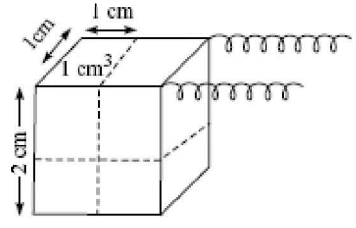


Fig. 16.2 *Relationship between equivalent conductivity and specific conductivity*

(b) Units of Equivalent Conductivity

$$\Lambda_{eq} = K \times V$$

$$= \text{ohm}^{-1}\text{cm}^{-1} \times \frac{\text{cm}^3}{\text{Gram Eq.}}$$

$$= \text{ohm}^{-1}\ \text{cm}^{-2}\ (\text{g eq})^{-1} \text{ or } S\ \text{cm}^2\ \text{eq}^{-1} \text{ or } \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

SI units

The units of Λ_{eq} are $Sm^2\ eq^{-1}$

$$1\ \text{S cm}^2\ \text{eq}^{-1} = 10^4 \times S\ \text{cm}^2\ \text{eq}^{-1}$$

5. Molar Conductivity The molar conductivity of a solutions is defined as under:

Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from one mole of the electrolyte dissolved in V cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them. It is usually represented by Λ_m.

Relationship Between Molar Conductivity and Specific Conductivity ***Molar*** conductivity is related to specific conductivity as follows:

Molar conductivity = Specific conductivity × Volume in cm^3 containing 1 mole of the electrolyte

or $$\Lambda_m = K \times V = K \times \frac{1000}{C} = K \times \frac{1000}{\text{Molarity}}$$

where K is the specific conductivity and V is the volume of the solution containing one mole of the electrolyte and C is the molar concentration.

Units of Λ_m are $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ (or $S\ \text{cm}^2\ \text{mol}^{-1}$) or $\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

SI Units

Units of Λ_m are $S\ \text{m}^2\ \text{mol}^{-1}$

$$1\ S\ \text{m}^2\ \text{mol}^{-1} = 10^4 \times S\ \text{m}^2\ \text{mol}^{-1}$$

16.3 MEASUREMENT OF ELECTROLYTIC CONDUCTANCE, SPECIFIC CONDUCTIVITY, EQUIVALENT CONDUCTIVITY AND MOLAR CONDUCTIVITY

1. Electrolyte Conductance Conductance is the reciprocal of resistance. Hence, the conductance can be obtained by measurement of the resistance and the latter can be found by Wheatstone bridge method shown in Fig. 16.3. It consists of four resistances R_1, R_2, R_3 and R_4 arranged in a manner as shown in the figure. R_1 is the variable resistance and R_2 is the unknown resistance. At the null point, i.e., when there is no deflection in the galvanometer G, the following relation holds:

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

Knowing the values of R_1, R_3, and R_4, R_2 can be calculated.

To find the resistance of the solution of an electrolyte, a special type of cell has to be used such that the solution is present between the two electrodes. The cell thus used is called a ***conductivity cell.*** It is made up of pyrex glass and two platinum electrodes at a fixed distance apart.

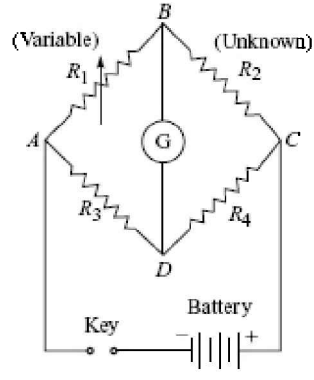


Fig. 16.3 *Principle of Wheatstone bridge*

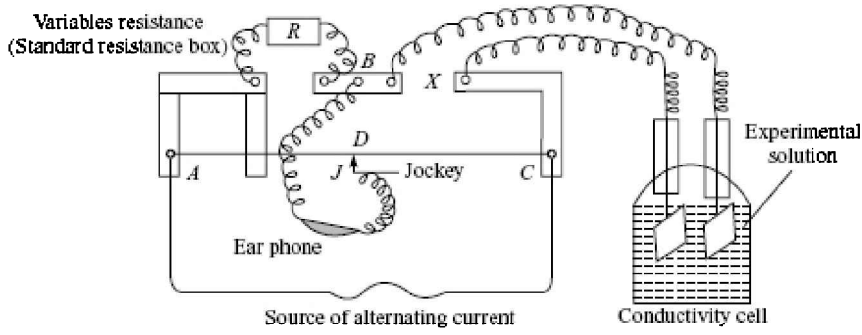


Fig. 16.4 *Apparatus for the measurement of electrolytic conductance.*

Various designs of conductivity cells are in use. If direct current is used, it causes electrolysis of the solution and this results in the change in the resistance of the solution. These effects are called ***polarisation effects.*** To overcome this problem, an alternating current of frequency of 50-200 cycles per second is used. Also, we have to use a headphone instead of a galvanometer to detect the null point.

The complete assembly for the measurement of the electrolytic conductance is shown in Fig. 16.4.

A resistance '*R*' is introduced from the standard resistance box such that when the sliding contact, i.e., the jockey *J* is moved along the stretched wire, the sound in the earphone is reduced to minimum at a point somewhere in the middle of the wire *AC*, say at the point *D*. This represents the null point. If *X* is the resistance of the electrolytic solution then by Wheatstone bridge principle, we have,

$$\frac{\text{Resistance } R}{\text{Resistance } X} = \frac{\text{Resistance of wire } AD}{\text{Resistance of wire } CD} = \frac{\text{Length } AD}{\text{Length } CD}$$

$$\text{Resistance } X = \text{Resistance } R \times \frac{\text{Length } CD}{\text{Length } AD}$$

Knowing the resistance *R* and the balance point *D*, the resistance *X* of the electrolytic solution can be calculated

$$\text{Conductance, } C = \frac{1}{X}$$

2. Specific Conductivity Specific conductivity (*K*) is related to the conductance (*C*) by the expression

$$K = C \times \frac{l}{a}$$

Thus, the specific conductivity of a solution can be determined by measuring its conductance and the distance (*l*) between the electrodes and the area of cross section (*a*) of each of the electrodes. However, for a particular cell, l/a is constant and this constant is called ***cell constant.*** The value of the cell constant is generally written on the cell. It can also be determined experimentally.

$$\frac{l}{a} = \text{Constant}$$

∴ Specific conductivity (*K*) = Conductance × Cell constant

The cell constant of a particular cell can be found by measuring the conductance of a solution whose specific conductivity is known. The solution usually taken for this purpose is *N*/50 KCl solution whose specific conductivity at 298 K has been determined accurately to be 0.002765 $\text{ohm}^{-1}\ \text{cm}^{-1}$.

Having determined the value of the cell constant, the specific conductivity of the given solution

can be obtained by measuring its conductance and multiplying the value with the cell constant.

3. Equivalent Conductivity Equivalent conductivity (Λ_{eq}) is related to the specific conductivity (K) by the equation

$$\Lambda_{eq} = K \times \frac{1000}{C_{eq}}$$

where C_{eq} is the concentration of the solution in gram equivalents per litre (i.e. the normality of the solution). Thus knowing the normality of the solution and the specific conductivity K, Λ_{eq} can be calculated.

4. Molar Conductivity The molar conductivity is related to the specific conductivity according to the relation

$$\Lambda_m = K \times \frac{1000}{C}$$

where c stands for the molar concentration. Thus, knowing molar concentration c and the specific conductivity K, Λ_m can be calculated.

These days, low-cost conductivity meters are available which can directly read the conductance or resistance of the solution in the conductivity cell. The cell constant is generally etched on the conductivity cell. Thus, knowing the cell constant and resistance of the solution, we can calculate conductivity of the solution by using the relation

$$K = \frac{\text{Cell constant}}{R}$$



Fig. 16.5 *Conductivity meter*

16.4 NUMERICAL PROBLEMS ON SPECIFIC, EQUIVALENTAND MOLAR CONDUCTIVITIES

Formulae to be Used

1. $R = \rho \frac{l}{a}$ or $\rho = R \frac{a}{l}$

2. $K = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a} = C \times \frac{l}{a} =$ Observed conductance $\times$ Cell constant

3. $$\text{Cell constant} = \frac{l}{a} = \frac{\text{Specific conductivity}}{\text{Observed conductance}} = \text{Specific conductivity} \times \text{Observed resistance}$$

4. $\Lambda_{eq} = K \times \frac{1000}{C}$

where, C = Concentration of a solution in gram equivalent/litre, i.e. normality of the solution.

5. $\Lambda_m = K \times \frac{1000}{C}$

where C = Molar concentration of the solution. **Sometimes, the term conductivity is used in place of specific conductivity. It can be understood from the units attached to it. If the units attached to conductivity are ohm^{-1} cm^{-1}, it is obvious that it is specific conductivity.**

Example 1 *The resistance of 0.01 N NaCl solution at 298 K is 200 ohms. Cell constant of the conductivity cell is unity. Calculate the equivalent conductance.*

Solution:

Specific conductance, $K = \frac{1}{R} \times \text{Cell constant} = \frac{1}{200 \text{ ohms}} \times 1 \text{ cm}^{-1} = 5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$

Equivalent conductance $\Lambda_m = \frac{K \times 1000}{\text{Normality}} = \frac{5 \times 10^{-3} \times 1000}{0.01} = 5 \times 10^2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

Example 2 *The resistance of a conductivity cell when filled with 0.02 M KCl solution is 164 ohms at 298 K. However, when filled with 0.05 M $AgNO_3$ solution, its resistance is found to be 78.5 ohms. If specific conductivity of 0.02 M KCl is 2.768 x 10^{-3} ohm^{-1} cm^{-1}, calculate*

(a) The conductivity of 0.05 M$AgNO_3$

(b) The molar conductivity of $AgNO_3$ solution

Solution: *Calculation of cell constant*

Specific conductivity of 0.02 M KCl = 2.768×10^{-3} ohm^{-1} cm^{-1}
Resistance = 164 ohm

$$\text{Specific conductivity} = \frac{1}{R} \times \text{Cell constant}$$

$$\text{Cell constant} = R \times \text{Specific conductivity}$$
$$= 164 \times 2.768 \times 10^{-3} = 0.4539 \text{ cm}^{-1}$$

$$\text{Conductivity} = \frac{1}{R} \times \text{Cell constant} = \frac{1}{78.5} \times 0.4539 = 0.00578 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Calculation of Λ_m of 0.05 M $AgNO_3$

$$\Lambda_m = \frac{1000 \times K}{\text{Molarity}} \quad \Lambda_m = \frac{1000 \times 0.0058}{0.05} = 115.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Example 3 *The conductivity of a solution containing 1 gram of anhydrous $BaCl_2$ in 200 cm^3 of water has been found to be 0.0058 mho cm^{-1}. What are the molar conductivity and equivalent conductivity of the solution (At. mass of Ba = 137, and Cl = 35.5)?*

Solution: Conductivity (K) = 0.0058 mho cm^{-1}

Mol. wt. of $BaCl_2$ = 137 + 2 × 35.5 = 208

As 1 gram of $BaCl_2$ is present in 200 cm^3 of the solution,

$$\text{Molar concentration, } (C) = \frac{1}{208} \times \frac{1}{200} \times 1000 \text{ mol } L^{-1} = 0.0240 \text{ mol } L^{-1}$$

Molar conductivity,

$$\Lambda_m = K \times \frac{1000}{C} = 0.0058 \times \frac{1000}{0.0240} = 241.67 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

In case of $BaCl_2$, equivalent weight $\frac{\text{Mol. wt.}}{2} = \frac{208}{2} = 104$

∴ Concentration of the solution in gram equivalent per litre, $C_{eq} = \frac{1}{104} \times \frac{1}{200} \times 1000 = 0.0480$

$$\Lambda_{eq} = K \times \frac{1000}{C_{eq}}$$

∴ equivalent conductivity, $$= 0.0058 \times \frac{1000}{0.480} = 120.83 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Example 4 *The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes 1.8 cm apart and 5.4 sq. cm in area was found to be 320 ohms. Calculate the equivalent conductance of the solution.*

Solution:

$$R = \frac{1}{K} \cdot \frac{l}{a} \quad \text{or} \quad K = \frac{1}{R} \cdot \frac{l}{a}$$

Substituting the values,
Specific conductance

$$K = \frac{1}{32} \times \frac{1.8}{5.4} = 0.0104 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Equivalent conductance = Specific conductance × Vol. in ml containing 1 g equivalent of electrolyte

$$= 0.0104 \times 10000 = 104 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Example 5 *Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 ohms. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M KCl solution. Conductivity of 0.1 M KCl solution is 1.29 S m^{-1}.*

Solution:

$$\text{Cell constant} = \text{Conductivity } (K) \times \text{Resistance } (R)$$
$$= 1.29\ S\ m^{-1} \times 100\ \text{ohm} = 129\ m^{-1} = 1.29\ cm^{-1}$$
$$K = \frac{1}{R} \times \frac{l}{A} = \frac{1}{520\ \Omega} \times 129\ cm^{-1} = 2.48 \times 10^{-3}\ S\ cm^{-1}$$
$$\Lambda_m = \frac{1000\ K}{M} = \frac{1000 \times 0.248 \times 10^{-2}}{0.02} = 124\ S\ cm^2\ mol^{-1}$$

16.5 EFFECT OF DILUTION ON SPECIFIC CONDUCTANCE AND EQUIVALENT CONDUCTANCE

The specific conductance shows a decrease with dilution. This is due to the fact that the number of current-carrying particles, i.e. ions per ml of the solution become less. Of course on dilution, the degree of dissociation also increases but the number of ions per ml is decreased to such an extent that even complete dissociation does not produce as many ions per ml as were present before dilution.

The equivalent conductance and molecular conductance on the other hand, show increase with dilution and finally attain a maximum value at infinite dilution.

This is due to the fact that this value is the product of specific conductance and the volume V of the solution containing 1 g equivalent (or 1 mole) of the electrolyte. The decreasing value of specific conductance is more than compensated by the increasing value of V and, therefore, the value of Λ_v increases with dilution.

PROBLEMS FOR PRACTICE

1. Calculate the equivalent conductivity of 1 M H_2SO_4 solution, if its conductivity is 26×10^{-2} $ohm^{-1}\ cm^{-1}$ (Atomic weight of sulphur = 32).

[Ans. 130 $ohm^{-1}\ cm^2\ eq^{-1}$]

2. Specific conductivity of a 0.12 normal solution of an electrolyte is 0.024 $ohm^{-1}\ cm^{-1}$. Determine its equivalent conductivity.

[Ans. 200 $ohm^{-1}\ cm^2\ eq^{-1}$]

3. The resistance of a decinormal solution of an electrolyte in a conductivity cell was found to be 245 ohms. Calculate the equivalent conductivity of the solution if the electrodes in the cell were 2 cm apart and each has an area of 3.5 sq. cm.

[Ans. 23.32 $ohm^{-1}\ cm^2\ eq^{-1}$]

4. The specific conductivity of 0.01 N KCl solution is 0.0014106 ohm cm^{-1} at 25°C. When a conductivity cell was filled up with the same solution, it offered a resistance of 484 ohms at 25°C. The same cell was then filled with 0.001 N solution of NaCl at same temperature which gave a resistance of 5194 ohms. Calculate the value of equivalent conductivity of 0.001 N solution of NaCl.

[Ans. 131.4 $ohm^{-1}\ cm^2\ eq^{-1}$]

5. The specific conductivity of N/50 solution of KCl at 298 K is 0.002765 ohms cm^{-1}. If the resistance of the same solution placed in the cell is 2000 ohms, what is the cell constant?

[Ans. 5.53 cm^{-1}]

6. The specific conductivity of N/50 KCl solution at 25°C is 2.768×10^{-3} ohms per cm. The resistance of the solution at 25°C when measured with a particular cell is 250.2 ohms. The

resistance of M/100 $CuSO_4$ solution at 25°C measured with the same cell was 8331 ohms. Calculate the molar conductivity of copper sulphate solution.

[Ans. 8.3 $ohm^{-1}\ cm^2\ mol^{-1}$]

7. The conductivity of an aqueous solution of sodium chloride in the cell is $92 \times 10^{-4}\ ohm^{-1}\ cm^{-2}$. The resistance offered by this cell is 247.8 ohms. Calculate the cell constant for this cell.

[Ans. 2.28 cm^{-1}]

8. The resistance of 0.01 N NaCl solution at 25°C is 200 Ω. Cell constant of the conductivity cell is unity. Calculate the equivalent conductance of the solution.

[Ans. 500 $\Omega^{-1}cm^2$]

9. A cell with N/50 KCl solution showed a resistance of 550 ohms at 25°C. The specific conductivity of N/50 KCl at 25°C is 0.002768 $ohm^{-1}\ cm^{-1}$. The cell filled with N/10 $ZnSO_4$ solution at 25°C shows a resistance of 72.18 ohms. Find the cell constant and molar conductivity of $ZnSO_4$ solution.

[**Ans.** 1.5224 cm^{-1}, 421.8 $ohm^{-1}\ cm^2\ mol^{-1}$]

10. In a particular cell, 0.01 M solution of potassium chloride gave a resistance of 150 ohms at 298 K while 0.01 M solution of hydrochloric acid gave a resistance of 51.40 ohms at the same temperature. At 298 K, the specific conductivity of 0.01 M potassium chloride solution is 0.0014088 $ohm^{-1}\ cm^{-1}$. Calculate equivalent conductivity of given hydrochloric acid.

[Ans. 411.12 $ohm^{-1}\ cm^2\ eq^{-1}$]

16.6 ARRHENIUS THEORY OF IONISATION

1. Postulates of Arrhenius' Theory of Ionisation Arrhenius, a Swedish chemist, carried out elaborate experiments to study the phenomenon of ionisation.

The main points of Arrhenius' theory are given below:

1. When dissolved in water, an electrolyte splits or dissociates into positively and negatively charged particles called ***ions.*** This process is called electrolytic dissociation or ionisation.

$$NaCl \rightarrow Na^+ + Cl^-$$
$$MgCl \rightarrow Mg^{2+} + 2Cl^-$$
$$Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$$

2. On passing electricity, the positive ions migrate towards the cathode and are, therefore, called ***cations.*** Similarly, negative ions, called the ***anions,*** move towards the positive electrode, the viz. anode.
3. The solution of the electrolyte is electrically neutral as a whole. That means total charge carried by the positive ions is equal to the charge carried by the negative ions.
4. The ions obtained by dissociation of electrolyte combine back to give the undissociated molecules. Ultimately, an equilibrium is reached between the ions and the undissociated molecules.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

The fraction of the total number of molecules of the electrolyte that dissociates into ions is called the ***degree of ionisation*** or ***dissociation.*** It is usually denoted by α, i.e.

$$\text{Degree of dissociation } (\alpha) = \frac{\text{No. of molecules dissoicated}}{\text{Total no. of molecules taken}}$$

5. The degree of dissociation increases with dilution and becomes maximum at infinite dilution.
6. The conductance of an electrolytic solution is due to be presence of the ions, produced by the dissociation, of the electrolyte. Greater the dissociation, higher is the conductance.
7. The ions produced by the dissociation of an electrolyte behave like molecules towards colligative properties. For example, each NaCl molecule dissociates to give two ions, viz. Na^+ and Cl^-. Hence, the observed value of any colligative property is double the expected value.
8. The properties of an electrolyte are the properties of its ions. For example, the properties of an acid are due to the H^+ ions furnished by it in the aqueous solution. Similarly, the properties of a base are due to the OH^- ions produced in the aqueous solution.

2. Factors that Govern Degree of Dissociation of an Electrolyte The degree of dissociation of an electrolyte in the solution depends upon the following factors:

(a) Nature of the Solute Some electrolytes like mineral acids, alkalis and most of the salts are almost completely ionised in water. These are called ***strong electrolytes.*** On the other hand, some electrolytes like organic acids and bases, and some inorganic acids and bases ionise only to a small extent. These are called ***weak electrolytes.***

(b) Nature of the Solvent Every solvent has some definite value of the ***dielectric constant*** which is defined as its power to weaken the forces of attraction present between the ions of the electrolyte. Water has the highest dielectric constant ($\approx$ 80 compared with vacuum taken as unity). Thus, the dissociation of an electrolyte is maximum in water.

(c) Concentration Degree of dissociation of an electrolyte increases with dilution and becomes maximum at infinite dilution, i.e. zero concentration.

(d) Presence of Common Ions The degree of dissociation of an electrolyte decreases when another electrolyte is present which furnishes a common ion. This effect is called ***common ion effect.***

For example, dissociation of NH_4OH decreases in presence of NH_4Cl.

3. Evidence in Support of Arrhenius' Theory of Ionisation Arrhenius' theory finds support on the following observations:

(a) Electrolytic Conductance Arrhenius' theory says that, the conductance of the solution of an electrolyte is due to the presence of the ions, produced by the electrolyte on aissociation. Strong electrolytes possess high degree of dissociation and hence show greater conductance, whereas weak electrolytes dissociate to the small extent and hence, show low conductance.

(b) Variation of Conductance with Dilution It is observed that the specific conductance decreases whereas conductance as well as equivalent conductance increases with dilution. The explanation is evidently based on the postulates of the Arrhenius' theory. The equivalent conductance and the dissociation of the electrolyte vary in such a similar manner with dilution that the degree of dissociation (α) of an electrolyte at any concentration can be expressed in terms of equivalent conductance as follows:

$$\alpha = \Lambda_c/\Lambda_o$$

where Λ_c is the equivalent conductance at a given concentration and Λ_o is equivalent conductance at infinite dilution.

(c) Electrolysis According to Arrhenius' theory, an electrolyte when dissolved in water

dissociates into ions. Thus, the function of the electricity is only to direct the ions towards the electrodes. The ions are already present in the solution of an electrolyte.

(d) Colligative Properties Anomalous results are obtained while measuring colligative properties like osmotic pressure, elevation in boiling points, etc., of the strong electrolytes. This is because every ion produced from the electrolyte acts as an independent particle as far as colligative properties are concerned.

(e) Ionic Nature of Reactions According to Arrhenius' theory, the properties of an electrolyte are the properties of the ions. Thus, the reaction between the NaCl solution and $AgNO_3$ solution forming a precipitate of AgCl may be explained as follows:

NaCl in aqueous solution ionises as

$$NaCl \rightarrow Na^+ + Cl^-$$

$AgNO_3$ also ionises in aqueous solution as

$$AgNO_3 \rightarrow Ag^+ + NO_3^-$$

When the above two solutions are mixed, we have

$$Na^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl + Na^+ + NO_3^-$$

The reaction between any two ionic compounds in aqueous solution takes place in a similar manner.

(f) Salt Hydrolysis It is defined as the process in which a salt reacts with water to give back the acid and base.

$$\text{Salt} + \text{Water} \rightarrow \text{Acid} + \text{Base}$$

Depending upon the relative strengths of the acid and the base produced, the resulting solution is acidic, basic or neutral. These observations are satisfactorily explained on the basis of Arrhenius' theory.

(g) Heat of Neutralisation The heat of neutralisation is defined as the amount of heat evolved when one gram equivalent of the acid is neutralised by the base or one gram equivalent of the base is neutralised by the acid. The heat of neutralisation of the strong acid with strong base is always the same, viz. 13.7 kcal (or 57.3 KJ). This is explained by Arrhenius' theory as under:

If the strong acid is HCl and the strong base is NaOH, both are completely dissolved in the aqueous solution and the reaction between them may be written as

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ Cl^- + H_2O$$

Cancelling out the common ions on both sides, the above reaction reduces to

$$H^+ + OH^- \rightarrow H_2O$$

Thus, neutralisation may be defined simply as the process in which H^+ ions given by acid combine with the OH^- ions given by the base to form unionised water molecules.

One gram equivalent of any strong acid in aqueous solution gives the same number of H^+ ions as the number of OH^- ions given by one gram equivalent of any strong base. The neutralisation involves the combination between the same number of H^+ ions and OH^- ions. Hence, the heat of strong acid with strong base is always the same.

4. Limitations of Arrhenius' Theory Arrhenius' theory suffers from some limitations as listed below:

(a) Arrhenius suggested that ***ionisation*** of the electrolyte takes place when dissolved in water. However, *X*-ray studies have shown that many such electrolytes are already in the ionised state

(e.g. $Na^+ Cl^-$)

(b) As an electrolyte can conduct electricity even in the molten state, it shows that the dissociation of the electrolyte takes place even in the molten state. As such, the function of water could not be explained by Arrhenius' theory.

(c) The most serious objection against the Arrhenius theory was its ***failure when applied to strong electrolytes:***

(i) Ostwald's dilution law which is derived on the basis of Arrhenius' theory, using the concept of ionic equilibrium, fails for the strong electrolytes, i.e. a constant value of the dissociation constant K is not obtained.

(ii) The degree of dissociation (α) of strong electrolytes calculated from conductance measurements ($\alpha = \Lambda_c/\Lambda_o$) was found to be different from that calculated from colligative properties.

(iii) Strong electrolytes are almost completely dissociated even at moderate concentrations, i.e., α = 1 or 100% at all concentrations. Hence, the Arrhenius view that conductance increases with dilution because the dissociation increases, does not hold in case of strong electrolytes. The increase in conductance with dilution is, therefore, due to some other factors.

16.7 OSTWALD DILUTION LAW

This law gives us a relationship between the concentration of the electrolyte and degree of dissociation. According to Arrhenius' theory of ionisation, when an electrolyte is dissolved in water, there is an equilibrium between the ions and the undissociated molecules. For example, for a binary electrolyte AB, we have

$$AB \rightleftharpoons A^+ B^-$$

Ostwald pointed out that the law of chemical equilibrium is applicable to this ***ionic equilibrium.***

Suppose the initial concentration of the binary electrolyte AB in solution is C moles/litre and α is the degree of dissociation. Then we will have

	AB	$\rightleftharpoons A^+$	$+ B^-$
Initial concentration	C moles/litre	0	0
Concentration at equilibrium = $C(1-\alpha)$		$C\alpha$	$C\alpha$ moles/litre

Applying the law of chemical equilibrium to the above process,

We have the following relation:

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

or

$$\boxed{K = \frac{C\alpha^2}{1-\alpha}} \quad \text{(Exact formula)} \qquad \ldots(16.2)$$



Fig. 16.6 *Wilhelm ostwald*
Friedrich Wilhelm Ostwald was a Baltic German chemist. He received the Nobel Prize in chemistry in 1909 for his work on catalysis, chemical equilibrium and electrochemical phenomenon

This is the ostwald dilution law.

The equilibrium constant K for the equilibrium $AB \rightleftharpoons A^+ + B^-$ is called the ***dissociation constant*** or ***ionisation constant*** of the electrolyte AB and may be represented by K_d (or K_i). Like any other equilibrium constant, K_d is constant only at constant temperature. The units of K_d will be same as those of the concentration.

If the degree of dissociation α is very small, as in the case of ***weak electrolytes at ordinary concentrations,*** α can be neglected in comparison to 1 in the denominator of expression (16.2). Then the approximate formula can be written as

$$K_d = C\alpha^2 \text{ or } \alpha^2 = \frac{K_d}{C}$$

or
$$\boxed{\alpha = \sqrt{\frac{K_d}{C}}} \text{ (Approx. formula)} \qquad \ldots(16.3)$$

Equations (16.2) and (16.3) are the two expressions of Ostwald's dilution law. Expression (16.3) can be stated as follows:

For a weak binary electrolyte, with a small degree of dissociation, the degree of dissociation is inversely proportional to the square root of the initial molar concentration.

1. Validity of Ostwald's Dilution Law To verify the law experimentally, the degree of dissociation α is determined from conductance measurements (using formula $\alpha = \Lambda_c/\Lambda_o$) at different concentrations for a number of electrolytes. For each electrolyte, the data are substituted in Eq. (16.2) to see whether the value of K_d comes out to be constant or not.

The following observations have been made:

(a) The value of K_d comes out to be constant only for weak electrolytes and that too when the concentration of the solution is not too high, i.e. for dilute solutions only.

(b) The value of K_d does not come out to be constant for strong electrolytes. It may be concluded that ***Ostwald's dilution law is valid only for weak electrolytes in dilute solutions. (that is why it is called dilution law) and it does not hold good for strong electrolytes.***

2. Importance of Ostwald's Dilution Law Ostwald's dilution law is applicable to weak

electrolytes only. It is very useful in the calculation of dissociation constants (K_d) of the weak acids and weak bases, by determining the degree of dissociation (α) from conductance measurements (Λ_c/Λ_0) at any concentration C. Having determined the value of K_d, which is constant for a particular weak acid or weak base, at a particular temperature, the degree of dissociation (α) of that weak acid or weak base can be obtained at any concentration (C).

Example 6 *A solution of ammonia gives the following values of equivalent conductivities at different dilutions.*

V (in litres)	8	16	32
Λ_V	3.20	4.45	6.32 $ohm^{-1}\ cm^2$

If equivalent conductivity at infinite dilution of NH_4OH is 237 $ohm^{-1}\ cm^2$, show that the above given data establish the truth of Ostwald's dilution law.

Solution: The ionisation constant K_d for weak electrolytes is given by the following relation:

$$K_d = \frac{C\alpha^2}{1-\alpha} \text{ or } K_d = \frac{\alpha^2}{(1-\alpha)V}$$

where C is the concentration of the solute in mol/litre and V is the volume of the solution in litre containing 1 mole of the solute.

Putting the values of α and V in the above expression, we have

S.No.	V (litres)	$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$	$K = \frac{\alpha^2}{(1-\alpha)V}$
1.	8	$\frac{3.2}{237} = 0.0135$	$\frac{(0.0135)^2}{(1-0.0135)8} = 2.31 \times 10^{-5}$
2.	16	$\frac{4.45}{237} = 0.0188$	$\frac{(0.0188)^2}{(1-0.0188)16} = 2.26 \times 10^{-5}$
3.	32	$\frac{6.32}{237} = 0.0265$	$\frac{(0.0265)^2}{(1-0.0265)32} = 2.25 \times 10^{-5}$

We find that the value of K comes out to be almost constant. Hence, the truth of the law is established.

Example 7 *Conductivity of 0.00241 M acetic acid is 7.896 × 10^{-5} S cm. Calculate its molar conductivity. If Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?*

Solution: Using the following relation and substituting the values, we get

$$\Lambda_m^c = \frac{K \times 1000}{\text{Molarity}} = \frac{(7.896 \times 10^{-5}\ S\ cm^{-1}) \times 1000\ cm^3\ L^{-1}}{0.00241\ mol\ L^{-1}} = 32.76\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

Degree of dissociation may be obtained as under:

$$K_d = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1 - 0.084} = 1.86 \times 10^{-5}$$

PROBLEMS FOR PRACTICE

1. The dissociation constant of ammonium hydroxide is 2.5×10^{-5}. Calculate the hydroxyl ion concentration in an N/100 solution of the base.

[Ans. 5×10^{-4} g ion/litre]

2. A 0.10 M solution of ammonium hydroxide is 1.3 per cent ionised at 25°C. Calculate the dissociation constant of ammonium hydroxide.

[Ans. 1.71×10^{-5}]

3. The weak acid HA in its 0.1 M aqueous solution is 50% dissociated. What will be the value of its dissociation constant?

[Ans. 0.05]

[Hint: Here, $\alpha = 0.5$ which is not small; hence, exact formula, viz. $K_d = \frac{C\alpha^2}{1-\alpha}$ should be used]

4. A 0.04 N solution of acetic acid has specific conductance of $4.23 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ while its equivalent conductivity at infinite dilution is $390\ \Omega^{-1}\ cm^2 equi^{-1}$. Calculate the concentration of hydrogen ions in the solution.

[Ans. $\alpha = 0.0271$, $[H^+] = 1.08 \times 10^{-3}$]

5. A 0.01 N solution of a weak monobasic acid dissociates to the extent to 10%. Calculate the dissociation constant of the acid.

[Ans. 1.11×10^{-4} moles/litre]

6. At 18°C, the equivalent conductivities of 0.01 N solutions of HCl, NaCl, CH_3COONa and CH_3COOH are 369.3, 101.7, 71.7 and 14.3 $ohm^{-1}\ cm^2$ respectively. Calculate the hydrogen-ion concentration of 0.01 N acetic acid at 18°C.

[Ans. 4.2×10^{-4} g ion/litre]

7. Calculate the concentration of hydrogen ions in a solution containing 0.04 mole of acetic acid in 250 ml of solution. ($K = 1.8 \times 10^{-5}$ moles/litre)

[Ans. 1.7×10^{-3} g ion/litre]

8. Calculate the H^+ ion concentration of 1.0 N solution of HCN if the dissociation constant of the latter is 4.0×10^{-10}.

[Ans. 2×10^{-5} g ion/litre]

9. Calculate the hydrogen-ion concentration of a solution of formic acid containing 0.092 g of acid per litre. The dissociation constant at 25°C is 2.14×10^{-4}.

[Ans. 6.54×10^{-4} g ion/litre]

16.8 VARIATION OF CONDUCTIVITY WITH CONCENTRATION OF STRONG ELECTROLYTES (DEBYE–HUCICEL–ONSAGAR EQUATION)

The following equation governs the change of a strong electrolyte with concentration

$$\Lambda_m^c = \Lambda_m^\circ - b\sqrt{C}$$

where, Λ_m^c = Molar conductance of the solution at the concentration C
Λ_m° = Molar concentration at infinite dilution
C = Concentration of the solution. b is a constant for a particular solvent at a particular temperature

The equation is known as Debye-Huckel-Onsagar equation. A plot of Λ_m^c against $\sqrt{C}$ is a straight line as shown in Fig. 16.7. Taking the case of KCl, which is a strong electrolyte, we find that there is not much variation in conductance with dilution. This is because of the fact that a strong electrolyte is 100% ionised even in a concentration solution. In a concentrated solution, there are inter-ionic attractions which decrease the mobility of the ions. Thus, there is slight increase in the conductance of a solution of a strong electrolyte on dilution.

In order to obtain the value of Λ_m° for a strong electrolyte, the plot which becomes linear at low concentration is extrapolated to the Y-axis (zero concentration). However, this is not possible for a weak electrolyte like CH_3COOH. Experimentally, it is impossible to determine Λ_m° for a weak electrolyte from the plot because it does not approach a limiting value. This problem was solved by Kohlrausch, as discussed in the next section.

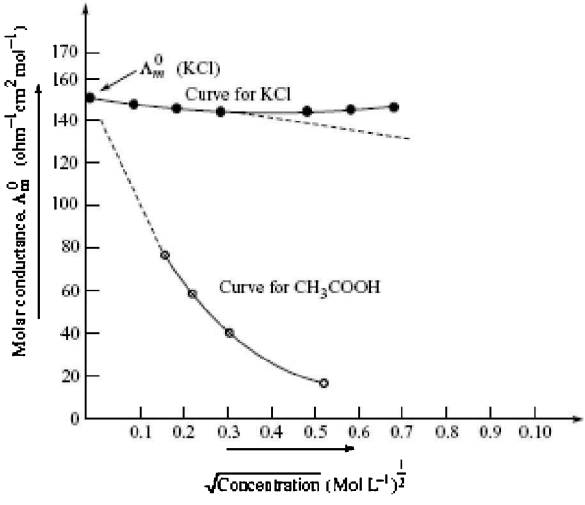


Fig. 16.7 *Variation of molar conductivity of a strong electrolyte (KCl)*

16.9 KOHLRAUSCH'S LAW

Kohlrausch studied the molar conductivities at infinite dilution, Λ_m° for a number of pairs of strong electrolytes each having a common cation or anion. He calculated the difference of these Λ_m° values of each pair. A few of these results are given in Table 16.2.

Table 16.2 Λ_m° *values of some pairs of electrolytes (at 298 K) having common ions (in ohm^{-1} cm^2)*

Electrolyte	Λ_m° at 298 K	Difference	Electrolyte	Λ_m° at 298 K	Difference
KCl	149.86	23.41	KBr	151.92	2.06
NaCl	126.45		KCl	149.86	
KBr	151.92	23.41	NaBr	128.51	2.06
NaBr	128.51		NaCl	126.45	
KNO_3	144.96	23.41	LiBr	117.09	2.06
$NaNO_3$	121.55		LiCl	115.03	

We find that differentce between Λ_m° values for each pair of sodium and potassium salts having a common anion is same, irrespective of the anion. Similarly, the differences in the Λ_m° values for each pair of salts having the same different anions and a common cation is same, irrespective of the cation. In fact, column 3 in the table gives the Λ_m° values for K^+ ions minus the Lm values for Na+ ions. Similarly, the last common gives the Λ_m° value for Br^- ions minus Λ_m° value for Cl^- ions.

Kohlrausch concluded that ***each ion makes a definite contribution to the total molar conductivity of an electrolyte at infinite dilution, irrespective of the nature of the other ion of the electrolyte. This individual contribution of an ion towards the total molar conductivity is called molar ionic conductivity.*** Kohlrausch, in 1876, put forward a generalisation known as ***Kohlrausch Law.*** It states as under: ***Molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of the electrolyte.*** Mathematically,

$$\Lambda_m^\circ \text{ for } A_xB_y = x\lambda_{A^+}^\circ + y\lambda_{B^-}^\circ$$

where Λ_m° is the molar conductivity of the electrolyte at infinite dilution, $\lambda_{A^+}^\circ$ and $\lambda_{B^-}^\circ$ are the molar conductivities of the cation and anion respectively at infinite dilution.

Thus,

$$\Lambda_m^\circ \text{ for } NaCl = \lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ$$
$$\Lambda_m^\circ \text{ for } BaCl_2 = \lambda_{Ba^+}^\circ + 2\lambda_{Cl^-}^\circ$$
$$\Lambda_m^\circ \text{ for } Al_2(SO_4)_3 = 2\lambda_{Al^{3+}}^\circ + 3\lambda_{SO_4^{2-}}^\circ$$

In terms of equivalent conductivities, Kohlrausch's law is defined as follows:

The equivalent conductivity of an electrolyte at infinite dilution is the sum of the two values, one depending upon the cation and the other upon the anion, i.e.

$$\Lambda_{eq}^\circ = \lambda_c^\circ + \lambda_a^\circ$$

where λ_c° and λ_a° are called the ***ionic conductivities*** at infinite dilution of the cation and the anion respectively.

Molar conductivity, Λ_m, is related to equivalent conductivity, Λ_{eq}, according to the equation

$$\Lambda_{eq} = \frac{\Lambda_m}{n_+ z_+} \quad \text{or} \quad \Lambda_{eq} = \frac{\Lambda_m}{n_- z_-}$$

where n_+ and n_- are the number of cations and anions present per formula unit of the electrolyte and z_+ and z_- are the charges on the cation and the anion respectively.

Applications of Kohlrausch's Law Different applications of Kohlrausch's law are discussed as under:

(a) Calculation of Molar Conductivities at Infinite Dilution (Λ°) for Weak Electrolytes Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally. However, this can be calculated using Kohlrausch's law.

Consider the example of acetic acid [CH_3COOH] as the weak electrolyte. By Kohlrausch's law,

$$\Lambda^\circ(CH_3COOH) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

This equation can be arrived at by knowing the molar conductivities at infinite dilution for the strong electrolytes KCl, CH_3COOK and HCl. As per Kohlrausch's law,

$$\Lambda^\circ(KCl) = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-}$$
$$\Lambda^\circ(CH_3COOK) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{K^+}$$
$$\Lambda^\circ(HCl) = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}$$



Fig. 16.8 *Friedrich Kohlrausch was a German physicist who investigated the conductive properties of electrolytes and contributed to knowledge of their behaviour*

Hence, we have

$$\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} = (\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{K^+}) + (\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}) - (\lambda^\circ_{K^+} + \lambda^\circ_{Cl^-})$$

i.e.
$$\Lambda^\circ(CH_3COOH) = \Lambda^\circ(CH_3COOK) + \Lambda^\circ(HCl) - \Lambda^\circ(KCl)$$

(b) Calculation of the Degree of Dissociation For a weak electrolyte, if Λ^c_m is the molar conductivity of a solution at any concentration C and Λ°_m is the molar conductivity at infinite dilution (i.e., zero concentration) then we have,

$$\text{Degree of dissociation, } (\alpha) = \frac{\Lambda^c_m}{\Lambda^0_m}$$

The value of Λ°_m for the weak electrolytes can be calculated using Kohlrausch's law.

(c) Calculation of Solubility of a Sparingly Soluble Salt Salts such as AgCl, $BaSO_4$, $PbSO_4$, etc., which dissolve to a very small extent in water are called sparingly soluble salts. As they dissolve very little, their solutions are considered infinitely dilute. Further, as their solutions are saturated, their concentration is equal to their solubility. Thus, by determining the specific conductivity (K) and the molar conductivity (Λ_m) of such a solution, we can obtain solubility as follows:

$$\Lambda^\circ_m = K \times \frac{1000}{\text{Molarity}} = K \times \frac{1000}{\text{Solubility}}$$

or
$$\text{Solubility} = \frac{K \times 1000}{\Lambda^0_m}$$

Λ_m° can be obtained by using Kohlrausch law.

Example 8 *If the molar conductivities at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 426.1 and 91.0 ohm^{-1}cm^2 mol^{-1} respectively, what will be that of acetic acid?*

Solution: According to Kohlrausch's law,

$$\Lambda^\circ \text{ for } CH_3COOH = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

$$\Lambda^\circ \text{ for NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-} = 126.4 \text{ ohm}^{-1} \text{ cm}^2 \quad \ldots(i)$$

$$\Lambda^\circ \text{ for HCl} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} = 426.1 \text{ ohm}^{-1} \text{ cm}^2 \quad \ldots(ii)$$

$$\Lambda^\circ \text{ for } CH_3COONa = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+} = 91.0 \text{ ohm}^{-1} \text{ cm}^2 \quad \ldots(iii)$$

Adding equations (ii) and (iii) and subtracting (i), we get,

$$\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+} - \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} = 426.1 + 91.0 - 126.4 \text{ ohm}^{-1} \text{ cm}^2$$

$$\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ \text{ for } CH_3COOH = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Example 9 *From the following molar conductivities at infinite dilution:*

$$\Lambda^\circ_m \text{ for } Ba(OH)_2 = 457.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ_m \text{ for } BaCl_2 = 240.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda^\circ_m \text{ for } NH_4Cl = 129.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Calculate Λ°_m for NH_4OH.

Solution:

$$\Lambda^\circ_m \text{ for } [Ba(OH)_2] = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ_{OH^-} = 457.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad \text{(i)}$$

$$\Lambda^\circ_m \text{ for } (BaCl_2) = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ_{Cl^-} = 240.6 \text{ ohm}^{-1} \text{cm}^2 \text{ mol}^{-1} \quad \text{(ii)}$$

$$\Lambda^\circ_m \text{ for } NH_4Cl = \lambda^\circ_{NH_4^+} + {}^\circ_{Cl^-} = 129.8 \text{ ohm}^{-1} \text{cm}^2 \text{ mol}^{-1} \quad \text{(iii)}$$

In order to find Λ°_m (NH_4Cl), we need to find the values of $\lambda^\circ_{NH_4^+} + \lambda^\circ_{OH^-}$

Multiplying (iii) by 2, adding to (i) and substracting Eq. (ii) from the sum,

$$2\lambda^\circ_{NH_4^+} + 2\lambda^\circ_{Cl^-} + \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ_{OH^-} - \lambda^\circ_{Ba^{2+}} - 2\lambda^\circ_{Cl^-} = (2 \times 129.8) + 457.6 - 240.6$$

$$2(\lambda^\circ_{NH_4^+} + 2\lambda^\circ_{OH^-}) = 476.6$$

$$\lambda^\circ_{NH_4^+} + \lambda^\circ_{OH^-} = 238.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Example 10 *Λ°_m for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively. Calculate Λ° for HAc.*

Solution:

$$\Lambda_m^\circ(\text{HAc}) = \lambda_{H^+}^\circ + \lambda_{Ac^-}^\circ = \lambda_{H^+}^\circ + \lambda_{Cl^-}^\circ + \lambda_{Ac^-}^\circ + \lambda_{Na^+}^\circ - \lambda_{Cl^-}^\circ - \lambda_{Na^+}^\circ$$
$$= \Lambda_{m(HCl)}^\circ + \Lambda_{m(NaAc)}^\circ - \Lambda_{m(NaCl)}^\circ$$
$$= (425.9 + 91.0 - 126.4)\, S\ \text{cm}^2\ \text{mol}^{-1}$$
$$= 390.5\, S\ \text{cm}^2\ \text{mol}^{-1}$$

Example 11 *At 291 K, the molar conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 ohm^{-1} cm^2 respectively. If molar conductivity of a centinormal solution of NH_4OH is 9.33 ohm^{-1} cm^2, what is the percentage dissociation of NH_4OH at this dilution?*

Solution: We are given that,

$$\Lambda^\circ \text{ for } NH_4Cl = 129.8\ \text{ohm}^{-1}\text{cm}^2$$
$$\Lambda^\circ \text{ for NaOH} = 217.4\ \text{ohm}^{-1}\text{cm}^2$$
$$\Lambda^\circ \text{ for NaCl} = 108.9\ \text{ohm}^{-1}\text{cm}^2$$

By Kohlrausch's law

$$\Lambda^\circ \text{ for } NH_4OH = \lambda_{NH_4^+}^\circ + \lambda_{OH^-}^\circ$$
$$= \Lambda^\circ(NH_4Cl) + \Lambda^\circ(NaOH) - \Lambda^\circ(NaCl)$$

Substituting the values,

$$\Lambda^\circ(NH_4OH) = 129.8 + 217.4 - 108.9 = 238.3\ \text{ohm}^{-1}\text{cm}^2$$
$$\Lambda_c = 9.33\ \text{ohm}^{-1}\text{cm}^2 \text{ (Given)}$$

Degree of dissociation $(\alpha) = \dfrac{\Lambda_c}{\Lambda^\circ} = \dfrac{9.33}{238.3} = 0.0392$

Percentage dissociation = 0.0392 × 100 = 3.92

PROBLEMS FOR PRACTICE

1. Equivalent conductance of NH_4Cl at a certain dilution is 149.7 Ω^{-1} cm^2 and the ionic conductance of $OH^-$and Cl^- ions are 198 and 76.3 Ω^{-1} cm^2 respectively. Calculate the equivalent conductance of NH_4OH at this dilution.

[Ans. 271.1 Ω^{-1} cm^2 eq^{-1}]

2. From the following equivalent conductances at infinite dilution,

$$\Lambda_o \text{ for } Ba(OH)_2 = 288.8\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equivalent}^{-1}$$
$$\Lambda_o \text{ for } BaCl_2 = 120.3\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equivalent}^{-1}$$
$$\Lambda_o \text{ for } NH_4Cl = 129.8\ \text{ohm}^{-1}\text{cm}^2\ \text{equivalent}^{-1}$$

Calculate Λ_o for NH_4OH

[Ans. 238.3 ohm^{-1} cm^2 eq^{-1}]

3. The equivalent conductivity at infinite dilution of HCl and CH_3COONa are 396 and 78 ohm^{-1} cm^2 equivalent^{-1} respectively. If the equivalent conductivity of NaCl at infinite dilution is 109 ohm^{-1} cm^2 equivalent^{-1}, calculate the equivalent conductivity of acetic acid at infinite dilution.

[**Ans.** 365 ohm^{-1}cm^2 eq^{-1}]

4. Calculate Λ_m° for $CaCl_2$ and $MgSO_4$ given that molar conductivities for Ca^{2+}, Mg^{2+}, Cl^- and

SO_4^{2-} are 119.0, 106.0, 76.3 and 160.0 *S* cm^2 mol^{-1} respectively.

[Ans. $CaCl_2$: 271.6 *S* cm^2 mol^{-1}, $MgSO_4$: 266 *S* cm^2 mol^{-1}]

Example 12 *Calculate the hydrogen-ion concentration of a solution of formic acid containing 0.092 g of acid per litre. The dissociation constant at 25°C is 2.14 × 10^{-4}.*

Solution: Concentration of formic acid (HCOOH) in moles/litre $= \frac{0.092}{46} = 0.002$

Using Ostwald's dilution law,

$$K = C\alpha^2$$
$$2.14 \times 10^{-4} = 0.002\,\alpha^2$$
$$\alpha^2 = \frac{2.14 \times 10^{-4}}{2 \times 10^{-3}}$$
$$\alpha^2 = 0.107$$
$$\alpha = 0.327$$

Hence, $[H^+] = 0.002 \times 0.327$ ions/litre $= 2 \times 10^{-3} \times 3.27 \times 10^{-1}$
$= 6.54 \times 10^{-4}$

Example 13 *The specific conductance of a 0.01 N solution of acetic acid at 25°C is 1.63 × 10^{-4} ohm cm^{-1} and the ionic conductance at infinite dilution but at the same temperature for H^+ and CH_3COO^- ions are 349.8 and 40.9 mhos cm^2 $equiv^{-1}$ respectively. Calculate the dissociation constant of acetic acid at 25°C.*

Also, calculate the H^+ ion concentration in the solution.

Solution: Here, we are given that

$$K = 1.63 \times 10^{-4} \text{ mhos cm}^{-1}$$
$$\lambda^\circ_{H^+} = 349.8 \text{ mhos cm}^2 \text{ equiv}^{-1}$$
$$\lambda^\circ_{CH_3COO^-} = 40.9 \text{ mhos cm}^2 \text{ equiv}^{-1}$$

Calculation of Λ_o for CH_3COOH

$$\Lambda_o \text{ for } CH_3COOH = 349.8 + 40.9 \text{ (By Kohlrausch's Law)}$$
$$= 390.7 \text{ mhos cm}^2 \text{ equiv}^{-1}$$

Calculation of Λ_c for CH_3COOH

As the solution is 0.01 N, the volume of the solution in cm^3 containing one gram equivalent of acetic acid $= \frac{1000}{0.01} = 10^5$ cm^3

$\therefore$ Λ_c = sp. conductance × vol. in cm^3 containing one gm equiv. of electrolyte

$\Lambda_c = 1.63 \times 10^{-4} \times 10^5 = 16.3$ mhos cm^2 $equiv.^{-1}$

Calculation of α

$\therefore$ $$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{16.3}{390.7} = 0.0417$$

Calculation of K_d

	$CH_3COOH \rightleftharpoons$	$CH_3COO^- +$	H^+
Initial concentration	0.01	0	0
Concentration at equilibrium	$0.01(1-\alpha)$	$0.01\,\alpha$	$0.01\,\alpha$

$$K_d = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{0.01\alpha \times 0.01\alpha}{0.01(1-\alpha)} = \frac{0.01\,\alpha^2}{1-\alpha}$$

$$= 0.01\,\alpha^2 \text{ [Taking } 1-\alpha = 1, \text{ as } \alpha \text{ is negligible compared to 1]}$$

$$= 0.01 \times (0.0417)^2 = 1.74 \times 10^{-5}$$

Calculation of H^+

$$[H^+] = 0.01\,\alpha = 0.01 \times 0.0417 = 4.17 \times 10^{-4} \text{ g ions/litre}$$

Example 14 *At 18°C, equivalent conductivities of 0.01 N solutions of hydrochloric acid, NaCl, CH_3COONa and CH_3COOH are 369.3, 101.7, 71.7 and 14.3 ohm^{-1} cm^2 respectively. Calculate the hydrogen-ion concentration in 0.01 Nacetic acid at 18°C.*

Solution: Equivalent conductance at infinite dilution Λ_o of CH_3COOH can be obtained using Kohl-rausch's law,

$$\Lambda_o(CH_3COOH) = 369.3 + 71.7 - 101.7 = 339.3$$

Degree of dissociation of $CH_3COOH = \frac{\Lambda_c}{\Lambda_o} = \frac{14.3}{339.3} = 0.042$

$\therefore$ hydrogen-ion concentration in $CH_3COOH = 0.042 \times 0.01 = 4.2 \times 10^{-4}$ g ion/litre

16.10 ANOMALOUS BEHAVIOUR OF STRONG ELECTROLYTES DEBYE—HUCKEL THEORY

The increase of equivalent conductance with dilution in case of weak electrolytes can be explained on the basis of Arrhenius's theory which suggests that the conductance increases because the dissociation of the weak electrolyte increases with dilution. However, in case of strong electrolytes, as they are almost completely dissociated even at moderate concentration, the increase in equivalent conductance with dilution must be due to some other factors.

The Debye-Huckel theory proposes that the increase in conductance of strong electrolytes on dilution is based upon the following two effects:

16.10.1 Relaxation Effect or Asymmetry Effect

Each ion in a solution is surrounded by an ionic atmosphere of opposite charge. As long as no electric field is applied, the ionic atmosphere remains symmetrical around the central ion [Fig. 16.9 (a)]. However, when current is passed through the solution, the central ion moves towards the oppositely charged electrode. As it is moving out of the ionic atmosphere, it has to rebuild an ionic atmosphere of opposite charge around it and the old ionic atmosphere is destroyed. However, the destruction of the old ionic atmosphere and the formulation of new ionic atmosphere do not take place at the same time. There is some time lag called **time of relaxation** between the destruction of the old and the formation of new ionic atmosphere. During this time, the old ionic atmosphere pulls the moving ion backward and hence retards its motion, Fig. 16.9 (b). Hence, this effect is called relaxation effect. Alternatively, it may be argued that as the central ion moves, the symmetry of the ionic atmosphere is lost, more ions of the ionic atmosphere are left behind than those present in the front [Fig. 16.9 (b)]. The excess ions

of the ionic atmosphere present behind the moving ion drag the ion backward and retard its motion. Thus, the effect arises because of the asymmetry of the ionic atmosphere of the moving ion and, hence, is also called asymmetry effect.

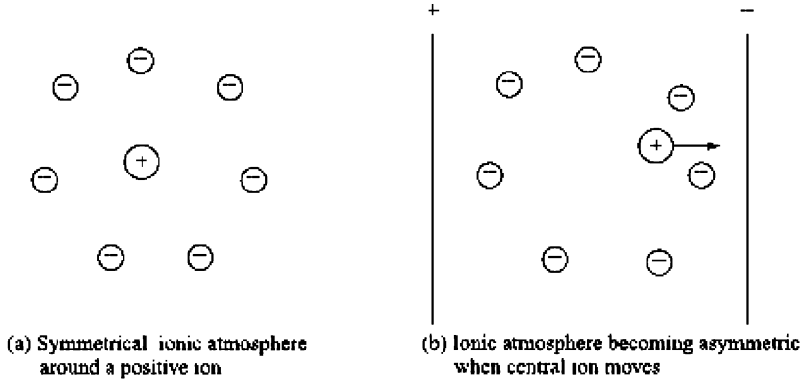


Fig. 16.9 *Relaxation or a symmetric effect*

16.10.2 Electrophoretic Effect

On applying emf, the central ion moves in one direction and the oppositely charged ionic atmosphere moves in the opposite direction. As this ionic atmosphere moves, the solvent molecules associated with it also move. Thus, the flow of the ionic atmosphere and that of the solvent molecules attached to it takes place in a direction opposite to that of the movement of the central ion. In other words, the central ion is moving against the stream. Thus, motion of the ions is retarded. This effect is called electrophoretic effect (Fig. 16.10)

Besides these two effects, the third retarding force is the normal frictional resistance offered by the medium which depends on the viscosity of the medium, its dielectric constant, etc.

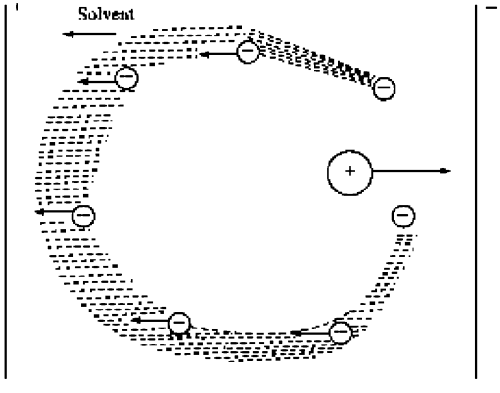


Fig. 16.10 *Movement of a central ion in a direction opposite to that of the ionic atmosphere and the associated solvent molecules.*

Based upon the above ideas, Debye and Huckel (1923) derived an equation for the variation of equivalent conductance with concentration. This equation was further improved by Onsagar (1926-27) and now the equation is known as ***Debye-Huckel-Onsagar equation*** or simply ***Onsagar equation.*** For a uni-univalent electrolyte, it is written in the form,

$$\Lambda_c - \Lambda_o \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20 \times 10^5}{(DT)^{3/2}} \Lambda_o \right] \sqrt{C} \qquad \ldots(16.4)$$

where

Λ_c = Equivalent conductance at concentration C

Λ_o = Equivalent conductance at infinite dilution

D = Dielectric constant of the medium

η = Viscosity of the medium

T = Temperature of the solution in degrees absolute

C = Concentration of the solution in moles/litre.

As D and η are constants for a particular solvent, therefore, at constant temperature, the above equation can be written in the form

$$\Lambda_c = \Lambda_o - (A + B\Lambda_o)\sqrt{C} \qquad \ldots(16.5)$$

where A and B are constants for a particular solvent at a particular temperature.

1. Verification of Onsagar Equation Validity of the Onsagar equation is established by the following two observations:

(a) The plot of Λ_c, vs $\sqrt{C}$ is linear

(b) The slope of the line obtained is equal to $A + B\Lambda_o$ after putting the values of $A + B$.

2. Significance of Debye-Huckel Theory The theory explains satisfactorily why the equivalent conductance of a strong electrolyte at any concentration Λ_c. is less than the limiting value of Λ_o at infinite dilution, in spite of complete ionisation of the strong electrolyte in terms of relaxation effect and asymmetry effect.

Example 15 *How does the Debye-Huckel equation explain the behaviour of strong electrolytes?*

Solution: Strong electrolytes are completely ionised even in concentrated solutions. But their ionic mobility is small. This is explained by the Debye-Huckel theory in terms of asymmetry effect and electrophoretic effect. Both these effects retard the movement of ions of the strong electrolyte, thereby bringing down ionic mobility.

Increase in ionic conductance of strong electrolytes on dilution can be explained by saying that asymmetry, and electrophoretic effects will be diluted when the solution is made dilute. There will be a smaller number of ions in the oppositely charged ionic sphere per unit volume of the solution. Also, for similar reasons, electrophoretic effect will also be weakened. This will result in higher conductance on dilution.

16.11 MIGRATION OF IONS AND TRANSPORT NUMBER

On passing electricity through an electrolyte, the ions move towards the oppositely charged electrodes and are deposited there. This movement of ions towards oppositely charged electrodes on passing electricity is called ***migration*** of ions.

Set-up of the apparatus to study migration of the ions is given below.

Take a U-tube. Fill its lower portion by $Cu_2Cr_2O_7$ jelly obtained by mixing a 5% solution of agar-agar and a mixture of $CuSO_4$ and $K_2Cr_2O_7$; and allow it to set (Fig. 16.11). The jelly is coloured green. To mark the position of the jelly, some charcoal is scattered over the green jelly. Over charcoal in both the limbs, is added KNO_3 solution in agar-agar, i.e., KNO_3 jelly and then aqueous solution of

KNO_3. On passing current, blue-coloured Cu^{2+} ions are seen moving towards the negative electrode and yellow-coloured $Cr_2O^{2-}_7$ ions are seen moving towards the positive electrode. After some time, the two types of ions are seen moving with well-defined boundaries. This experiment clearly shows the migration of ions.

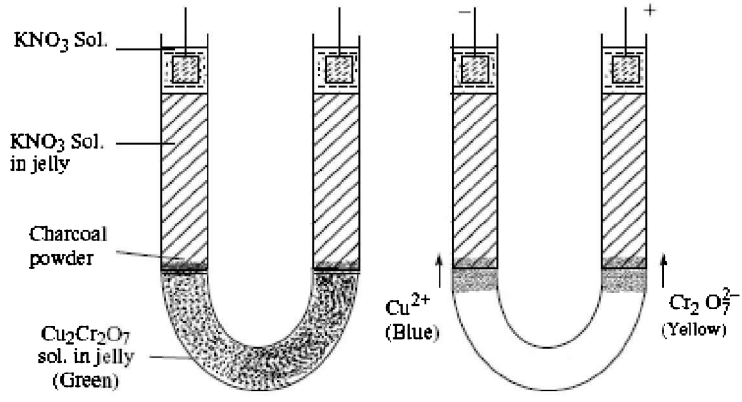


Fig. 16.11 *Demonstration of the migration of ions*

16.12 HITTORF'S THEORETICAL DEVICE-CHANGE IN CONCENTRATION

Consider a cell containing the solution and provided with anode *A* and the cathode *C* (Fig. 16.12). Let the solution lying between the electrodes *A* and *C* be divided into three imaginary compartments (the anodic, the middle and cathodic) with the help of porous partitions *(a* and *c)* shown by vertical dotted lines. Before electrolysis, suppose there are 13 pairs of ions, 4 being present in each of the anodic and the cathodic compartments and 5 in the middle (as shown in the position I). The following cases are considered when the electrodes are not attacked and when they are attacked.

16.12.1 When The Electrodes are not Attackable

Case I When Only Anions (–) Move Let two anions leave the cathodic compartment and enter the anodic compartment. We get the position II. Although the cations have not moved, still we see that the number of ions liberated is the same (viz. 2) at both the electrodes. But we see that concentration in the anodic chamber has not altered while that in the cathodic chamber has fallen by two molecules.

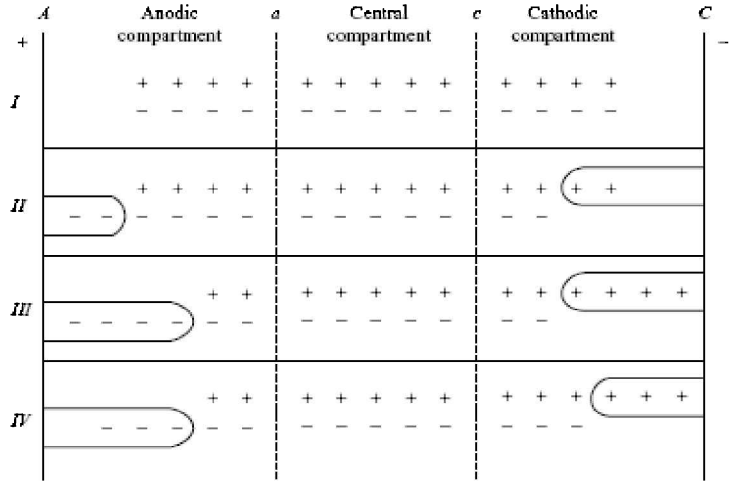


Fig. 16.12 *Migration velocity of ions and change in concentration when the electrodes are not attacked*

Similarly, if cations are capable of movement and two of them enter the cathodic compartment from the anodic compartment then there will be a fall in concentration of two molecules in the anodic chamber. Thus, we see that the fall of concentration of chamber is proportional to the speed of the ion leaving the chamber.

Case II When Cations (+) and Anions (–) Move at the Same Rate Assume that two cations move from the anodic compartment to the cathodic compartment and the two anions move from the cathodic compartment to the anodic compartment. Then we get the position III. In this case, there is fall in the concentration of 2 molecules in each compartment. But we find that the number of ions liberated at both the electrodes is same, i.e. 4.

Case III When Cations (+) Move at Double the Speed of Anions (–) Assume that two cations (+) from the anodic compartment leave and enter the cathodic compartment. Since the speed of anions is half the speed of cations, only one anion enters the anodic compartment. The position is shown in IV. We also observe that the fall in concentration of anodic and cathodic compartments are 2 and 1 molecules respectively. The number of ions discharged is again the same, viz. 3, on each electrode.

From the above observation, we draw the following conclusions:

1. Fall in concentration around any electrode is proportional to the speed of the ion moving away from it.

   It means fall in concentration around the cathode is proportional to the speed of the anion (u_a) and fall in concentration around the anode is proportional to speed of the cation (u_c)

   i.e.,
   $$\frac{\text{Fall in concentration around anode}}{\text{Fall in concentration around cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}}$$

2. Irrespective of the speeds of the ions, the number of ions liberated on both the electrodes is equal.

16.12.2 When the Electrodes are Attackable

In a silver voltameter (containing $AgNO_3$ solution and having silver electrodes), each NO^-_3 ion

that reaches the anodic compartment reacts with Ag of the electrode forming $AgNO_3$ and instead of decrease, there is an increase of concentration in the anodic compartment. In a silver voltameter, the above three cases are reproduced in Fig. 16.13.

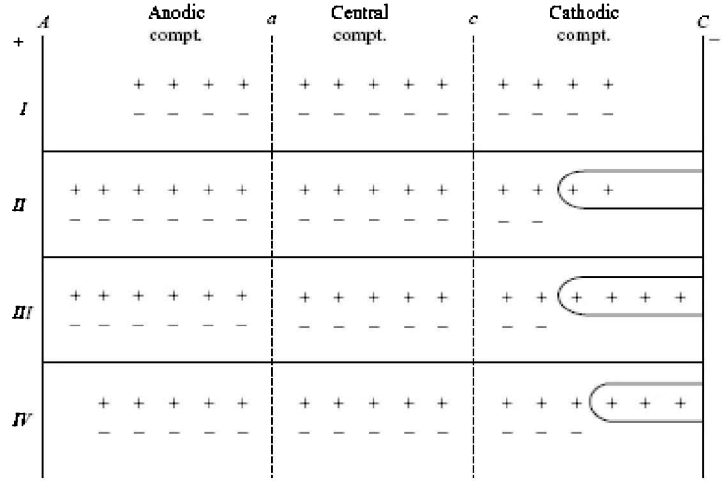


Fig. 16.13 *Migration velocity of ions and change in concentration when the electrodes are attacked*

We observe that there is always an increase in concentration in the anodic compartment.

This increase in concentration takes place even when the Ag^+ ions migrate from the anodic compartment to the cathodic compartment (Cases III and IV). In order to find the increase in concentration that would have taken place, if no Ag^+ ions had migrated from the anodic compartment to the cathodic compartment, a silver or a copper voltameter or coulometer is connected in series. Let the number of gram equivalents of Ag and Cu deposited in this voltameter be *x*. Obviously, *x* gram equivalents would have been the increase in the concentration of anodic compartment if no Ag^+ ions had migrated from this compartment. However, the actual increase is less due to migration of Ag^+ ions. Suppose the actual increase in the concentration of Ag in the anodic compartment is *y* gram equivalents. Then,

$$\left.\begin{array}{l}\text{Fall in concentration in anoidc comparment}\\ \text{due to migration of } Ag^+ \text{ ions}\end{array}\right\} (x - y) \text{ gram equivalents}$$

From Fig. 16.13, we can infer that,

Fall in conc. around cathode= Increase in conc. around anode = *y* gram equivalents.

Thus, the speed ratio in this case will be given by

$$\frac{\text{Speed of } Ag^+ \text{ ions}}{\text{Speed of } NO_3^- \text{ ions}} = \frac{x - y}{y}$$

16.13 TRANSPORT NUMBER

The fraction of the total current carried by an ion is called its ***transport number*** or ***transference number*** or ***Hittorf's number.***

Greater the speed of the ion, greater is the amount of current it will carry with it and hence, greater will be its transport number.

If u_a and u_c are the speeds of the anion and the cation respectively then

Current carried by the anion $\propto u_a = K \cdot u_a$

Current carried by the cation $\propto u_c = K \cdot u_c$

Since current is carried by the ions,

$$\therefore \quad \text{Total current carried} = \text{Current carried by anion} + \text{Current carried by cation}$$
$$= K \cdot u_a + K \cdot u_c = K(u_a + u_c)$$

$\therefore$ Transport number of anion $$n_a = \frac{u_a}{u_a + u_c}$$

Similarly, transport number of the cation $n_c = \dfrac{u_c}{u_a + u_c}$

The sum of the transport numbers of the cation and anion comes out to be unity.

$$n_a + n_c = 1$$

DETERMINATION OF TRANSPORT NUMBER

Two methods are available for the determination of transport numbers. These are described separately as under:

Hittorf's Method

This method is based upon the principle that the fall in the concentration around the electrode is proportional to the speed of the ion moving away from it.

$$\frac{\text{Fall in concentration around cathode}}{\text{Fall in concentration around anode}} = \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{u_a}{u_c}$$

Adding 1 to both sides, we get

$$1 + \frac{\text{Fall in concentration around cathode}}{\text{Fall in concentration around anode}} = \frac{u_a}{u_c} + 1$$

or $$\frac{\text{Fall in concentration around anode} + \text{Fall in concentration around cathode}}{\text{Fall in concentration around anode}} = \frac{u_a + u_c}{u_c}$$

or $$\frac{\text{Total fall in concentration around both the electrodes}}{\text{Fall in concentration around anode}} = \frac{u_a + u_a}{u_c}$$

or $$\frac{\text{Fall in concentration around anode}}{\text{Total fall in concentration around both the electrodes}} = \frac{u_c}{u_a + u_c} = n_c$$

If the concentrations are expressed in gram equivalents, the above expression may be written as

$$n_c = \frac{\text{Number of gram equivalents lost from anodic compartment}}{\text{Number of gram equivalents lost from both the compartments}}$$

It may be seen that the number of gram equivalents lost from both the compartments is equal to the number of gram equivalents discharged at each electrode. This can be found by connecting a silver or copper voltameter in series. According to Faraday's second law, when the same quality of electricity flows through the silver voltameter, the same number of gram equivalents of Ag or Cu will be deposited. The above formula reduces to,

$$n_c = \frac{\text{Number of gram equivalents lost from the anodic compartment}}{\text{Number of gram equivalents deposited in the voltameter}}$$

Hence, the determination of the transport number of the cation (n_c) involves the determination of the number of gram equivalents lost from the anodic compartment and the number of gram equivalents

of Ag or Cu deposited in the voltameter placed in series with the apparatus.

To determine the transport number of the anion (n_a), there is no need to find the loss in concentration of the cathodic compartment because it can be calculated directly from the equation,

$$n_a = 1 - n_c$$

1. Apparatus It consists of a *U*-tube joined on its two sides to two vertical bulbed glass tubes (Fig. 16.15). The *U*-tube and the two vertical tubes do not have stopcocks at their bottom. The *U*-tube is also provided with two stopcocks, one on either side at the top so as to cut off the various compartments from each other when required. In the two vertical tubes are placed the anode and the cathode separately. These are made of platinum, as it is desired that these should not be attacked by the ions. Alternatively, the anode and the cathode of silver or copper are taken depending upon whether transport number of Ag^+ ions or Cu^{2+} ions is to be determined, in which case the anode is attacked by the anions. The apparatus is connected to a silver or copper voltameter in series with the apparatus along with a battery, a rheostat, a key and a milli-ammeter, as shown in Fig. 16.15.



Fig. 16.14 *Wilhelm Hittorf He was a pioneer in electrochemical research. He investigated the migration of ions during electrolysis and developed expressions for transport numbers.*

2. Procedure

(a) The apparatus is filled with the solution of the electrolyte, containing ions whose transport number is to be determined.

(b) A silver or copper voltameter is placed in series with the apparatus and the various connections are made as shown in Fig. 16.15.

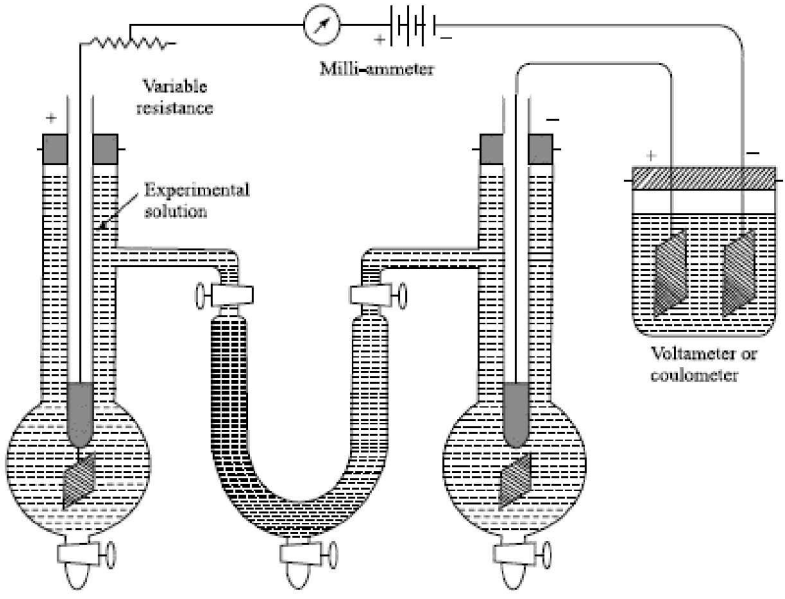


Fig. 16.15 *Apparatus for the determination of transport number by Hittorf's method*

(c) Before electrolysis, the concentration of the electrolyte is found by titrating a known weight of the solution against a suitable reagent.

(d) A current of 0.01 to 0.02 ampere is passed for 2–3 hours. A low current is used so that the change in concentration around the electrodes is not too fast as otherwise the diffusion may take place.

(e) After electrolysis, the solution from anodic compartment is taken out, weighed and then titrated as before to know the amount of the electrolyte present.

(f) The weight of the silver deposited in a silver voltameter (or that of copper in case a copper voltmeter is used) is also determined.
Presumably, there is no change in concentration of the middle compartment during the experiment.

3. Calculations The method of calculation is illustrated by taking the example of $AgNO_3$ as the electrolyte and using silver voltameter in series.

(a) When the Electrodes are not Attacked (i.e. when platinum electrodes are used)

(i) After Electrolysis Let the weight of the anodic solution taken out = w_1g

Weight of $AgNO_3$ found to be present (by titration) = w_2g

$\therefore$ Weight of water present = $(w_1 - w_2)$g

Thus, $(w_1 - w_2)$g of water contains w_2g of $AgNO_3$ after electrolysis.

$$w_2 \text{ g of } AgNO_3 = \frac{w_2}{170} \text{ g eq of } AgNO_3 = \frac{w_2}{170} \text{ g of Ag} = x \text{ g eq. (say)}$$

Thus, we can say that after electrolysis, $(w_1 - w_2)$g of water contains x g eq. of Ag.

(ii) Before Electrolysis Suppose w_3 g of solution contains w_4 g of $AgNO_3$

$\therefore$ Weight of water present = $(w_3 - w_4)$g

Thus, $(w_3 - w_4)$g of water contains w_4 g of $AgNO_3$ before electrolysis.

$$\therefore (w_1 - w_2)\text{g of water contains} = \frac{w_4}{(w_3 - w_4)} \times (w_1 - w_2)\text{g of } AgNO_3$$

$$= \frac{w_4}{(w_3 - w_4)} \times \frac{(w_1 - w_2)}{170} \text{ g eq. of } AgNO_3$$

$$= \frac{w_4}{(w_3 - w_4)} \times \frac{(w_1 - w_2)}{170} \text{ g eq. of Ag} = y \text{ g eq. (say)}$$

When the electrodes are not attacked, $x < y$

$\therefore$ Fall in the concentration of the anodic compartment = $(y - x)$g eq. of Ag Suppose the weight of silver deposited in the silver voltameter

$$= w \text{ g} = \frac{w}{108} \text{ g eq. of Ag} = z \text{ g eq. (say)}$$

$\therefore$ Transport number of Ag^+ ion (n_{Ag^+})

$$= \frac{\text{Fall in concentration around anode in g eq}}{\text{Amonut of Ag deposited in voltameter in g eq.}} = \frac{y - x}{z}$$

$\therefore$ transport number of NO_3^- ions $(n_{NO_3^-}) = 1 - n_{Ag^+}$

(b) When the Electrodes are Attacked (i.e. When Silver Electrodes are Used) In this case, NO_3^- ions reaching the anode attack the silver anode. Therefore, there is increase in the concentration of Ag^+ ions in the anodic solution (instead of decrease), i.e. in this case, we will have

$$x > y$$

$\therefore$ increase in concentration of the anodic solution

$$= (x - y) \text{ g eq. of Ag}$$

This increase in the concentration takes place in spite of the migration of Ag^+ ions from the anodic compartment to the cathodic compartment. If no Ag^+ ions had migrated from the anodic compartment, the increase in the concentration of Ag^+ ions in the anodic compartment would have been higher and equal to z g eq. of Ag (i.e. the same as the amount deposited in the silver voltameter). Hence, we can say

Fall in concentration in anodic solution due to migration of Ag^+ ions = $z - (x - y)$g eq. of Ag

$\therefore$ Transport number of Ag^+ ion = $\frac{z - (x - y)}{z}$

Transport number of NO_3^- ions = $1 - n_{Ag^+}$

In Case a Copper Voltameter is Used the number of gram equivalents of copper deposited in the voltameter is obtained by dividing the weight of copper deposited (W g) by its equivalent weight i.e. 31.75

Example 16 *A solution containing 10.09 g of $CuSO_4$ in 189.9 g of water was electrolysed. After electrolysis, 275.4 g of the solution around the anode was found to contain 15.4 g of $CuSO_4$ and 3.096 g of silver was deposited in a coulometer placed in series calculate the Hittorf's number of Cu^{2+} and SO^{2-}_4 ions.*

Solution: The data for 'after electrolysis' and 'before electrolysis' is complied as under.

After electrolysis

Weight of the anode solution = 275.4 g

Weight of $CuSO_4$ present = 15.4 g

Weight of water present = 275.4 – 15.4 g = 260 g

Before electrolysis

Weight of water = 189.9 g

Weight of $CuSO_4$ = 10.09 g

i.e. 189.9 g of water are associated with = 10.09g $CuSO_4$

$\therefore$ 260g of water is associated with

$$= \frac{10.09}{189.9} \times 260 \text{ g } CuSO_4 = 13.815 \text{ g}$$

Increase in the concentration of $CuSO_4$ around anode = 15.4 – 13.815 = 1.585 g

$$= \frac{1.585}{79.75} \text{ g eq.} \left\{ \because \text{Eq. wt of } CuSO_4 = \frac{63.5 + 32 + 64}{2} = 79.75 \right\}$$

$$= 0.01987 \text{ g eq.}$$

Since we find an increase in concentration around anode it is a case of attack of electrode.

Silver deposited in coulometer

$$= 3.096 \text{ g} = \frac{3.06}{108} \text{ g eq.} = 0.02867 \text{ g eq.} \quad \{\because \text{Eq. wt. of Ag} = 108\}$$

If no Cu^{2+} ions had migrated from the anodic compartment to the cathodic compartment, the increase around anode would have been 0.02867 g eq. Actual increase = 0.01987 g eq. Hence, ***fall in concentration around anode*** due to migration of Cu^{2+} ions is given by,

$$= 0.02867 - 0.01987 = 0.0088 \text{ g eq.}$$

$\therefore$ $$n_{Cu^{2+}} = \frac{\text{No. of g eq. of ion lost from anodic compartment}}{\text{No. of g eq. deposited in the coulometer}}$$

$$= \frac{0.0088}{0.02867} = 0.307$$

$\therefore$ $$n_{SO_4^{2-}} = 1 - 0.307 = 0.693$$

Example 17 *A solution of $AgNO_3$ containing 0.5066 g of the salt in 60 g of solution was electrolysed between silver electrodes. After electrolysis, 50 g of the anode liquid was found to contain 0.5186 g of $AgNO_3$. A current of one ampere was passed for 1 minute and 58 second. What are the transport number of Ag^+ and NO^- ions?*

Solution:

Here, quantity of electricity passed = Current (amperes) × Time (seconds)

$$= 1 \times 118 = 118 \text{ coulombs}$$

96,500 coulombs of electricity deposit 1 g eq. of Ag.

$\therefore$ 118 coulombs of electricity deposit Ag = $\frac{118}{96500}$ g eq.

After electrolysis	Before electrolysis
Weight of anode solution = 50 g	Weight of anode solution = 60 g
Weight of $AgNO_3$ = 0.5186 g	Weight of $AgNO_3$ = 0.5066 g
Weight of water = 49.4814 g	Weight of water = 59.4934 g

59.4934 g water contains 0.5066 g of $AgNO_3$ (Before electrolysis)

$$\therefore \quad 49.4814 \text{ g water contains } \frac{0.5066}{59.4934} \times 49.4814 \text{ g } AgNO_3 = 0.4213 \text{ g } AgNO_3$$

$$\text{Increase in conc. of } AgNO_3 = 0.0973 \text{ g } AgNO_3 = \frac{0.0973}{170} \text{ g equivalent}$$

$$= 0.00057 \text{ g equivalent}$$

$$\text{Silver deposited in the coulometer} = \frac{118}{96500} \text{ g eq.} = 0.00122$$

Hence, decrease in conc. of $AgNO_3$ due to migration of cations from the anodic compartment

$$= 0.00122 - 0.00057 = 0.00065 \text{ g eq.}$$

$$\therefore \text{ Transport number of } Ag^+ = \frac{0.00065}{0.00122} = 0.533$$

$$\therefore \text{ Transport number of } NO_3^- = 1 - 0.533 = 0.467$$

Example 18 *During the electrolysis of a solution of potassium chloride between platinum electrodes, 0.0137 g of the chloride was lost from the anodic compartment and 0.0857 g of silver was deposited in a silver coulometer connected in series with the cell. Determine the transport number of K^+ and Cl^- ions.*

Solution: No. of g eq. of the Cl^- ions lost from the anodic compartment

$$= \frac{0.0137}{35.5} = 0.0003859 \quad \{\because \text{Eq. wt. of Cl} = 35.5\}$$

No. of g eq. of Ag deposited in the coulometer

$$= \frac{0.0857}{108} = 0.0007935 \quad \{\because \text{Eq. wt. of Ag} = 108\}$$

$\therefore$ Transport number of the cation (i.e. K^+) is given by,

$$n_{K^+} = \frac{\text{No. of g eq. lost from the anodic compartment}}{\text{No. of g eq. deposited in the coulometer}} = \frac{0.0003859}{0.0007935} = 0.486$$

$$n_{Cl^-} = 1 - n_{K^+}$$

$$= 1 - 0.486 = 0.514$$

Example 19 *A solution of silver nitrate was electrolysed between silver electrodes. Before electrolysis, 10 g of the solution contained 0.01788 g of silver nitrate. After the experiment, 20.09 g of the anodic solution contained 0.06277 g of silver nitrate and 0.00947 g of copper was deposited in the copper coulometer placed in the series. Calculate the transport numbers of silver and nitrate ions. The atomic weights of Ag and Cu are 108 and 63.6 respectively.*

Solution:

After electrolysis

Weight of the anodic solution = 20.09 g

Weight of $AgNO_3$ present = 0.06277 g

$\therefore$ Weight of water present = 20.09 – 0.06277

= 20.02723 g

Before electrolysis

Weight of solution = 10 g

Weight of $AgNO_3$ solution = 0.01788 g

$\therefore$ Weight of water present = 10 – 0.01788

= 9.98212 g

9.98212 g water is association with = 0.01788 g of $AgNO_3$

$\therefore$ 20.02723 g of water is associated with

$$= \frac{0.01788}{9.98212} \times 20.02723 = 0.03587 \text{ g } AgNO_3$$

Increase in conc. of $AgNO_3$ around anode = 0.06277 – 0.03587 = 0.0269 g

$$= \frac{0.0269}{170} \text{ g eq.} = 0.0001582 \text{ g eq.} \qquad \{\because \text{Eq. wt. of } AgNO_3 = 170\}$$

Copper deposited in the coulometer = 0.00947 g

$$= \frac{0.00947}{31.8} \text{ g eq.} \qquad \left\{\because \text{Eq. wt. of Cu} = \frac{63.6}{2} = 31.8\right\}$$

$$= 0.0002977 \text{ g eq.}$$

If no Ag^+ ions had migrated from the anodic compartment to the cathodic compartment, the increase in concentration of the anodic compartment would have been 0.0002977 g eq.

Actual increase in conc. = 0.0001582 g eq. Hence, fall in concentration around anode due to migration of Ag^+ ions from the anodic compartment

$$= 0.0002977 - 0.0001582 \text{ g eq.} = 0.0001395 \text{ g eq.}$$

$$n_{Ag^+} = \frac{\text{No. of g eq. lost from the anodic compartment}}{\text{No. of eq. deposited in the coulometer}}$$

$$= \frac{0.0001395}{0.0002977} = 0.469$$

$$n_{NO_3^-} = 1 - n_{Ag^+} = 1 - 0.469 = 0.531$$

PROBLEMS FOR PRACTICE

1. During the electrolysis of nitrate solution between platinum electrodes, the fall in concentration of silver ions in the anode chamber is 1.06 g per unit volume while the corresponding fall in cathode chamber is 0.1 g, what are the transport numbers of the silver ion and the nitrate ion?

   [Ans. $n_{Ag^+} = 0.567$, $n_{NO_3^-} = 0.433$]

2. A current which deposited 0.047 g of copper in a voltameter containing $CuS0_4$ solution was passed through a solution of $AgNO_3$ using silver electrodes. The liquid from the cathode contained before the experiment 1.315 g of silver and after the experiment, 1.231 g of silver. Calculate the transport number of Ag^+ and NO^-_3 ions.

   [Ans. $NO^-_3 = 0.525$, $Ag^+ = 0.475$]

3. A solution of $AgNO_3$ having the composition 28.435 g of H_2O and 0.2099 g of $AgNO_3$ was electrolysed using silver electrodes. The current passed deposited 0.000702 g eq. of silver. At the close of the electrolysis, the anode solution was found to have the composition: 28.435 g

H_2O and 0.2874 g $AgNO_3$. Calculate the transport number of Ag^+ and NO^-_3 ions.

[Ans. $Ag^+ = 0.424$, $NO^- = 0.576$]

4. A solution of $AgNO_3$ containing 1.139 mg of silver per unit gram of solution was electrolysed between silver electrodes, and the anode liquid after electrolysis contained 39.66 mg silver in 20.09 g of solution. In a silver voltameter in series with the electrolytic cell, 32.10 mg of silver was deposited. Calculate the transport number of Ag^+ and NO_3^- ions.

[Ans. $Ag^+ = 0.477$, $NO_3^- = 0.523$]

5. A solution of $AgNO_3$ containing 0.510 g of salt in 60.40 g of the solution was electrolysed using silver electrodes. After electrolysis, 54 g of the anode solution was found to contain 0.56 g of $AgNO_3$. A current of 0.04 ampere was passed for 2950 seconds. Calculate the transport number of Ag^+ and NO^-_3 ions.

[Ans. $Ag^+ = 0.498$, $NO^-_3 = 0.502$]

6. A current, which deposited 30.0 mg of silver in silver voltameter, was passed through a solution of $AgNO_3$ using silver electrodes. The increase in concentration of silver corresponded to 15.9 mg of silver. Calculate the transport number of Ag^+ and NO^-_3 ions.

[Ans. $Ag^+ = 0.47$, $NO^-_3 = 0.53$]

7. In determining the transport number of silver and nitrate ions, the following results were obtained: Before the experiment, 1.0 g anode solution contained 0.001788 g of $AgNO_3$. After the experiment, 20.0 g of anode solution contained 0.065227 g of $AgNO_3$. In a voltameter placed in the circuit, 0.03222 g of silver was deposited. Calculate the transport number of Ag^+ and NO^-_3.

[Ans. $Ag^+ = 0.477$, $NO^-_3 = 0.523$]

8. The original strength of a solution of caustic soda was 0.06315 g per 100 cc. After electrolysis between platinum electrodes, 100 cc of anode solution contained 0.059 g NaOH and the same current deposited 0.05216 g silver in a silver voltameter. Find the transport number of Na^+ and OH^- ions.

   As the solution is dilute, weights of the solvent and solution may be taken as equal.

[Ans. $n_{Na^+} = 0.215$, $n_{OH^-} = 0.785$]

9. A solution of $AgNO_3$ containing 1.06 mg of silver per g of the solution was electrolysed between silver electrodes and anode liquid, after electrolysis contained 42.94 mg of silver in 25 g of solution. In a silver voltameter in series, 32.10 mg of Ag^+ were deposited. Calculate the transport number of Ag^+ ions.

[Ans. 0.488]

16.14 MOVING BOUNDARY METHOD FOR THE DETERMINATION OF TRANSPORT NUMBERS

This method is based upon the generalisation that the transport numbers of the cation and the anion are given by,

$$n_c = \frac{u_c}{u_c + u_a}$$

and

$$n_a = \frac{u_a}{u_c + u_a}$$

Thus, by determining the speed of cation and the anion (u_c and u_a), the transport number can be calculated.

The apparatus used for transport-number determination is shown in Fig. 16.16. It consists of a long tube mounted vertically and fitted with the platinum electrodes on the two sides. The salt *BA* under investigation is dissolved in water and then placed between the solutions of two other salts *B′A* and *BA′*, one having a common cation and other having common anion. For example, if *BA* is KCl, *B′A* may be LiCl and *BA′* may be CH_3COOK. The three solutions are placed in order of increasing density downwards to avoid mixing solutions. The original boundaries between solutions are *a* and *b*. Even if the solutions are colourless, the boundaries can be observed because of the differences in the refractive indices of the solution. In order that the boundaries may remain sharp throughout the experiment, *B′* and *A′* must have smaller velocities than *B* and *A* respectively, so that *B′* does not overtake *B* and *A′* does not overtake A. On passing the current, the boundaries move to *a′* and *b′*.

Speed of cation (B^+), $u_c \propto$ length aa'

Speed of anion (A^-) $u_a \propto$ length bb'

Hence,

$$n_c = \frac{aa}{aa' + bb'}$$

and

$$n_a = \frac{bb'}{aa' + bb'}$$

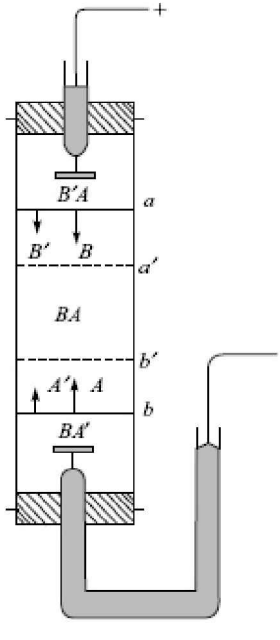


Fig. 16.16 *Moving-boundary method for determination of transport number*

Factors that Influence Transport Number of Ions

The factors that influence the transport number of ions are discussed as under:

1. Nature of the Ion Smaller the size of the ion, greater is its speed and hence, higher is its transport number. For example, the transport number H^+ ions in 0.1 N HCl is greater than that of Na^+ ions in 0.1 N NaCl or K^+ ions in 0.1 N KCl, etc.

2. Nature of the Other Ion Present The transport number of Cl^- ion (n_{Cl^-}) in HCl is different from that of Cl^- ion in NaCl. This may be explained as follows:

$$n_{Cl^-} \text{ in HCl} = \frac{u_{Cl^-}}{u_{H^+} + u_{Cl^-}} \quad \ldots(16.6)$$

$$n_{Cl^-} \text{ in NaCl} = \frac{u_{Cl^-}}{u_{Na^+} + u_{Cl^-}} \quad \ldots(16.7)$$

where u_{H^+}, u_{Na^+}, u_{Cl^-} represent the speeds of H^+ ions, Na^+ and Cl^- ions respectively in their respective solutions. As the Na^+ ion is larger in size than the H^+ ion, $u_{H^+} > u_{Na^+}$. As a result, the denominator of expression (16.6) is greater than that of expression (16.7) and hence, n_{Cl^-} in HCl is smaller than n_{Cl^-} in NaCl. The same applies to other ions also.

3. Temperature With increase of temperature, the ions tend to approach a transport number value of 0.5, i.e. equal fraction of the current is carried by the cation and the anions. In case of ions having transport number less than 0.5 at ordinary temperature, the transport number increases with increase of temperature. In case of ions having transport number greater than 0.5 at ordinary temperature, the transport number decreases with increase of temperature.

4. Hydration of the Ions The speed of an ion and, hence, its transport number are very much affected by the hydration of the ions. For example, Li^+ ions being smaller in size than Na^+ ions are expected to have higher transport number than Na^+ ions but the actual position is otherwise. This is because Li^+ ions are more hydrated than Na^+ ions.

5. Concentration The transport number of ion changes with concentration but the change is very small. However, if there is an increase in concentration and it results into the formation of a complex ion, the transport number changes significantly. For example, the transport number of Cd^{2+} ions in cadmium iodide solution falls from 0.444 in 0.005 M solution to 0.003 in 0.025 M solution. At still higher concentration, the transport number appears to be zero or even negative. This is explained on the basis of formation of complex CdI_4^{2-} ions at higher concentrations as per the following equations:

$$CdI_2 \rightarrow Cd^{2+}(aq) + 2I^-(aq)$$

$$Cd^{2+}(aq.) + 4I^-(aq) \rightarrow CdI_4^{2-}(aq)$$

As the concentration is increased, more and more of CdI_4^{2-} ions are formed, which migrate to the anodic compartment. A stage comes when as many CdI_4^{2-} ions migrate into the anodic compartment as the number of Cd^{2+} ions migrating from it to the cathodic compartment. Thus, there is no change in the concentration of Cd^{2+} ions in the anodic compartment and so the Cd^{2+} ions appear to have zero transport number.

(a) Relationship Between the Ionic Conductance and Transport Number

Ionic conductance (λ) $\propto$ ionic mobility (u),

i.e. $$\lambda_c \propto u_c \text{ or } \lambda_c = ku_c \quad \ldots(16.8)$$

and $\lambda_a \propto u_a$ or $\lambda_a = ku_a$ ...(16.9)

where, λ_c and λ_a are the ionic conductances and u_c and u_a are the ionic mobilities of the cation and the anion respectively and k is constant.

Dividing Eq. (16.8) by Eq. (16.9), we have

$$\frac{\lambda_c}{\lambda_a} = \frac{u_c}{u_a}$$

Adding 1 to both sides,

$$\frac{\lambda_c}{\lambda_a} + 1 = \frac{u_c}{u_a} + 1 \quad \text{or} \quad \frac{\lambda_c + \lambda_a}{\lambda_a} = \frac{u_c + u_a}{u_a}$$

Taking reciprocal of both the sides,

$$\frac{\lambda_a}{\lambda_c + \lambda_a} = \frac{u_a}{u_c + u_a}$$

But $\frac{u_a}{u_c + u_a} = \lambda_a$, transport number of the anion

and $\lambda_c + \lambda_a = \Lambda_o$, equivalent conductance at infinite dilution (By Kohlrausch's law)

$$\frac{\lambda_a}{\Lambda_o} = n_a \text{ or } \lambda_a = n_a \times \Lambda_o$$

Similarly, $\lambda_c = n_c \times \Lambda_o$

(b) Ionic Mobilityand Ionic Conductance

Ionic mobility is the absolute velocity of an ion. It is the distance travelled by an ion in cm/s under a potential gradient of 1 V/cm. Contribution by an ion towards total equivalent conductance of an electrolyte at infinite dilution is called ionic conductance. The relationship between the two is given below:

$$\text{Ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

Example 20 *The equivalent conductance of very dilute solution of $NaNO_3$ at 18°C is 105.2 ohm^{-1} cm^2. If the ionic conductance of NO^-_3 ion in the solution is 61.7 ohm^{-1} cm^2, calculate the transport number of Na^+ ions in the solution.*

Solution: Given that,

$$\Lambda_o \text{ for } NaNO_3 = 105.2 \text{ ohm}^{-1} \text{ cm}^2$$
$$\lambda_{NO_3^-} = 61.7 \text{ ohm}^{-1} \text{ cm}^2$$

Substituting the values in the equation,

$$\lambda^\circ_{NO_3^-} = n_{NO_3^-} \times \Lambda^\circ_{NaNO_3}$$
$$61.7 = n_{NO_3^-} \times 105.2$$
$$n_{NO_3^-} = \frac{61.7}{105.2} = 0.586$$

$\therefore$ transport no. of $Na^+ = 1 - 0.516 = 0.414$

Example 21 *If ionic conductance for H^+ and OH^- ions are 394.8 and 198.5 ohm^{-1} cm^2 respectively at 25°C and if the specific conductance of water at this temperature is 5.54 × 10^{-8} ohm^{-1} cm^2, calculate the ionic product of water.*

Solution: Given that,

$$\lambda_{H^+} = 394.8 \text{ ohm}^{-1} \text{ cm}^2$$

$$\lambda_{OH^-} = 198.5 \text{ ohm}^{-1} \text{ cm}^2$$

$$\therefore \quad \Lambda_o(H_2O) = \lambda_{H^+} + \lambda_{OH^-} \text{ (By Kohlrausch's law)}$$

$$= 349.8 + 198.5 \text{ ohm}^{-1} \text{ cm}^2$$

$$= 548.3 \text{ ohm}^{-1} \text{ cm}^2$$

Specific conductance of pure water at 25°C is found to be,

$$K = 5.54 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^2$$

As water dissociates to a very small extent to give H^+ ions and OH^- ions, water may be considered to be a very dilute solution of H^+ ions and H^- ions in water so that we have

Eq. conductance of water = Specific conductance of water × Vol. in cm^3 containing 1 g eq. of ions

∴ volume in cm^3 containing 1 g eq. of ions

$$= \frac{\text{Eq. conductance of water}}{\text{Sp. conductance of water}} = \frac{548.3}{5.54 \times 10^{-8}}$$

$$= 9.897 \times 10^9$$

9.897×10^9 cm^3 of water contains 1 g eq. of H^+ ions or OH^- ions.

∴ 1 cm^3 of water contains H^+ ions or OH^- ions

$$= \frac{1}{9.897 \times 10^9} = 1.01 \times 10^{-10} \text{ g eq.}$$

or 1000 cm^3 of water contains H^+ ions or OH^- ions

$$= 1.01 \times 10^{-10} \times 1000 = 1.01 \times 10^{-7} \text{ g eq.}$$

i.e. $$[H^+] \text{ or } [OH^-] = 1.01 \times 10^{-7} \text{ g eq. per litre} = 1.01 \times 10^{-7} \text{ moles/litre}$$

Pure water dissociates to give equal number of H^+ ions and OH^- ions so that we have,

$$[H^+] = [OH^-] = 1.01 \times 10^{-7} \text{ M at } 25°C$$

Hence, $$K_w = [H^+][OH^-]$$

$$= (1.01 \times 10^{-7}) \times (1.01 \times 10^{-7}) = 1.02 \times 10^{-14} \text{ at } 25°C$$

6. Applications of Conductance Measurement

Conductance measurements find a number of applications, some of which are described as under:

(a) Determination of Ionic Conductance and Absolute Velocity of Ions, i.e. Ionic Mobilities The relation between ionic mobility and ionic conductance is

$$\text{Ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

This has also been explained along with solved examples in a previous section of the chapter.

(b) Determination of Equivalent Conductance at Infinite Dilution (Λ_o) for Weak Electrolytes Equivalent conductance of a weak electrolyte at infinite dilution cannot be determined directly. It is obtained using Kohlrausch's law. This has been explained along with solved examples in previous sections in this chapter.

(c) Determination of Degree of Dissociation of Weak Electrolyte Degree of dissociation of weak electrolyte (α) is given by,

$$\alpha = \frac{\Lambda_c}{\Lambda_o}$$

where Λ_c = Equivalent conductance at the concentration C, and Λ_o = Equivalent concentration at zero concentration (or infinite dilution). Knowing the values of Λ_c and Λ_o, α can be calculated.

(d) Determination of the Solubility of a Sparingly Soluble Salt Salts such as AgCl, $BaSO_4$, $PbSO_4$, etc., dissolve in water to a very small extent. That is why these salts are called ***sparingly soluble salts.*** The solubility of such salts can be calculated by the application of Kohrausch's law and conductance measurements as follows:

Specific conductance of the solution is determined first. Suppose it comes out to be k. If S is the solubility of the salt in ***gram equivalents per litre*** then the volume of the solution in cm^3 containing 1 g eq. will be 1000/S.

$\therefore$ Eq. conductance of the solution = Specific conductance $\times \frac{1000}{S}$

i.e.
$$\Lambda = K \times \frac{1000}{S}$$

Since, the salt dissolves very little, the solution is very dilute so that Λ may be considered as equal to Λ_o, i.e. equivalent conductance at infinite dilution.

Therefore,

$$\Lambda_o = K \times \frac{1000}{S} \text{ so that } \boxed{S = \frac{1000 \times K}{\Lambda_o}}$$

The value of Λ_o can be found by the application of Kohrausch's law, e.g. for AgCl,

$$\Lambda_o = \lambda_{Ag^+} + \lambda_{Cl^-}$$

This will give the solubility in gram-equivalent per litre. The solubility in grams/litre can be obtained by multiplying S with the equivalent weight of the substance.

Example 22 *Specific conductivity of a saturated solution of AgCl at 25°C was found to be 3.41 × 10^{-5} ohm^{-2} cm^{-1}. The specific conductivity for water used to make up the solution was 1.60 × 10^{-6} ohm^{-1} cm^{-1}. Determine the solubility of AgCl in water. Ionic conductances of Ag^+ and Cl^- at 25°C are 60.3 and 78.0 ohm^{-1} cm^2 respectively.*

Solution: Given that,

$$\begin{aligned} K \text{ for AgCl solution} &= 3.41 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1} \\ K \text{ for } H_2O &= 1.60 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1} \\ \lambda_{Ag^+} &= 60.3 \text{ ohm}^{-1} \text{ cm}^2 \\ \lambda_{Cl^-} &= 78.0 \text{ ohm}^{-1} \text{ cm}^2 \end{aligned}$$

By Kohlrausch's law, we have

$$\Lambda_o \text{ for AgCl} = \lambda_{Ag^+} + \lambda_{Cl^-}$$
$$= 60.3 + 78.0 = 138.3 \text{ ohm}^{-1} \text{ cm}^2$$
$$K \text{ for AgCl} = K \text{ for solution} - K \text{ for } H_2O$$
$$= (3.41 - 1.60) \times 10^{-6} = 1.81 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Substituting the values in the formula,

$$S = \frac{1000 \times K}{\Lambda_o}, \text{ we get}$$
$$S = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} \text{ g eq/litre}$$
$$= \frac{1000 \times 1.81 \times 10^{-6}}{138.3} \times 143.5 \text{ g/litre} = 0.001878 \text{ g/litre}$$

16.15 CONDUCTOMETRIC TITRATIONS

Conductometric methods help us obtain accurate end points in titration. The basic principle in conductomet-ric titrations is that when one solution from the burette is added to the other solution in the titration flask, the conductance value changes. This helps us arrive at the end point. The following examples will illustrate.



Fig. 16.17 *Conductometric titration*

1. Conductometric Titration of a Strong Acid with a Strong Base Suppose a solution of HCl is to be titrated against NaOH solution. The acid solution is taken in a beaker and the NaOH solution in the burette. The conductance of the acid solution is noted initially as well as after successive additions of small amount of NaOH solution. Evidently, the conductance of acid solution in the beginning is very high as it contains highly mobile H^+ ions ($HCl \rightarrow H^+ + Cl^-$). On adding NaOH solution to the HCl solution, the H^+ ions are replaced by the slow-moving Na^+ ions and hence the conductance of the solution keeps on falling till the end point is reached (i.e. all the H^+ ions replaced by Na^+ ions).

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

Beyond the end point, further addition of NaOH solution brings in fast-moving OH^- ions and

hence, the conductance of the solution again starts increasing. If the conductance values are plotted against the volume of the alkali added, a curve of type *ABC* is obtained as shown in Fig. 16.18. Point of intersection (i.e. the point *B*) corresponds to the end point.

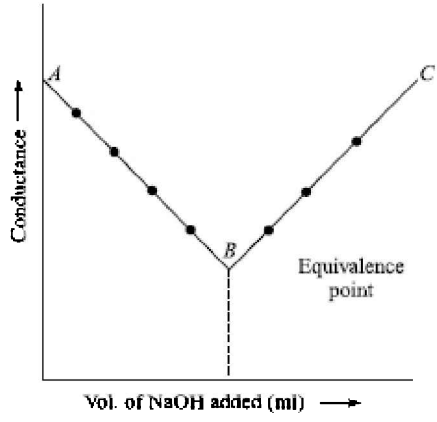


Fig. 16.18 *Conductometric titration of a strong acid with a strong base*

2. Titration of a Strong Acid with a Weak Base Let us consider the titration of HCl against NH_4OH solution. The conductance of HCl solution is initially high because of the presence of the fast-moving H^+ ions. As NH_4OH solution is added, the fast-moving H^+ ions are replaced by the slower $NH4^+$ ions and hence, the conductance falls along the line *AB*.

$$H^+ + Cl^- + NH_4OH \longrightarrow NH_4^+ + Cl^- + H_2O.$$

When the end point is reached further addition of NH_4OH does not cause much change in the conductance because NH_4OH is a weakly ionised substance. The line *BC* is thus almost horizontal. (Fig. 16.19).

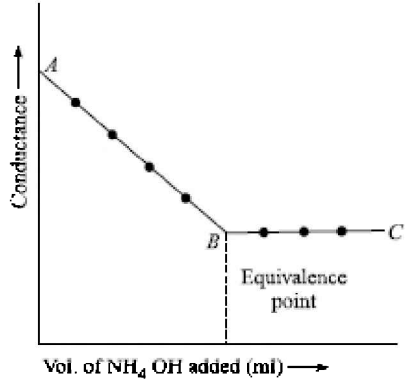


Fig. 16.19 *Conductometric titration of a strong acid against a weak base*

3. Titrations of a Weak Acid with a Strong Base (say CH_3COOH vs NaOH) Let us say a weak acid like acetic acid is titrated against a strong base like NaOH. The conductance of the acid initially is very low because of the low ionisation of the acid. However, on adding NaOH solution to the acid solution, the salt produced, viz. CH_3COONa, is highly ionized and hence the conductance

keeps on increasing along the line *AB* as shown in Fig. 16.20. When the whole of acetic acid has been neutralised, further addition of NaOH solution causes the conductance to increase sharply along the line *BC* because the NaOH added introduces the fast-moving OH^- ions. Intersection of the two lines *AB* and *BC* at the point *B* gives the equivalent point.

4. Titration of a Weak Acid Against a Weak Base Conductometric titrations are particularly valuable because we do not get sharp end points with indicators in normal titrations. Consider the titration of acetic acid (weak acid) with ammonium hydroxide (weak base). Initially, the conductance of solution is low due to poor dissociation of acetic acid. As the base is added to it, the conductance starts picking up due to the formation of ionisable ammonium acetate. After the neutralisation point, conductance remains almost constant, because the free base NH_4OH is a weak electrolyte. The end point is quite sharp. This is illustrated in Fig. 16.21.

5. Titration of Silver Nitrate Against KCl (Precipitation Reaction) $AgNO_3$ solution has some definite value of conductance in the beginning. As KCl solution is added to the $AgNO_3$ solution, the following reaction takes place.

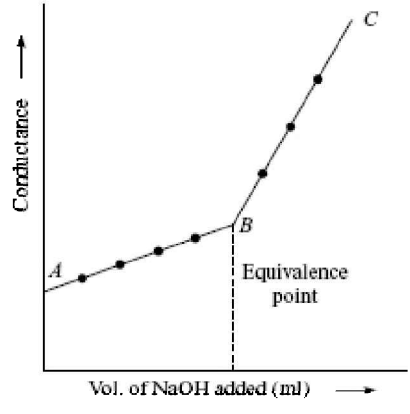


Fig. 16.20 *Conductometric titration of a weak acid with a strong base*

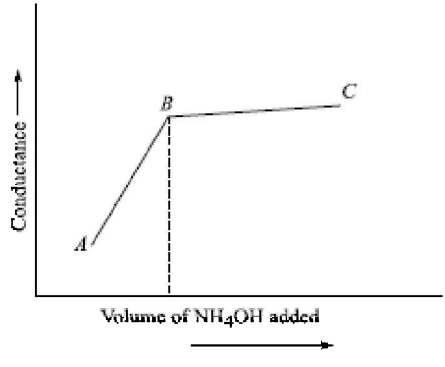


Fig. 16.21 *Conductometric titration of a weak acid with a weak base*

$$Ag^+ + NO_3^- + K^+ + Cl^- \rightarrow K^+ + NO_3^- + AgCl(ppt)$$

Thus, the net result is the replacement of Ag^+ ions of the $AgNO_3$ solution by the K^+ ions. Since

both these ions have nearly equal ionic mobility, the conductance remains almost constant till the end point is reached (Fig. 16.22). After the end point, further addition of KCl brings in K^+ and Cl^- ions. Thus, the conductance begins to increase along the line *BC*. Point of intersection *(B)* corresponds to the equivalence point.

Advantages of Conductometric Titrations Conductometric titrations have a number of advantages over ordinary titrations as listed below:

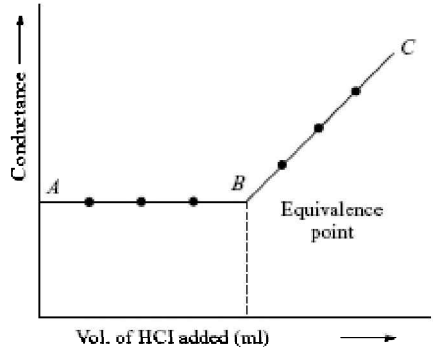


Fig. 16.22 *Conductometric titration of $AgNO_3$ sol. against KCl sol.*

(a) As the end point in these titrations is the intersection of two lines, no extra care is needed near the end point.

(b) These titrations can be used for ***coloured solutions*** where ordinary indicators fail.

(c) These can be used for titration of even ***very dilute solutions.***

(d) These can be used for the titration of mixture of ***weak and strong acids.***

PROBLEMS FOR PRACTICE

1. Equivalent conductance of $AgNO_3$ at infinite dilution is 133.3 ohm^{-1} cm^2 $equivalent^{-1}$. The transport number of Ag^+ ions in very dilute $AgNO_3$ solution is 0.454. Calculate the equivalent ionic conductances of Ag^+ and NO^-_3 ions at infinite dilution.

[Ans. $\lambda°_{Ag^+}$ = 60.158 ohm^{-1} cm^2 and $\lambda°_{NO\bar{3}}$ = 72.782 ohm^{-1} cm^2]

2. At 18°C, the equivalent conductivity of HCl acid solution is 379.6 ohm^{-1} cm^2. The transport number of chloride in HCl is 0.16. Calculate the ionic conductances of hydrogen and chloride ions.

[Ans. $\lambda°_{H^+}$ = 318.87 ohm^{-1} cm^2 and $\lambda°_{Cl^-}$ = 60.73 ohm^{-1} cm^2]

3. A dilute solution of $AgNO_3$ has an equivalent conductivity of 115.3 ohm^{-1} cm^2 eq^{-1} and the transport number of silver ion is 0.47. Calculate the ionic conductance and ionic mobilities of silver and nitrate ions.

[Ans. $\lambda°_{Ag^+}$ = 54.144 ohm^{-1} cm^2, $\lambda°_{NO\bar{3}}$ = 61.056 ohm^{-1} cm^2, $u(Ag^+)$ = 0.000561 cm/sec, $u(NO_{\bar{3}})$ = 0.000633 cm/sec]

4. If the equivalent conductance at infinite dilution at 293 K for aqueous hydrochloric acid, sodium acetate and sodium chloride solution are 383.5, 78.4 and 102.0 ohm^{-1} cm^2 respectively. Calculate the equivalent conductance of acetic acid at this temperature and dilution. If the equivalent conductance of acetic acid at some other dilution is 100.0 ohm^{-1} cm^2 at 293 K.

Calculate the degree of ionization of acetic acid at that dilution.

[Ans. $\Lambda_o = 359.9$ ohm^{-1} cm^2, $\propto = 0.278$**]**

5. The equivalent conductivity of acetic acid at infinite dilution is 387 Ω^{-1} cm^2 (g equivalent)$^{-1}$. At the same temperature, but at a concentration of 1 g equivalent weight in 1000 litres, it is 55 Ω^{-1}cm^2 (g equivalent)$^{-1}$. What is the percentage dissociation of 0.001 N acetic acid?

[Ans. 14.21%**]**

6. The molar conductances at infinite dilution of potassium chloride, hydrochloric acid and potassium acetate are 130.1, 379.4 and 95.6 ohm^{-1} cm^2 mol^{-1} respectively. Calculate the value of molar conductance at infinite dilution for acetic acid. If a molar conductance of a given acetic acid solution is 48.5 ohm^{-1} cm^2 mol^{-1} at 298 K, calculate the degree of dissociation of acetic acid at this temperature.

[Ans. $\Lambda_0 = 344.9$ ohm^{-1} cm^2 mol^{-1}, $\alpha = 0.141$**]**

7. The equivalent conductivity of a very dilute solution of KCl is 130.1 ohm^{-1} cm^2. The transport number of K^+ ion in such a solution is 0.496. Calculate the absolute velocities of the ions under unit fall of potential.

[Ans. $K^+ = 0.000669$ cm/s $Cl^- = 0.000679$ cm/s**]**

8. The molecular conductance of an aqueous solution of $AgNO_3$ at 20°C is 120 ohm^{-1} cm^2. If the transport number of nitrate ions is 0.55 at this temperature, how much distance would the silver ions move under a unit potential gradient?

[Ans. 0.00056 cm/s**]**

9. The equivalent conductivity at infinite dilution of NH_4Cl was found to be 150.4 ohm^{-1} cm^2 at 25°C. The transport number of NH_4^+ ion was found to be 0.491. Calculate the ionic conductances of NH_4^+ and Cl^-ions.

[Ans. $NH_4^+ = 73.84$ ohm^{-1} cm^2, $Cl^- = 76.54$ ohm^{-1} cm^2**]**

SOLVED EXAMPLES

Example 23 *Why is Ostwald's dilution law is not applicable to strong electrolytes?*

Solution: Strong electrolytes dissociate completely. Hence, there is no equilibrium between ions and the undissociated molecules, i.e., degree of dissociation $\alpha = 1$ at all concentrations. Thus, the dilution law is not applicable.

Example 24 *In the conductometric titration, the solution to be added from above should be much stronger than the solution taken in the conductometric cell. Why?*

Solution: The solution taken in the burette is usually about ten times stronger than that taken in the titration flask so that the volume change of the latter solution is minimum on the addition of the form or solution. This is required because conductance changes with dilution.

Example 25 *The Li^+ ion is smaller in size than Na^+ ion, yet transport number of Li^+ in LiCl solution is less than that of Na^+ ion in NaCl solution. Why?*

Solution: This is because Li^+ ions are more hydrated than Na^+ ions. The effective size of Li^+ ions becomes much bigger than Na^+ ions.

Example 26 *Molar conductivities of both strong and weak electrolytes increase with dilution.*

What is the difference in the cause of increase in the two cases?

Solution: A strong electrolyte is completely ionised even at high concentration. But ions are not completely free to move. On dilution, the interionic attractions decrease and ions become more free. Hence, the conductance increases. A weak electrolyte is very little ionised at high concentration. On dilution, dissociation increases, i.e. number of ions increases, and hence, the conductance increases.

Example 27 *Specific conductivity decreases with dilution whereas molar conductivity increases with dilution. Explain why.*

Solution: Specific conductivity is the conductance of ions present in 1 cm^3 of the solution. On dilution, the number of ions per cm^3 decreases. Hence, specific conductivity decreases. Molar conductivity (Λ_m) is product of sp. conductivity (K) and volume (V) of the solution in cm^3 containing 1 mole of the electrolyte. While K decreases on dilution, but V increases much more. Hence, their product increases with dilution.

SUMMARY

1. Electrical conductors are of two types, viz. electronic conductors for example, metals, graphite and electrolytic conductors for example, solutions of strong electrolytes.
2. Inter-ionic attraction, solvation of ions, viscosity of solvent and temperature determine the electrical conductivity of solutions.
3. If one ampere current flows through a conductor when a voltage of one volt is applied to it, the resistance (R) of the conductor is taken as 1 ohm (written as 1 Ω)
4. The reciprocal of electrical resistance is called conductance (C).
5. Specific conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 sq cm as the area of cross section. Alternatively, it is defined as the conductance of one centimetre cube of the solution of the electrolyte.
6. Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from one mole of the electrolyte dissolved in V cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them.
7. Resistance of an electrolytic solution is measured using the Wheatstone bridge principle.
8. Specific conductance shows a decrease with dilution. However, equivalent and molar conductances increase with dilution.
9. Ostwald dilution law may be stated as: *For a weak electrolyte with a small degree of dissociation, the degree of dissociation is inversely proportional to the square root of the initial molar concentration.*
10. Kohlrasch law states: *Molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions, each multiplied by the number of ions present in one formula unit of the electrolyte.*
11. The Kohlrausch law can be used to calculate molar conductivities at infinite dilution, degree of dissociation and solubility of a sparingly soluble salt.
12. According to Debye-Huckel theory, increase in equivalent conductance of a strong electrolyte on dilution is due to relaxation effect or asymmetry effect and electrophoretic effect.
13. Transport number is the fraction of the total current carried by anions. It can be determined by Hittorf method and moving-boundary method.
14. The basic principle in conductometric titrations is that when one solution from the burette is added to the other solution in the titration flask, the conductance value changes. This helps us arrive at the end point.

KEY RELATIONS

1. $R = \frac{E}{I}$ (ohm's law)
2. $C = \frac{1}{R}$ C and R stand for conductance and resistance respectively.
3. $R = \rho\frac{l}{a}$ ρ is called resistivity
4. $\rho = \frac{1}{K}$ where K is specific conductivity
5. $\Lambda_m = K \times V = K \times \frac{1000}{C} = K \times \frac{1000}{\text{Molarity}}$
6. Cell constant $= \frac{l}{a}$
7. Degree of dissociation, $\alpha = \frac{\Lambda_c}{\Lambda_o}$
8. $K = \frac{C\alpha^2}{1-\alpha}$ [Ostwald dilution law]
9. $\Lambda_m^c = \Lambda_m^\circ - b\sqrt{C}$ [Debye–Huckel–Onsagar equation for strong electrolytes]
10. Λ_m° for $A_xB_y = x\Lambda_{A^+}^\circ + y\lambda_{B^-}^\circ$
11. The complete Debye-Huckel-onsagar equation for strong electrolytes is

$$\Lambda_c = \Lambda_o - \left[\frac{82.4}{(DT)^{\frac{1}{2}}\eta} + \frac{8.20 \times 10^5}{(DT)^{\frac{3}{2}}}\Lambda_o\right]\sqrt{C}$$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. The Hittorf's rule states that
   (a) the loss of concentration around any electrode is proportional to the speed of the ions moving towards it
   (b) the loss of concentration around any electrode is proportional to the speed of the ions moving away from it
   (c) the loss of concentrations around both the electrodes is proportional to the sum of speed of cations and anions
   (d) none of the above
2. The statement of Kohlrausch's law is
   (a) the equivalent conductance of an electrolyte at infinite dilution is equal to the product of equivalent conductance of the component ions

(b) the equivalent conductance of an electrolyte at infinite dilution is equal to the difference of equivalent conductances of the component ions

(c) the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions

(d) none of the above

3. On passing electrical current through an electrolyte solution, the cations

(a) move towards cathode with speed equal to that of anions towards anode

(b) move with faster speed than that of anions

(c) move with different speed as compared to that of anions

(d) move with slower speed than that of anions

4. Kohlrausch's law can be used to determine

(a) λ_∞ for weak electrolyte

(b) absolute ionic mobilities

(c) solubility of a sparingly soluble salt

(d) all of these

5. The fraction of total current carried by the cation or anion is termed as

(a) fractional number

(b) speed number

(c) carrier number

(d) transport number

6. If λ_∞ is the equivalent conductance at infinite dilution and λ_v is the equivalent conductance of the electrolyte at the dilution v, the degree of dissociation is given by

(a) $\alpha = \dfrac{\lambda_\infty}{\lambda_v}$

(b) $\alpha = \dfrac{\lambda_v}{\lambda_\infty}$

(c) $\alpha = \lambda_\infty - \lambda_v$

(d) $\alpha = \lambda_v - \lambda_\infty$

7. The equivalent conductance at infinite dilution of NaCl, HCl and CH_3COONa at 25°C are 126.0, 426.0 and 91.0 ohm^{-1} cm^2 respectively. The equivalent conductance of acetic acid at infinite dilution at 25°C will be

(a) 643.0

(b) 517.0

(c) 217.0

(d) 391.0

8. When a strong acid is titrated against a strong base, the end point is the point of

(a) zero conductance

(b) maximum conductance

(c) minimum conductance

(d) none of these.

9. The failure of Ostwald's dilution law in case of strong electrolytes is due to
   (a) strong electrolytes are almost completely dissociated at all dilutions and λ_v/λ_∞ do not give accurate value of α
   (b) the law of mass action in its simple form cannot be applied when the concentration of the ions is very high
   (c) the ions get hydrolysed and affect the concentration terms
   (d) all of the above
10. Which of the following statement is true?
   (a) Ostwald's dilution law holds good only for strong electrolytes and fails completely when applied to weak electrolytes.
   (b) Ostwald's dilution law holds good for both weak and strong electrolytes.
   (c) Ostwald's dilution law holds good only for weak electrolytes and fails completely when applied to strong electrolytes.
   (d) Ostwald's dilution law does not good hold good for both weak and strong electrolytes.
11. Kohlrasch's law can be expressed as
   (a) $\lambda_\infty = \lambda_a - \lambda_c$
   (b) $\lambda_\infty = \lambda_c - \lambda_a$
   (c) $\lambda_\infty = \lambda_a + \lambda_c$
   (d) $\lambda_\infty = \lambda_c + \lambda_a$
12. Which of the following postulatales of Debye-Huckel theory is/are true?
   (a) The strong electrolyte is completely ionised at all dilutions.
   (b) The oppositely changed ions are completely distributed in the solution but the cations tend to be found in the vicinity of anions and vice versa.
   (c) Decrease in equivalent conductance with increase in concentration is due to fall in mobilities of ions due to inter-ionic effect.
   (d) All of the above.
13. During titration of a weak acid against a weak base, there is a sharp increase in — at the end point.
   (a) conductivity
   (b) equivalent conductance
   (c) specific conductance
   (d) none of these
14. The effect that trends to retard the mobilities of ions in solution is
   (a) asymmetry effect
   (b) relaxation effect
   (c) electrophoretic effect
   (d) all of these
15. If λ_∞ and λ_v are the equivalent conductances at infinite dilution and at V dilution, the degree of dissociation, α is given by

(a) $\alpha = \frac{\lambda_\infty}{\lambda_v}$

(b) $\alpha = \frac{\lambda_\infty}{\lambda_v^2}$

(c) $\alpha = \frac{\lambda_v}{\lambda_\infty}$

(d) None of these

Answers

1. (b)
2. (c)
3. (c)
4. (d)
5. (d)
6. (b)
7. (d)
8. (c)
9. (d)
10. (b)
11. (c)
12. (d)
13. (a)
14. (d)
15. (c)

SHORT-ANSWER QUESTIONS

1. How do specific conductivity and equivalent conductivity vary with dilution and why?
2. Explain relaxation effect as used in Debye-Huckel theory
3. What are the limitations of Arrhenius' theory of ionisation?
4. Give three points of differences between metallic conductor and electrolytic conductor.
5. What is meant by degree of dissociation of a weak acid? How can we obtain it from conductance measurement?
6. Describe an experiment to show migration of ions towards the electrodes on passing electricity.
7. Draw the titration curves obtained when
   (a) HCl is titrated against NaOH
   (b) CH_3COOH is titrated against NH_4OH
8. How are conductivity, equivalent conductivity and molar conductivity of an electrolytic solution related?

9. Give three postulates of Arrhenius's theory of ionisation.
10. Write Debye-Huckel-Onsagar equation in complete form explaining the meaning of different quantities.
11. State and explain Ostwald's dilution law.
12. What is transport number? How is it related to velocity of ions?
13. Derive the relationship between equivalent conductance and specific conductance.
14. Show graphically how the molar conductivity of a strong electrolyte and a weak electrolyte vary with concentration.

GENERAL QUESTIONS

1. Briefly explain the terms *specific conductance, equivalent conductance* and *molar conductance*. How are they inter-related? How are they measured experimentally?
2. How do specific conductance, equivalent conductance and molar conductance vary with dilution? Discuss the variation of molar conductivity of strong and weak electrolytes with concentration.
3. What are the limitations of Arrhenius' theory? How does Debye-Huckel theory explain the anomalous behaviour of strong electrolytes?
4. Define *Transport number*. Briefly describe 'moving boundary method' for the determination of transport number. Briefly explain the factors on which transport number depends.
5. What are the postulates of Arrhenius' theory of ionisation? How does this theory explain the following?
   (a) Anomalous result about colligative properties of electrolytic solutions
   (b) Constancy in the value of heat of neutralisation of any strong acid by any strong base
   (c) Acidic, basic or neutral nature of salt solutions
6. What do you mean by *transport number?* Briefly describe Hittorf's method for the determination of transport number of Ag^+ and NO^-_3 in $AgNO_3$ solution when
   (a) electrodes of platinum are used
   (b) electrodes of silver are used
7. State and explain Kohlrausch's law. Why is it called law of independent migration of ions? How does it help in the calculation of degree of dissociation of a weak electrolyte?
8. With the help of Hittorf's theoretical device, how can you justify that fall in concentration around any electrode is proportional to the speed of the ions moving away from it? What happens if the electrodes are attackable?
9. Explain the type of titration curves obtained when
   (a) $AgNO_3$ solution is titrated against KCl solution
   (b) CH_3COONa solution is titrated against HCl solution
10. What type of titration curve is obtained when
    (a) Acetic acid is titrated against NaOH solution?
    (b) HCl is titrated against NaOH solution? Explain why such curves are obtained.
11. List the important advantages of conductometric titrations over ordinary titrations.
12. Briefly explain 'moving-boundary method' for determination of transport numbers of K^+ and Cl^- in KCl solution.
13. Derive the relationship between ionic conductance and transport number of an ion.

14. State Kohlrausch's law. How can it be used to determine (a) ionic product of water, and (b) solubility of a sparingly soluble salt.
15. State and explain Ostwald's dilution law. Briefly describe its limitations and importance.
16. (a) What do you understand by 'ionic mobility'? How is it related to ionic conductance? Derive the relationship.

    (b) What is the effect of the following on the ionic conductance?

    (i) Viscosity of the solvent

    (ii) Temperature

    (iii) Pressure
17. Explain the method of calculation of transport number by Hittorf's method if the electrodes are attackable.
18. Taking a suitable example, explain how conductometric titrations can be used for the titration of a mixture of a weak acid and a strong acid against NaOH solution.
19. How can conductance measurement be used to find solubility of a sparingly soluble salt?
20. Briefly explain the principle of conductometric titrations taking the example of titration of HCl versus NaOH.
21. Briefly explain the factors on which transport number of an ion depends.
22. How can conductance measurements be used to find the degree of dissociation of a weak acid?
23. Why cannot limiting molar conductivities of weak electrolytes be found experimentally? How has the problem been solved? State and explain the law.
24. (a) What is the principle underlying conductometric titrations?

    (b) Discuss the titration curve obtained in the conductometric titration of

    (i) An aqueous solution of HCl with an aqueous solution of NaOH.

    (ii) NaOH against CH_3COOH

    (iii) CH_3COOH with NH4OH solution

    (iv) HCl solution with NH_4OH solution

    (v) A mixture of HCl and CH_3COOH with NaOH

    (vi) Oxalic acid solution with NaOH solution

    (vii) $AgNO_3$ solution with KCl solution

    (viii) Sodium acetate solution with hydrochloric acid
25. Define Kohlrausch's law. How can it be applied to determine the ionic product of water?



Electrochemistry-II 17

LEARNING OBJECTIVES

- Define buffer solutions and categorise them into different types
- Study the buffer action of a mixture of acetic acid and sodium acetate (acidic buffer)
- Study the buffer action of a mixture of ammonium hydroxide and ammonium chloride (basic buffer)
- Realise the importance of buffer solutions
- Derive Henderson equation for the pH of a buffer mixture
- Buffer capacity and buffer index
- Understand the neutralisation phenomenon
- Study neutralisation of a strong/weak acid with a strong/weak base
- Understand salt hydrolysis
- Derive expressions for hydrolysis constant, degree of hydrolysis and pH of the solution for salts of
    - Strong acid and weak base
    - Weak acid and strong base
    - Weak acid and weak base

17.1 BUFFER SOLUTION—INTRODUCTION

A buffer solution is defined as a solution whose pH remains practically constant even when small amounts of an acid or base are added to it.

Types of Buffer Solutions There are two types of buffer solutions.

(a) Solutions of Single Substances The solution of the salt of a weak acid and weak base, e.g. ammonium acetate (CH_3COONH_4), acts as a buffer.

(b) Solutions of Mixtures These are further classified as under:

(i) Acidic Buffer It is the solution of a mixture of equimolar quantities of a weak acid and a salt of this weak acid with a strong base (e.g. $CH_3COOH + CH_3COONa$)

(ii) Basic Buffer It is the solution of a mixture of equimolar quantities of a weak base and a salt of this weak base with a strong acid (e.g. $NH_4OH + NH_4Cl$). Buffer action of different kinds of buffer solutions is explained separately as under:

17.1.1 Buffer Action of Ammonium Acetate

Ammonium acetate is almost completely dissociated in the aqueous solution as

$$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+$$

Thus, in the solution, there are plenty CH_3COO^- ions and NH^+_4 ions.



Fig. 17.1 *Buffer solutions with specific pH values are available in the market.*

When a small amount of an acid is added to the above solution, the H^+ ions given by the acid combine with CH_3COO^-ions to form almost unionised CH_3COOH molecules.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

Thus, the H^+ ion concentration of the solution does not change practically and hence, the pH of the solution remains almost constant. Similarly, when a small amount of base is added to the above solution, the OH^- ions given by the base combine with NH^+_4 ions to form almost unionised NH_4OH molecules.

$$NH^+ + OH^- \rightarrow NH_4OH$$

Thus, the OH^- ion concentration and, hence, the H^+ ion concentration or the pH of the solution remains almost constant.

Role of buffer solutions in everyday life

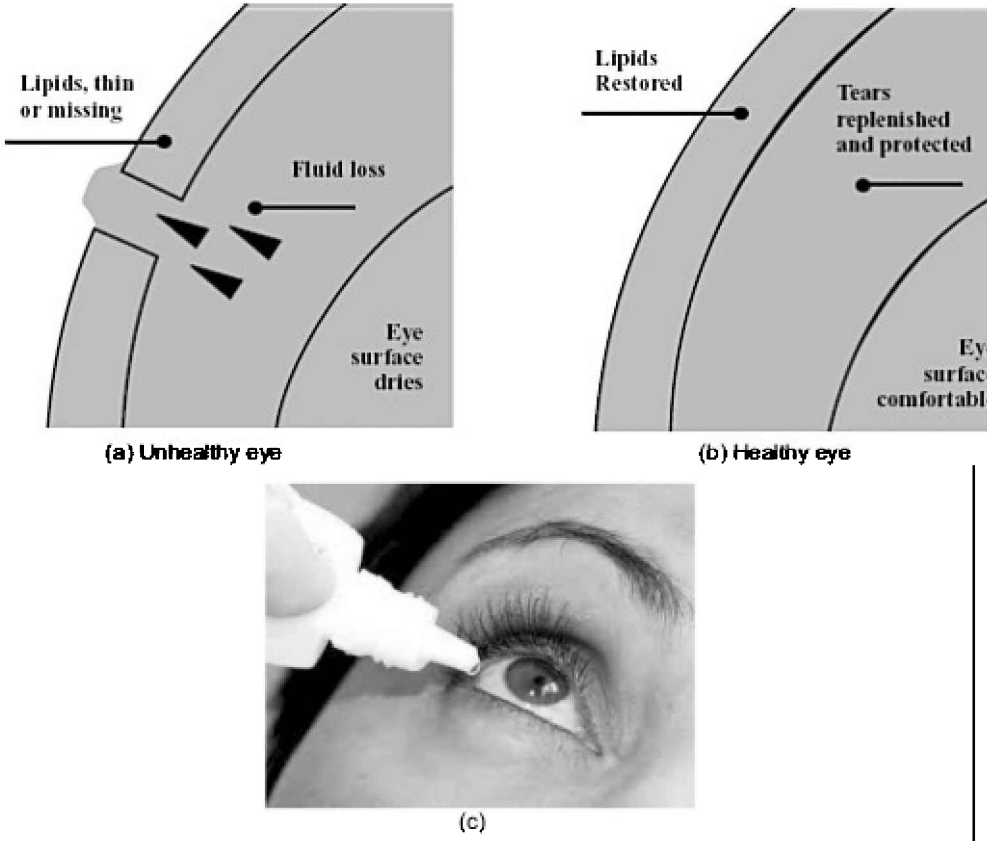


Fig. 17.2 *Administration of eye drops*

There is an outer lipid (fat) layer in the human eye. People with dry eyes lack a complete lipid layer which results in inadequate amount of tear fluid. Without this tear fluid, the person may experience a burning sensation and blurred vision. The pH of healthy tears is in the range 7.4–7.6. Eye drops meant for lubrication of the eye conform to this pH range. They compensate for the tear loss.

17.1.2 Buffer Action of a Mixture of Acetic Acid and Sodium Acetate (Acidic Butter)

Acetic acid dissociates to a small extent whereas sodium acetate is almost completely dissociated in the aqueous solution as follows:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \ldots(17.1)$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \quad \ldots(17.2)$$

By common-ion effect, the ionisation of CH_3COOH is further suppressed. Thus, in the solution, there are excess of acetate (CH_3COO^-) ions and a small amount of H^+ ions.

When a small amount of an acid is added to the above mixture solution, the H^+ ions given by the acid combine with the CH_3COO^- ions to form CH_3COOH which is almost unionised.

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH$$

Thus, the H^+ ion concentration and hence, the pH of the solution does not change much.

Similarly, when a small amount of a base is added, the OH^- ions given by the base combine with the H^+ ions already present to form almost unionised H_2O.

$$H^+ + OH^- \longrightarrow H_2O$$

From [17.1] [Given by the base (17.2)]

As the H^+ ions are consumed, the equilibrium (17.1) shifts towards right (according to Le Chatelier's principle). Thus, more of CH_3COOH dissociates to make up the loss of H^+ ions. Hence, the H^+ ion concentration of the pH of the solution remains almost the same.

17.1.3 Buffer Action of a Mixture of Ammonium Hydroxide and Ammonium Chloride (Basic Buffer)

NH_4OH dissociates to a small extent whereas NH_4Cl dissociates completely in the aqueous solution as follows:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad \ldots(17.3)$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \quad \ldots(17.4)$$

By common-ion effect, the ionisation of NH_4OH is further suppressed. Thus, in solution, there are excess of NH^+_4 ions and a small amount of OH^- ions.

When a small amount of base is added, the OH^- ions given by it immediately combine with NH^+4 ions to form the almost unionised NH_4OH.

$$NH_4^+ + OH^- \longrightarrow NH_4OH$$

Thus, the H^+ ion concentration or the pH of the solution is not affected much.

Similarly, when a small amount of an acid is added, the H^+ ions given by it combine with the OH^-ions already produced by NH_4OH in equilibrium (17.3)

$$H^+ + OH^- \longrightarrow H_2O$$

[Given by the acid] [Given by (17.3)]

As the OH^- ions are consumed away, the equilibrium (17.3) shifts in the forward direction. Thus, more of NH_4OH dissociates to produce OH^- ions which make up the loss of OH^- ions. Hence, the OH^-ion concentration and, therefore, the H^+ concentration or the pH of the solution does not change much.

17.1.4 Importance of Buffer Solutions

Importance of buffer solutions is discussed as under:

1. In industrial Processes The use of buffers is an important part of many industrial process, e.g.,

(a) In electroplating

(b) In the manufacture of leather, photographic materials and dyes

(c) In bacteriological research, culture media are generally buffered to maintain the pH required for the growth of the bacteria being studied

(d) In analytical chemistry

2. In Biological Processes The pH of our blood is maintained constant (at about 7.4) in spite of the various acid and base-producing reactions going on in our body. In the absence of its buffer nature, we cannot eat a variety of foods.

The two primary components of ***blood*** are ***blood plasma*** and ***Red Blood Cells*** (RBC). Blood plasma contains proteins, metal ions and inorganic phosphates. RBC contain haemoglobin molecules as well as the enzyme ***carbonic anhydrase*** which catalyses both the formation and decomposition of carbonic acid.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad \text{Carbonic acid}$$

The pH of blood plasma is maintained at about 7.40 by the HCO_3^-/H_2CO_3 buffer system. The pH of RBC is maintained at 7.25 again by HCO_3^-/H_2CO_3 and haemoglobin.

PH of our body fluids plays a fig role in leading a healthy and stress-free life. Overeating and eating of oily and junk food rises pH in our stomach which leads to stress and ageing. On the other hand, raw vegetables and fruits, which are alkaline in nature help to maintain ideal pH values in the body.

17.2 HENDERSON EQUATION FOR THE pH. OF A BUFFER MIXTURE

Henderson provided a solution to determine the pH of buffer mixtures of different types. These are reproduced as under:

1. For Acidic Buffer Mixture Suppose it is required to calculate the pH of an acidic buffer mixture, obtained by mixing a weak acid HA and its salt with a strong base BA. The former, being weak, dissociates to a small extent whereas the latter being a strong electrolyte, dissociates almost completely in the solution, i.e. we have,

$$HA \rightleftharpoons H^+ + A^-$$
$$BA \longrightarrow B^+ + A^-$$

If we apply the law of chemical equilibrium to the dissociation equilibrium of the weak acid, we get the following equation:

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \ldots(17.5)$$

where K_a is the dissociation constant of the acid.

$$\therefore \qquad [H^+] = K_a \frac{[HA]}{[A^-]} \qquad \ldots(17.6)$$

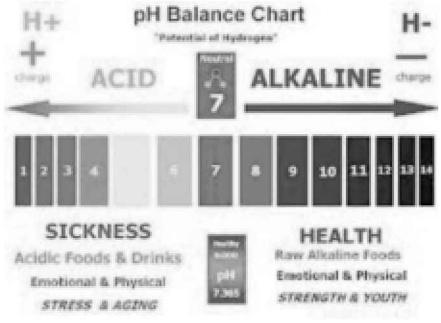


Fig. 17.3 *pH chart*

pH of our body fluids plays a big role in leading a healthy and stress-free life. Overeating and eating of oily and junk food raises pH in our stomach which leads to stress and ageing. On the other hand, raw vegetables and fruits, which are alkaline in nature help to maintain ideal pH values in the body.

Let the concentration of acid and the salt taken originally in the buffer solution be C_1 and C_2 moles/litre respectively.

As HA dissociates to a small extent which is further suppressed by the common-ion effect, the A^- ions in the mixture are mainly those produced from the salt BA. As the salt BA dissociates completely, we have

$$[A^-] = [BA] = c_2 \text{ moles/litre} \qquad \ldots(17.7)$$

As HA dissociates to a very small extent, the concentration of HA at equilibrium will be almost same as the original concentration.

$$[HA] = c_1 \text{ moles/litre} \qquad \ldots(17.8)$$

Substituting the values of $[A^-]$ and [HA] from equations (17.7) and (17.8) in Eq. (17.6), we get

$$\boxed{[H^+] = K_a \frac{c_1}{c_2}}$$

or
$$[H^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]} \qquad \ldots(17.9)$$

Taking logarithm of the sides, we get

$$\log [H^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

or
$$-\log [H^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

or
$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \ldots(17.10)$$

This equation is known as ***Henderson equation.*** Using this equation, we can calculate the pH of an acidic buffer mixture from the known concentrations of an acid and salt provided the dissociation constant of the acid is known.

2. For Basic Buffer Mixture Following the same steps as above, the expression for the pOH of a basic buffer mixture (BOH + BA) can be obtained. The Henderson equation for the basic buffer is

$$pOH = pK_b + \log\frac{[Salt]}{[Base]} \qquad \ldots(17.11)$$

where k_b is the dissociation constant of the base.

The pH of the basic buffer solution can be obtained from the following expression:

$$pH + pOH = 14$$

17.3 BUFFER CAPACITY AND BUFFER INDEX

Besides the general meaning of buffer capacity as given earlier, there are precise definitions of buffer capacity as given below.

Buffer capacity is defined as the number of moles of the acid or base which may be added to one litre or one dm^3 of a buffer solution for changing its pH by unity.

Alternatively Buffer capacity is defined as the change in the concentration of the acid buffer HA or the base buffer BOH required for changing its pH by unity keeping the concentration of the acid + salt or base + salt constant.

Buffer Index This term was introduced by Van Slyke to express the buffer capacity of a buffer solution quantitatively. It is expressed by the letter β. Mathematically,

$$\text{Buffer index, } \beta = \frac{\text{No. of moles of the acid or base added to one litre of the buffer solution}}{\text{Change in pH value}}$$

Example 1 *Calculate the pH of a mixture containing 0.01 M acetic acid and 0.03 M sodium acetate solutions (pK_a = 4.8).*

Solution: pH of an acid buffer is given by,

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Substituting the values,

$$pH = 4.8 + \log\frac{0.03}{0.01}$$

or $\quad pH = 4.8 + \log 3 \quad$ or $\quad pH = 4.8 + 0.4771 \quad$ or $\quad pH = 5.2771$

Example 2 *What will be the pH value of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume to 500 ml ($K_{CH_3COOH} = 1.8 \times 10^{-5}$ at 25°C)?*

Solution: Concentration of acetic acid is computed as under:

$$\text{Concentration} = 5 \text{ g in } 500 \text{ ml} = 10/\text{g litre}$$

$$= \frac{10}{60} \text{ M} \quad [\because \text{ Mol. wt. of } CH_3COOH = 60]$$

i.e. $$[CH_3COOH] = \frac{1}{6} \text{ M}$$

Concentration of sodium acetate is computed as under:

$$\text{Concentration} = 7.5 \text{ g in } 500 \text{ ml} = 15 \text{ g/litre}$$

$$[CH_3COONa] = \frac{15}{82} \text{ M} \quad \{\because \text{ Mol. wt. of } CH_3COONa = 82\}$$

$$pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.7447$$

$\therefore$ $$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.7447 + \log\frac{15/82}{1/6} = 4.7447 + \log 1.097$$

$$= 4.7447 + 0.0402$$

or $$pH = 4.7849 \simeq 4.78$$

Example 3 *Determine the pH of a solution obtained by mixing equal volumes of 0.10 N ammonium nitrate and 0.02 N ammonium hydroxide, K_b for NH_4OH being 1.8×10^{-5}.*

Solution: Before mixing, the concentrations of NH_4NO_3 and NH_4OH are,

$$[NH_4NO_3] = 0.10 \text{ N} = 0.10 \text{ M}$$

$$[NH_4OH] = 0.02 \text{ N} = 0.02 \text{ M}$$

After mixing, the concentrations change.
As the volume of the solution becomes twofold,

$$[NH_4NO_3] = \frac{0.10}{2} = 0.05 \text{ M}$$

$$[NH_4OH] = \frac{0.02}{2} = 0.01 \text{ M}$$

Applying Henderson equation,

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{0.05}{0.01} = 4.7497 + 0.6990 = 5.4487$$

$$pH = 14 - pOH$$

or $$pH = 14 - 5.4487 = 8.5513 \simeq 8.55$$

PROBLEMS FOR PRACTICE

1. A buffer solution is prepared from an acid of 2×10^{-6} dissociation constant and its sodium salt. What will be the molar ratio of the salt to the acid per litre in a buffer solution of 6.8 pH?

$$\left[\text{Ans. } \frac{[\text{Salt}]}{[\text{Acid}]} = 12.62\right]$$

2. Calculate the hydrogen on concentration of a solution obtained by mixing 100 ml of 0.3 N NH_4OH with 50 ml of 0.6 N NH_4Cl. Dissociation constant of NH_4OH is 2×10^{-5} and the ionic product of water 1×10^{-14}.

[Ans. 5×10^{-10} g ions/litre]

[*Hint:* First calculate pH]

3. What will be the hydrogen-ion concentration of a solution obtained by mixing equal volumes of 0.05 M acetic acid and 0.5 M sodium acetate? Dissociation constant of acetic acid is 1.8×10^{-5}.

[Ans. 1.779×10^{-6} g ions/litre]

[*Hint:* First calculate pH]

4. Calculate the pH of a solution obtained by mixing 6.0 g of acetic acid and 12.3 g of sodium acetate and making the volume to 500 ml ($K_a = 1.9 \times 10^{-5}$).

[Ans. 4.8973]

5. Calculate the pH at 18°C of a solution, prepared by the mixing of equimolar amounts of acetic acid and sodium acetate. The pK_a of acetic acid at 18°C is 4.74.

[Ans. 4.74]

6. Calculate the pH of a solution prepared by mixing 100 ml of 0.1 N acetic acid and 100 ml of 0.15 M sodium acetate. (Dissociation constant of acetic acid is 1.8×10^{-5}).

[Ans. 4.9258]

17.4 NEUTRALISATION PHENOMENON

A reaction between an acid and a base is called neutralization reaction. The acid could be strong or weak. Similarly, the base could be strong or weak. Correspondingly, we have four different types of neutralizations which are discussed separately.

1. Neutralisation of Strong Acid with a Strong Base The strong acids and strong bases are completely dissociated in the aqueous solutions to give H^+ and OH^- ions respectively. Thus, the neutralisation reaction taking place is simply

$$H^+ + OH^- \rightleftharpoons H_2O$$

The other ions like Na^+ or Cl^- (from say, HCl and NaOH) do not participate in the neutralisation process.

(a) Heat of Neutralisation Obviously, the neutralisation reaction, as written above, does not

depend upon the nature of the acid and the base. If a solution containing equivalent amounts of the strong acid and the strong base is taken, they are dissociated completely and produce the same quantity of H^+ ions and OH^- ions respectively. On mixing the two solutions, the same amount of neutralisation takes place and hence, the same amount of heat, i.e. 13.7 kcal/mole or 54.3 kJ mol^{-1}, is produced always.

(b) pH of the Solution In the present case, concentration of H^+ ions in an acid solution is equal to the concentration of OH^- ions present in the solution of the base. On mixing, the H^+ ions and OH^- ions combine with each other to form a weakly ionised water.

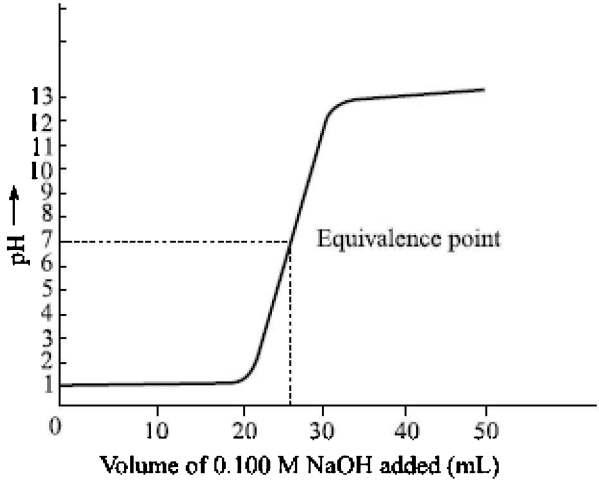


Fig. 17.4 *Titration curve for the neutralisation of strong acid with strong base.*

The water formed will have equal concentration of H^+ and OH^- ions.

$$[H^+] = [OH^-] = 10^{-7}\ M$$

$\therefore$ pH of the resulting solution will be = 7, i.e. the resulting solution will be neutral.

Titration curve (pH as a function of volume of titrant added is shown in Fig. 17.4.

This curve is obtained when we add 0.100 M NaOH to a beaker or flask containing 25 mL of 0.100 M HCl.

2. Neutralisation of a Strong Acid with a Weak Base Consider the reaction between HCl (strong acid) and NH_4OH (weak base). NH_4OH is not completely dissociated, while HCl is completely dissociated. Thus, we have

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$HCl \longrightarrow H^+ + Cl^-$$

(a) Heat of Neutralisation The reaction taking place may be represented as

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \qquad \Delta H = +1.4\ \text{kcal/mol}\ (5.9\ \text{kJ mol}^{-1})$$
$$H^+ + OH^- \rightleftharpoons H_2O \qquad \Delta H = -13.7\ \text{kcal/mole}\ (57.3\ \text{kJ mol}^{-1})$$
$$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O \qquad \Delta H = -12.3\ \text{kcal/mole}\ (51.4\ \text{kJ/mol}^{-1})$$

In this case, 1.4 kcal (5.9 kJ) of heat is used up for the dissociation of one mole of NH_4OH. Hence, the net heat evolved is only 12.3 kcal/mole (51.4 kJ mol^{-1}).

(b) pH of the Solution As represented by the final equilibrium equation above, the solution contains some undissociated NH_4OH molecules and an equal number of H^+ ions. Hence, the final solution is acidic, i.e. has pH < 7.

Titration curve for the neutralisation of a strong acid with weak base is given in Fig. 17.5.

This type of curve is obtained when we add 0.100 M HCl to 25 mL of NH_3 solution in a flask. As a result of hydrolysis, the pH at the equivalence point is less than 7.

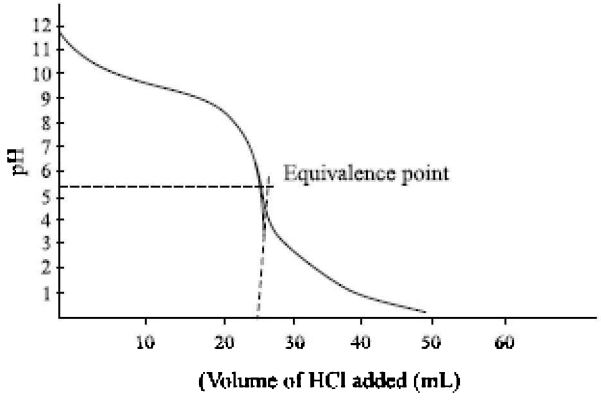


Fig. 17.5 *Titration curve for the neutralisation of strong acid with weak base*

3. Neutralisation of Weak Acid with a Strong Base Consider the reaction between CH_3COOH (weak acid) and NaOH (strong base). In this case, acetic acid is dissociated to a small extent while NaOH is dissociated completely in the aqueous solution as follows:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \ldots(17.12)$$

$$NaOH \longrightarrow Na^+ + OH^- \quad \ldots(17.13)$$

The heat of neutralisation and the pH of the resulting solution is explained below:

(a) Heat of Neutralisation The small amount of H^+ ions produced from the dissociation of acetic acid combine with OH^- ions produced from NaOH. Thus, as the H^+ ions are removed, the equilibrium (17.12) shifts towards right (according to Le Chatelier's principle). Thus, more of CH_3COOH dissociates producing more of H^+ ions which again combine with the OH^- ions. The process continues till all the H^+ ions produced combine with the OH^-. In this case, ***some heat is used up for the dissociation of acetic acid.*** Hence, the net reaction may be represented as,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \Delta H = 0.5 \text{ kcal/mole } (-2.1 \text{ kJ mol}^{-1})$$

$$H^+ + OH^- \longrightarrow H_2O, \Delta H = -13.7 \text{ kcal/mole } (-57.3 \text{ kJ mol}^{-1})$$

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O, \Delta H = -13.7 + 0.5 = -13.2 \text{ kcal/mole } (-55.2 \text{ kJ mol}^{-1})$$

Thus, the net heat evolved is less than in the first case.

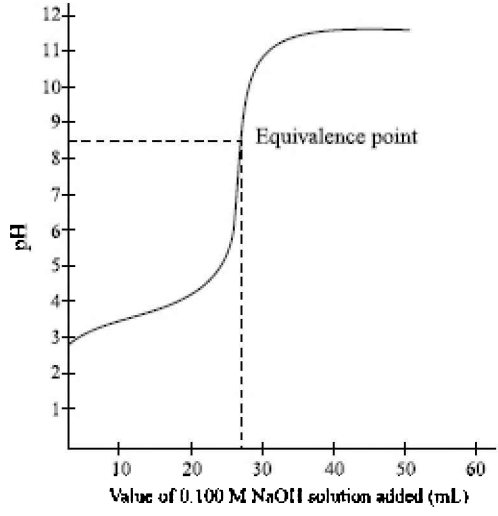


Fig. 17.6 *Titration curve for neutralisation of weak acid with strong base*

(b) pH of the Solution The final reaction does not proceed to completion. Instead, it reaches a state of equilibrium. The backward reaction produces some acetic acid (CH_3COOH) molecules and OH^- ions. Thus, the final solution contains some undissociat-ed acetic acid molecules and an equal number of OH^- ions. Hence, the solution obtained is alkaline, i.e. has pH > 7.

Titration curve of neutralisation of a weak acid with strong base is shown in Fig. 17.6.

The above curve is obtained when 0.100 M NaOH solution is added from a burette to 25.0 mL of a 0.100 M CH_3COOH solution in a flask. The pH of the solution at the equivalence point in such titration is greater than 7.



Fig. 17.7 *pH meter*

A pH meter is used to carry out the titration. After each addition of say 1 ml, the pH of the solution is noted. A graph is than plotted between pH and volume of the solution added.

4. Neutralisation of Weak Acid and a Weak Base Consider a reaction between

CH_3COOH (weak acid) and NH_4OH (weak base). Both the substances dissociate to a small extent in the aqueous solution.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \ldots(17.14)$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad \ldots(17.15)$$

(a) Heat of Neutralisation The small amount of H^+ ions and OH^- ions thus produced combine with each other as follows:

$$H^+ + OH^- \longrightarrow H_2O \quad \ldots(17.16)$$

As the H^+ ions and the OH^- ions are being removed from equilibria (17.14) and (17.15) respectively, these equilibria shift towards right producing more of H^+ ions and OH^- ions which again combine with one another and thus the process goes on. Here, some heat is required for the dissociation of CH_3COOH as well as NH_4OH. Hence, the net heat evolved is much less.

(b) pH of the Solution Although both the acid and the base involved dissociate to a small extent, yet depending upon their degrees of dissociation, one of the two may dissociate more than the other. Thus they may produce unequal number of H^+ ions and OH^- ions. Depending upon which of the two ions are in excess, the resulting solution may be alkaline or acidic.

17.5 SALT HYDROLYSIS

It is defined as the process in which salt reacts with water to give back the acid and the base.

$$\text{Salt} + \text{water} \longrightarrow \text{Acid} + \text{Base}$$

or

$$BA + H_2O \longrightarrow HA + BOH$$

Salt Water Acid Base

All salts are electrolytes and thus ionize completely in the aqueous solution. If the acid (HA) produced is strong and the base (BOH) produced is weak, we can write the above equation as,

$$B^+ + A^- + H_2O \longrightarrow H^+ + A^- + BOH$$

or

$$B^+ + H_2O \longrightarrow H^+ + BOH$$

Thus, in this case, the cation reacts with water to give an acidic solution. This is called ***cationic hydrolysis.***

Again, if the acid produced is weak and the base produced is strong, we can write

$$B^+ + A^- + H_2O \longrightarrow HA + B^+ + OH^-$$

or

$$A^- + H_2O \longrightarrow HA + OH^-$$

Here, the anion reacts with water to give the basic solution. This is called ***anionic hydrolysis.***

Hence, ***salt hydrolysis may be defined as the reaction of the cation or the anion of the salt with water to produce an acidic or basic solution.***

Salts can be divided into the following four categories.

1. Salts of Strong Acids and Strong Bases Examples of this category of salts are NaCl, KCl, K_2SO_4, Na_2SO_4, KNO_3, etc. Hydrolysis of NaCl is represented as under:

$$NaCl + aq \longrightarrow Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The overall process will be

$$NaCl + H_2O \rightleftharpoons Na^+ + Cl^- + H^+ + OH^-$$

i.e. there is only dissociation of sodium chloride and no hydrolysis.

2. Salts of Strong Acids and Weak Bases Examples of this category of salts are NH_4Cl, $CaCl_2$, NH_4NO_3. Hydrolysis of NH_4Cl is explained as under.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

or

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

Removing common anion from both sides

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

i.e. it is ***cationic hydrolysis.***

3. Salts of Weak Acids and Strong Bases Examples of this category are CH_3COONa, Na_3PO_4, Na_2CO_3. Hydrolysis of CH_3COONa is given below.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

or

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

Removing common cation from both sides

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

i.e. it is ***anionic hydrolysis.***

4. Salts of Weak Acids and Weak Bases Examples of this category of salts are CH_3COONH_4, NH_4CN. Hydrolysis of CH_3COONH_4 is explained as under:

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

The overall reaction will be

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

i.e. it involves both ***anionic as well as cationic hydrolysis.***

17.6 HYDROLYSIS CONSTANT AND DEGREE OF HYDROLYSIS

Hydrolysis of a salt (BA) may be presented as

$$BA + H_2O \rightleftharpoons HA + BOH$$

Applying the law of chemical equilibrium to the above reaction,

$$\frac{[HA][BOH]}{[BA][H_2O]} = K, \text{ the equilibrium constant.}$$

Since water is present in very large excess in the aqueous solution, its concentration $[H_2O]$ may be regarded as constant. Thus, we have

$$\frac{[HA][BOH]}{[BA]} = K[H_2O] = K_h$$

where k_h is called the ***hydrolysis constant.***

[HA] and [BOH] the molar concentrations of the free acid and the free base produced and [BA] represents the molar concentration of unhydrolysed salt. The general expression for the hydrolysis constant may be written as

$$K_h = \frac{[\text{Free Acid}][\text{Free Base}]}{[\text{Unhydrolysed salt}]}$$

Degree of Hydrolysis The degree of hydrolysis of a salt is defined as the fraction (or percentage) of the total salt which is hydrolysed. For example, if in a solution of aniline hydrochloride, 90% of the salt is hydrolysed into aniline and hydrochloric acid, the degree of hydrolysis is 0.90 or may be expressed as percentage, viz. 90%. It is usually represented by the symbol h.

17.7 EXPRESSIONS FOR THE HYDROLYSIS CONSTANT, DEGREE OF HYDROLYSIS AND pH OF SOLUTIONS OF SALTS OF STRONG ACID AND WEAK BASE

1. Hydrolysis Constant For the salt BA, the hydrolysis may be represented as

$$\underset{\text{Salt}}{BA} + H_2O \rightleftharpoons \underset{\text{Weak}}{BOH} + \underset{\text{Strong}}{HA}$$

$$\downarrow$$

or $$B^+ + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$$

or $$B^+ + H_2O \rightleftharpoons BOH + H^+$$

It is a case of ***cation hydrolysis***

The hydrolysis constant, k_h is given by,

$$K_h = \frac{[BOH][H^+]}{[B^+]} \qquad \ldots(17.17)$$

For the weak base BOH, the dissociation equilibrium is

$$BOH \rightleftharpoons B^+ + OH^-$$

$\therefore$ the dissociation constant k_b of the weak base BOH is given by,

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \ldots(17.18)$$

The ionic product of water, K_w, is given by,

$$K_w = [H^+][OH^-] \qquad \ldots(17.19)$$

Multiplying Eq. (17.17) with (17.18) and dividing by (17.19), we get,

$$\frac{K_h K_b}{K_w} = 1$$

or
$$K_h = \frac{K_w}{K_b} \quad \ldots(17.20)$$

2. Degree of Hydrolysis

Then	$B^+ + H_2O \rightleftharpoons$	BOH +	H^+
Initial molar concentration	c	0	0
Molar concentration at equilibrium	$c(1-h)$	ch	ch

The hydrolysis constant is given by

$$K_h = \frac{[H^+][BOH]}{[B^+]} = \frac{ch.ch}{c(1-h)} = \frac{ch^2}{1-h}$$

If h is very small as compared to 1, we can take $1 - h = 1$ so that the above expression may be written as

$$ch^2 \simeq K_h$$

or
$$h \simeq \sqrt{\frac{K_h}{c}} \quad \ldots(17.21)$$

If V is the volume of the solution is liters containing 1 mole of the solute, we have $c = 1/V$ so that expression (17.21) can be written as

$$h \simeq \sqrt{K_h . V} \quad \ldots(17.21a)$$

Substituting the value of K_h from (17.20) into (17.21) we get

$$h \simeq \sqrt{\frac{K_w}{K_b . c}} \quad \ldots(17.21b)$$

Then degree of hydrolysis of a salt of strong acid and weak base is inversely proportional to the square root of its molar concentration.

$$h \propto \sqrt{\frac{1}{c}}$$

3. pH The hydrolysis equation is

	$B^+ + H_2O \rightleftharpoons$	BOH +	H^+
Original concentration	C	0	0
Conc. at equilibrium	$c(1-h)$	ch	ch

i.e., $[H^+] = ch$

Substituting the value of h from Eq. (17.21b), we get

$$[H^+] = c\sqrt{\frac{K_h}{K_b \cdot c}} = \sqrt{\frac{K_w \cdot c}{K_b}} = \left(\frac{K_w \cdot c}{K_b}\right)^{1/2}$$

$$pH = -\log[H^+] = -\log\left(\frac{K_w \cdot c}{K_b}\right)^{1/2}$$

or
$$pH = -\frac{1}{2}[\log K_w - \log K_b + \log c] \quad \ldots(17.22)$$

17.8 EXPRESSIONS FOR THE HYDROLYSIS CONSTANT, DEGREE OF HYDROLYSIS AND pH OF SOLUTION OF A SALT OF WEAK ACID AND STRONG BASE

1. Hydrolysis Constant With the salt BA, the hydrolysis may be represented as follows:

$$BA + H_2O \rightleftharpoons BOH + HA$$

Salt ↓ Strong ↓

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA$$

or
$$A^- + H_2O \rightleftharpoons OH^- + HA$$

It is a case of ***anion hydrolysis***

The hydrolysis constant K_h for the above reaction is given by

$$K_h = \frac{[OH^-][HA]}{[A^-]} \quad \ldots(17.23)$$

For the weak acid HA, the dissociation equilibrium is

$$HA \rightleftharpoons H^+ + A^-$$

$\therefore$ the dissociation constant K_a of the acid HA is given by

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \ldots(17.24a)$$

The ionic product of the water K_w is given by,

$$K_w = [H^+][OH^-] \quad \ldots(17.24b)$$

Multiplying equations (17.23) with (17.24) and dividing by (17.25), we get

$$\frac{K_h K_a}{K_w} = \frac{[OH^-][HA]}{[A^-]} \times \frac{[H^+][A^-]}{[HA]} \times \frac{1}{[H^+][OH^-]} = 1$$

or
$$K_h = \frac{K_w}{K_a} \quad (17.25)$$

2. Degree of Hydrolysis Let the original concentration of the salt in the solution be c moles per litre and h be its degree of hydrolysis at this concentration.

Then

	$A^- + H_2O \rightleftharpoons$	OH^- +	HA
Original molar conc.	c	0	0
Molar conc. at equilibrium	$c(1-h)$	ch	ch

The hydrolysis constant (K_h), is given by

$$K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{1-h}$$

If h is very small as compared to 1, we can take $1 - h - 1$ so that the above expression reduces to

$$ch^2 \simeq K_h \quad \text{or} \quad h^2 \simeq \frac{K_h}{c}$$

or
$$h \simeq \sqrt{\frac{K_h}{c}} \qquad \ldots(17.26)$$

i.e.,
$$h \propto \sqrt{\frac{1}{c}}$$

Thus, ***the degree of hydrolysis of a salt of a weak acid and a strong base is inversely proportional to the square root of its molar concentration.***

If V is the volume of the solution in litres containing 1 mole of the solute, we have $c = \frac{1}{V}$ so that the expression (17.26) can also be written as,

$$h \simeq \sqrt{K_h \cdot V}$$

Substituting the values of K_h from Eq. (17.25) in Eq. (17.26) we get,

$$h \simeq \sqrt{\frac{K_w}{K_a \cdot c}} \qquad \ldots(17.27)$$

3. pH The hydrolysis equation is

	$A^- + H_2O \rightleftharpoons$	OH^- +	HA
original concentration	c	0	0
Conc. at equilibrium	$c(1-h)$	ch	ch

i.e. $$[OH^-] = ch$$

$\therefore$ $$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{ch}$$

Substituting the value of h from Eq. (17.27), we get

$$[H^+] = \frac{K_w}{c}\sqrt{\frac{K_a \cdot c}{K_w}} \quad \text{or} \quad [H^+] = \sqrt{\frac{K_w \cdot K_a}{c}}$$

$\therefore$ $$pH = -\log [H^+] = -\log \sqrt{\frac{K_w \cdot K_a}{c}} = -\log \left(\frac{K_w \cdot K_a}{c}\right)^{1/2}$$

or $$pH = -\frac{1}{2}[\log K_w + \log K_a - \log c]$$

17.9 EXPRESSIONS FOR HYDROLYSIS CONSTANT, DEGREE OF HYDROLYSIS AND pH OF SOLUTIONS OF SALTS OF WEAK ACID AND WEAK BASE

1. Hydrolysis Constant Representing the salt BA, we have

$$BA + H_2O \rightleftharpoons BOH + HA$$

Salt Weak Weak

$$\downarrow$$

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

If involves the ***anionic hydrolysis as well as cationic hydrolysis.*** Writing the various equations, we have

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} \qquad \ldots(17.28)$$

For the weak acid, $HA \rightleftharpoons H^+ + A^-$, so that

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \ldots(17.29)$$

For the weak base, $BOH \rightleftharpoons B^+ + OH^-$, so that

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \ldots(17.30)$$

Also, $$K_w = [H^-][OH^-] \qquad \ldots(17.31)$$

Multiplying equations (17.28), (17.29) and (17.30) and dividing by Eq. (17.31), we get,

$$\frac{K_h \cdot K_a \cdot K_b}{K_w} = 1$$

or $$K_h = \frac{K_w}{K_a K_b} \qquad \ldots(17.32)$$

2. Degree of Hydrolysis The hydrolysis equation is

	B^+	$+A^-$	$+H_2O \rightleftharpoons$	BOH	+ HA
Original concentration	c	c		0	0
Conc. at equilibrium	$c(1-h)$	$c(1-h)$		ch	ch

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \frac{h^2}{(1-h)^2} \qquad \ldots(17.33)$$

Here, the relationship between *Kh* and *h* does not involve *c*. Thus, the ***degree of hydrolysis of such a salt is independent of the concentration of the solution.***

If h is very small in comparison to 1, we can take $1 - h \simeq 1$, so that Eq. (17.33) becomes

$$K_h \simeq h^2 \quad \text{or} \quad h \simeq \sqrt{K_h}$$

Substitute the value of K_h from Eq. (17.32) in the above equation

$$h \simeq \sqrt{\frac{K_w}{K_a \cdot K_b}} \qquad \ldots(17.34)$$

3. pH For the weak acid, HA

$$HA \rightleftharpoons H^+ + A^-$$

$\therefore$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

or

$$[H^+] = K_a \frac{[HA]}{[A^-]} = K_a \frac{ch}{c(1-h)} = K_a \frac{h}{(1-h)}$$

But from Eq. (17.33), $\frac{h}{(1-h)} = \sqrt{K_h}$, so that we have

$$[H^+] = K_a \sqrt{K_h} = K_a \sqrt{\frac{K_w}{K_a \cdot K_b}} = \sqrt{\frac{K_a \cdot K_w}{K_b}}$$

$$pH = -\log H^+ = -\log \sqrt{\frac{K_a K_w}{K_b}} = -\log \left(\frac{K_a \cdot K_w}{K_b} \right)^{1/2}$$

or

$$pH = -\frac{1}{2}[\log K_a + \log K_w - \log K_b] \qquad \ldots(17.35)$$

Example 4 *Ionisation constant of acetic acid and ionic product of water at 25°C are 1.75 × 10^{-5} and 1 × 16^{-44} respectively. Calculate the hydrolysis constant of sodium acetate and its degree of hydrolysis in 0.1 molar solution at 25°C.*

Solution: Sodium acetate is a salt of weak acid and strong base; therefore,

$$K_h = \frac{K_w}{K_a}$$

Given that,

$$K_w = 10^{-14} \quad \text{and} \quad K_a = 1.75 \times 10^{-5}$$

$$K_h = \frac{10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

For a salt of weak acid and strong base,

$$h = \sqrt{\frac{K_h}{C}}$$

where, C is the molar concentration, i.e. number of moles/litre.

$$h = \sqrt{\frac{5.7 \times 10^{-10}}{0.1}} = 7.55 \times 10^{-5}$$

Example 5 *If the dissociation constant of HCN be 7.2×10^{-10} and that of ammonia be 1.75×10^{-5}, find out the hydrolysis constant for ammonium cyanide and also its degree of hydrolysis. Given $K_w = 1 \times 10^{-4}$*

Solution: For a salt of weak acid and weak base,

$$K_h = \frac{K_w}{K_a \cdot K_b}$$

In the present case, $K_a = 7.2 \times 10^{-10}$, $K_b = 1.75 \times 10^{-5}$, $K_w = 1 \times 10^{-14}$

Hence, $K_h = \dfrac{1 \times 10^{-14}}{7.2 \times 10^{-10} \times 1.75 \times 10^{-5}}$ or $K_h = \dfrac{10}{7.2 \times 1.75} = 0.7937$

Degree of hydrolysis

$$h = \sqrt{\frac{K_w}{K_a \cdot K_b}} \quad \text{or} \quad h = \sqrt{K_h}$$

or $h = \sqrt{0.7937} = 0.8909$

Example 6 *What would be the pH of a 0.1 molar sodium acetate solution when the dissociation constant for acetic acid is 1.8×10^{-5}?*

Solution: The pH of the solution of a salt depends upon the products of hydrolysis. In the present case, sodium acetate is hydrolysed as follows:

$$\begin{array}{ccc} CH_3COONa + H_2O & \rightleftharpoons & CH_3COOH + NaOH \\ \downarrow & & \downarrow \end{array}$$

or $$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

or $$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

If C is the initial concentration of the salt and h is the degree of hydrolysis, we have

	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$		
Before hydrolysis	c	0	0
After hydrolysis	$c(1-h)$	ch	ch

For a salt of weak acid and strong base,

$$[OH^-] = ch = c\sqrt{\frac{K_h}{c}}$$

$$[OH^-] = \sqrt{K_h \cdot c} = \sqrt{\frac{K_w}{K_a} \cdot c}$$

Substituting values, we have

$$[OH^-] = \sqrt{\frac{10^{-14}}{1.8\times10^{-5}} \times 0.1} = \sqrt{55.55\times10^{-12}} = 7.45\times10^{-6}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{7.45\times10^{-6}} = 1.342\times10^{-9}$$

$$pH = -\log[H^+] = -\log(1.342\times10^{-9}) = 8.8723$$

Alternatively, we can obtain the pH value by using the following relation directly,

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log c]$$

$$= -\frac{1}{2}[\log 10^{-14} + \log(1.8\times10^{-5}) - \log 10^{-1}]$$

$$= -\frac{1}{2}[-14 - 5 + 0.2553 + 1] = 8.8723$$

Example 7 *At 25°C, the ionisation constant of anilinium hydroxide is 4.6×10^{-10}. Taking the ionic product of water as 1×10^{-14}, calculate (a) the hydrolysis constant of anilinium chloride, (b) the degree of hydrolysis, and (c) pH value of 0.02 molar solution of the salt.*

Solution:

(a) ***Calculation of hydrolysis constant*** As anilinium chloride, $C_6H_5NH_3Cl$, is a salt of weak base (aniline) and strong acid (HCl), hydrolysis constant is given by,

$$K_h = \frac{K_w}{K_b}$$

Given that,

$$K_w = 10^{-14} \text{ and } K_b = 4.6\times10^{-10}$$

$$K_h = \frac{10^{-14}}{4.6\times10^{-10}} = 2.17\times10^{-5}$$

(b) ***Calculation of degree of hydrolysis.***

For such a salt $$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{2.17\times10^{-5}}{0.02}} = 3.29\times10^{-2}$$

(c) ***Calculation of pH***

For a salt of weak base and strong acid,

$$\text{pH} = -\frac{1}{2}[\log K_w - \log K_b + \log C]$$

$$= -\frac{1}{2}[\log 10^{-14} - \log(4.6 \times 10^{-10}) + \log 2 \times 10^{-2}]$$

$$= -\frac{1}{2}[-14 - (0.6628 - 10) + (0.3010 - 2)] = 3.18$$

PROBLEMS FOR PRACTICE

1. 0.05 molar solution of the potassium salt of a weak monobasic acid was found to have a pH of 9.25 at 25°C. Calculate the degree of hydrolysis and hydrolysis constant. Assuming the value of K_w to be 1×10^{-11} at 25°C, determine the dissociation constant of the weak acid.

[Ans. $K_a = 1.585 \times 10^{-6}$, $K_h = 6.31 \times 10^{-9}$, $h = 3.55 \times 10^{-4}$]

2. If the dissociation constant of HCN be 7.2×10^{-10} and that of ammonia be 1.75×10^{-5}, find out the hydrolysis constant for ammonium cyanide and also the degree of hydrolysis.

[Ans. $K_h = 0.794$, $h = 0.891$]

3. The dissociation constant of aniline as a base at 25°C is 593×10^{-10}. The ionic product of water at 25°C is 1.02×10^{-14}. Calculate the percentage hydrolysis of aniline hydrochloride in 1.0 N solution at 25°C.

[Ans. 0.415%]

4. Calculate the percentage hydrolysis of 0.01 N solution of sodium salt of organic acid. The ionication constant of water is 10^{-14} and dissociation constant of organic acid is 10^{-8}.

[Ans. 10%]

5. In a decinormal solution of KCN at 25°C, the salt is hydrolysed to 1.18%. Calculate (a) the hydrolysis constant, and (b) the degree of hydrolysis of N/20 solution of the salt at the same temperature.

[Ans. (a) 1.392×10^{-5} (b) 0.0167]

6. Calculate the degree of hydrolysis of 0.01 M solution of NH_4Cl. The dissociation constant of NH_4OH is 1.7×10^{-5} and ionic product of water = 1×10^{-14}. Also calculate the pH of the solution.

[Ans. $h = 2.42 \times 10^{-4}$, pH = 5.615]

7. Calculate the degree of hydrolysis of 0.1 N solution of sodium acetate. (The ionic product of water is 1.0×10^{-14} and the dissociation constant of acetic acid is 1.8×10^{-5}).

[Ans. 0.0002357]

8. At 18°C, the degree of hydrolysis of 0.01 N aniline acetate is 54%. Calculate the dissociation constant of aniline, given that K_a for acetic acid is 1.8×10^{-5} and $K_w = 1 \times 10^{-14}$.

[Ans. 1.91×10^{-9}]

9. The hydrolysis constant of a solution of potassium formate is 5×10^{-11}. The dissociation

constant for formic acid is 2×10^{-4}. Calculate the value of the ionic product (K_w) for water.

[Ans. 1×10^{-14}]

SUMMARY

1. A buffer solution is defined as a solution whose pH remains practically constant even when small amounts of acid or base are added to it.
2. There are buffers consisting of single substances and solutions of mixtures.
3. A solution of a mixture of equimolar quantities of a weak acid and a salt of this weak acid with a strong base (e.g. $CH_3COOH + CH_3COONa$) is called *acidic buffer.*
4. A solution of a mixture of equimolar quantities of a weak base and a salt of this weak base with a strong acid (e.g. $NH_4OH + NH_4Cl$) is called *basic buffer.*
5. Buffer solutions play an important role in industrial processes and biological processes.
6. *Buffer capacity* of a buffer solution is defined as the number of moles of the acid or base which may be added to one litre or one dm^3 of buffer solution for changing the pH by unity.
7. Buffer index, which is denoted by the letter β is given by

$$\text{Buffer Index} = \frac{\text{No. of moles of the acid or base added to one litre of the buffer solution}}{\text{Change in pH value}}$$

8. In the neutralisation of a strong acid and a strong base, the heat of neutralisation is constant and is equal to 57.3 kJ mol^{-1} and the pH of the solution at equivalence point is 7.
9. In the neutralisation of a strong acid with a weak base, the heat of neutralisation is less than 57.3 kJ mol$^-$and pH at the equivalence point is less than 7.
10. In the neutralisation of weak acid with a strong base, the heat of neutralisation is again less than 57.3 kJ mol^{-1} and pH at the equivalence point is more than 7.
11. In the neutralisation of a weak acid with a weak base, the heat of neutralisation is less than in the other types discussed and pH of the solution could be more than or less than 7 depending upon whether the acid is stronger or the base is stronger.
12. The process in which the salt reacts with water to give back the acid or base is called *salt hydrolysis.*
13. *Degree of hydrolysis* of a salt is defined as the fraction (or percentage) of the total salt which is hydrolysed.

KEY RELATIONS

1. Henderson equation for pH of a buffer solution:

For acidic buffer, $$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

For basic buffer, $$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

2. pH + pOH = 14
3. For a salt of strong acid and weak base,

$$K_h = \frac{K_w}{K_b}$$

$$h \simeq \sqrt{\frac{K_w}{K_b \cdot c}} \qquad \text{pH} = \frac{1}{2}\left[\log K_w - \log K_b + \log c\right]$$

4. For a salt of weak acid and strong base,

$$K_h = \frac{K_w}{K_a} \quad h \simeq \sqrt{\frac{K_w}{K_a \cdot c}}$$

$$\text{pH} = -\frac{1}{2}\left[\log K_w + \log K_a - \log c\right]$$

5. For a salt of weak acid and weak base

$$K_h = \frac{K_w}{K_a K_b} \quad h \simeq \sqrt{\frac{K_w}{K_a K_b}}$$

$$\text{pH} = -\frac{1}{2}\left[\log K_a + \log K_w - \log K_b\right]$$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. An example of an acid buffer is a solution of
   (a) ammonium acetate
   (b) a mixture of NH_4OH + NH_4Cl
   (c) a mixture of CH_3COOH + CH_3COONa
   (d) a solution of CH_3COONa
2. An example of a basic buffer is a solution of
   (a) NH_4OH + NH_4Cl
   (b) NH_4OH + HCl
   (c) CH_3COONH_4
   (d) NH_4OH + NaOH
3. In spite of various acid and base-producing reactions in our body, the pH of our blood is
   (a) 5.4
   (b) 6.4
   (c) 7.4
   (d) 8.4
4. The pH of an acidic buffer according to the Henderson equation is given by

(a) $pK_a - \log\frac{[\text{Salt}]}{[\text{Acid}]}$

(b) $pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

(c) $pK_a + \log\frac{[\text{Acid}]}{[\text{Salt}]}$

(d) $-pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

5. Choose the correct statement from the following:

(a) $\text{pOH} = -pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$

(b) $\text{pOH} = pK_b + \log\frac{[\text{Base}]}{[\text{Salt}]}$

(c) $\text{pOH} = -pK_b - \log\frac{[\text{Salt}]}{[\text{Base}]}$

(d) $\text{pOH} = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$

6. The pH value of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume to 500 mL ($K_{CH_3COOH} = 1.8 \times 10^{-5}$) is

(a) 4.78

(b) 3.78

(c) 5.78

(d) zero

7. The pH of a solution of strong acid and weak base at the equivalence point is

(a) 7

(b) more than 7

(c) less than 7

(d) none of the above

8. Heat of neutralisation of a strong acid and weak base is less than 57.3 kJ mol^{-1}. This is because

(a) all the acid is not ionised

(b) all the base is not ionised

(c) the ionisation is complete but further reaction does not take place

(d) some of the heat is transferred to the surroundings

9. Both anionic and cationic hydrolysis occur in the case of

(a) salts of strong acid and strong base

(b) salts of strong acid and weak base

(c) salts of weak acid and strong base

(d) salts of weak acid and weak base

10. The pH of a solution of salt of strong acid and weak base is given by

(a) $\frac{1}{2}(\log K_w + \log K_b + \log C)$

(b) $\frac{1}{2}(\log K_w - \log K_b - \log C)$

(c) $\frac{1}{2}(\log K_w - \log K_b + \log C)$

(d) $\frac{1}{2}(-\log K_w - \log K_b - \log C)$

Answers

1. (c)
2. (a)
3. (c)
4. (b)
5. (d)
6. (a)
7. (c)
8. (b)
9. (d)
10. (c)

SHORT-ANSWER QUESTIONS

1. Define buffer solution. What are the different types?
2. Explain with the help of equations the buffer action of ammonium acetate.
3. Explain one importance of buffer solution.
4. Write the equations for pH for acid buffer and basic buffer. Explain the terms involved in the equations.
5. Differentiate between buffer capacity and buffer index. Explain giving examples.
6. What will be the heat of neutralisation and pH of the solution at the neutralisation point in the case of a strong acid and a strong base?
7. Why is the pH of the solution at the neutralisation point less than 7 in case of a strong acid and weak base?
8. Estimate the heat of neutralisation in the case of a weak acid and weak base. Which factors determine the pH in such a case?
9. What is meant by salt hydrolysis?
10. Give the shape of neutralisation curve in the case of a weak acid and strong base.
11. Give two examples of salts of (a) strong acid and strong base, (b) strong acid and weak base, (c) weak acid and strong base, and (d) weak acid and weak base

12. Explain (a) cationic hydrolysis, and (b) anionic hydrolysis.
13. Explain the terms: (a) Hydrolysis constant (b) Degree of hydrolysis
14. Write the expressions for hydrolysis constant, degree of hydrolysis and pH of solution for the salt of a strong acid and weak base.

GENERAL QUESTIONS

1. What are different types of buffer solutions? Briefly describe each of them.
2. Discuss the buffer action of a mixture of acetic acid and sodium acetate.
3. Discuss the importance of buffer solutions in (a) industrial processes, and (b) biological processes.
4. Derive Henderson equation for the determination of pH of an acidic buffer mixture.
5. Explain the terms: (a) Buffer capacity (b) Buffer index
6. Discuss neutralisation phenomenon taking examples of
   (a) strong acid and weak base
   (b) weak acid and strong base
7. What is salt hydrolysis? Discuss the hydrolysis of salts of
   (a) strong acid and strong base
   (b) weak acid and weak base
8. What is meant by degree of hydrolysis? Derive expressions for the hydrolysis constant, degree of hydrolysis and pH of solutions of salts of weak acid and strong base.
9. Prove that degree of hydrolysis of a salt of weak acid and weak base is independent of the concentration of the solution.



Electrochemistry-III 18

LEARNING OBJECTIVES

- Understand electrochemical cell and electrolytic cell
- Represent an electrochemical cell as per convention
- Understand electrode potential and emf of a cell
- Know how to measure the emf of a cell
- Differentiate between a reversible cell and irreversible cell
- Learn different types of electrodes
- Derive a relationship between electrical energy and chemical energy
- Obtain expressions for ΔG, ΔH and ΔS in terms of temperature coefficient of emf
- Study reference electrodes
- Understand electrochemical series and its applications
- Learn activity and activity coefficient of electrolytes
- Derive Nernst equation for single electrode potential
- Study irreversible electrode processes
- Learn concentration cell and derive emf of electrode concentration cell and electrolyte concentration cell without transference and that of electrolyte concentration cell with transference.
- Have an idea of liquid junction potential
- Determine activity and activity coefficient from emf measurement
- Study the applications of emf measurement
- Study corrosion and its types
- Explain corrosion in terms of electrochemical theory and study the methods of prevention of corrosion

18.1 ELECTROCHEMICAL CELL

A device used to convert ***chemical energy*** of a reaction into ***electrical energy*** is called an ***electrochemical*** cell or ***galvanic cell.***

Working of an electrochemical cell is explained, taking the example of reaction between zinc metal and a solution of copper sulphate.

18.1.1 Reaction between Zn and $CuSO_4$

The reaction that takes place between the two is

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu\downarrow$$

It may also be written as

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

The above reduction oxidation (redox) reaction can be split into two half-reactions as under

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(oxidation half reaction)}$$
$$Cu^{2+} + 2e^- \longrightarrow Cu \quad \text{(Reduction half reaction)}$$

The first reaction is called ***oxidation half reaction*** whereas the second reaction is called ***reduction half reaction.*** The addition of the two half reactions gives the ***overall reaction.***



Fig. 18.1 *Lurgi Galvani (1737–1798) was the inventor of Galvamic cell*

If the redox reaction is allowed to take place in such a way that oxidation half reaction takes place in one beaker and the reduction half reaction in the other beaker, the electrons given out by the former will be taken up by the latter and the current will flow.

A zinc rod is placed in zinc sulphate solution in a beaker. A copper rod is placed in copper sulphate solution in another beaker. The two rods are connected by a wire and the two solutions are connected by a ***salt bridge*** (Fig. 18.2).

A salt bridge is a U-shaped tube containing concentrated solution of an electrolyte like KCI or K_2SO_4. The function of the salt bridge is to allow the movement of ions from one solution to another, without mixing of the two solutions. Electrons flow in the outer circuit in the wire but the inner circuit is completed by the flow of ions from one solution to the other through the salt bridge.

Some important features of the above cell are described as under:

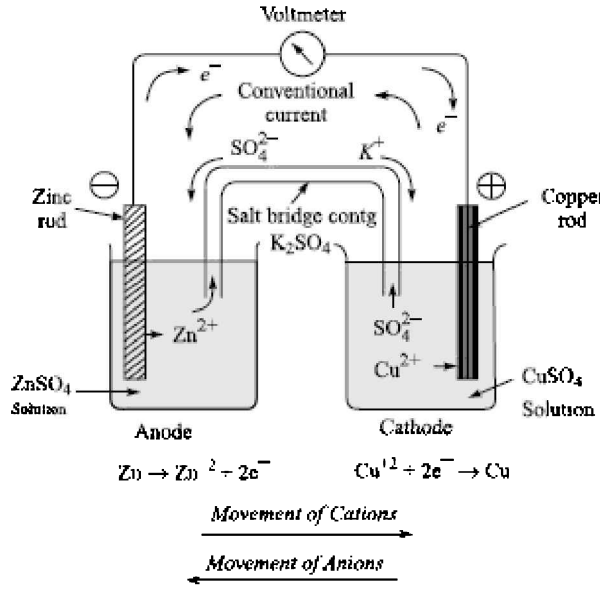


Fig. 18.2 *Electrochemical cell based on the reaction $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$*

1. Zinc electrode at which oxidation takes place is called ***anode.*** The copper electrode at which the reduction takes place is called ***cathode.***
2. Since electrons are produced at the zinc electrode, it is named the ***negative pole.*** The other electrode, i.e. the copper electrode acts as the ***positive pole.***
3. The electrons flow from the negative pole to the positive pole in the external circuit. Conventionally, the current is said to flow in the opposite direction.
   The oxidation of zinc into zinc ions produces excess of Zn^{2+} ions in the left beaker. Similarly, the reduction of copper ions to copper atoms leaves the excess SO^{2-}_4 ions in the solution in the right beaker. To maintain electrical neutrality of the solutions in the two beakers, the cations and the anions move through the salt bridge. This also completes the inner circuit.
5. As copper from copper sulphate solution is deposited on the copper electrode and sulphate ions migrate to the other side, the concentration of copper sulphate solution decreases as the cell operates. Consequently, the current falls with the passage of time.
6. The weight of copper rod will increase while that of zinc rod will decrease as the cell works.

18.1.2 Working of Ag-Cu Cell

The cell reactions that take place are represented under :

$$Cu + 2\ Ag\ NO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$$

or it may be written as

$$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

The two half reactions are

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

(oxidation half reaction)

$$2Ag^+ + 2e^- \longrightarrow Ag$$

(reduction half reaction)

Hence, the cell may be set up as shown in Fig. 18.3. Potassium nitrate may be taken as electrolyte in the salt bridge.

The oxidation takes place at the copper electrode. Therefore, it acts as an ***anode*** or negative pole. Reduction takes place at the silver electrode, it acts as ***cathode*** or ***positive pole.*** The conventional flow of current takes place from silver to copper.

KCl is used as Electrolyte in Salt Bridge KCl is specifically chosen as an electrolyte in salt bridge because the transport number of K^+ and Cl^- are almost equal. This eliminates the possibility of any kind of error in the measurement of cell voltage.

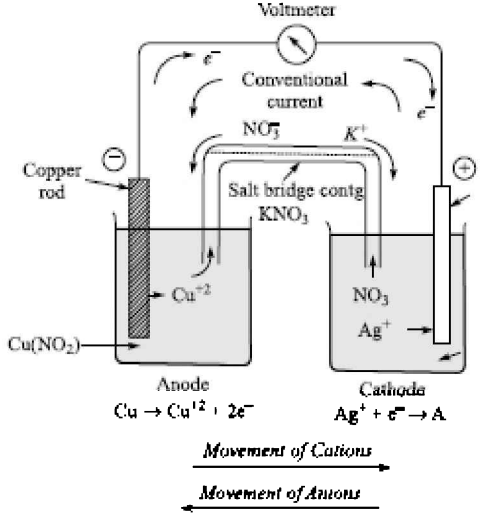


Fig. 18.3 *Electrochemical cell based on the* $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2A$

18.2 ELECTROLYTIC CELL

We take the aqueous solution of an electrolyte or the molten electrolyte in the vessel and two metal rods are immersed into it and then connected to a battery as shown in Fig. 18.4. We observe that cations (+ve ions) move towards the cathode and anions (–ve ions) towards the anode.

The anions on reaching the anode lose electrons. The cations on reaching the cathode gain electrons. Thus,

At anode: $B^- \longrightarrow B + e^-$ (oxidation)

At cathode: $A^+ + e^- \longrightarrow A$ (Reduction)

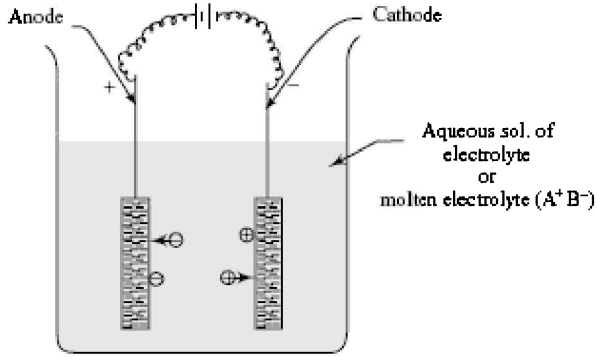


Fig. 18.4 *Electrolytic cell*

Thus, a redox reaction takes place on supplying electrical energy resulting into decomposition of the substance.

An ***arrangement in which electrical energy is supplied to bring about the redox reaction which was otherwise non-spontaneous i.e., to bring about the decomposition of the electrolyte is called an electrolytic cell.***

The main points of difference between an electrochemical cell and electrolytic cell are as follows:

Table 18.1 *Points ofdifference between an electrochemical cell and an electrolytic cell:*

Electrochemical cell	Electrolytic cell
1. This device converts chemical energy into electrical energy, i.e. electrical energy is produced as a result of the redox reaction taking place.	This device converts electrical energy into chemical energy, i.e. electrical energy is supplied to the electrolytic solution to bring about the redox reaction.
2. It is based upon redox reaction which is spontaneous.	The redox reaction is non-spontaneous in this case.
3. The two electrodes may be used in the solutions of the same or different electrolytes.	The two electrodes are used in the same electrolytic solution.
4. The electrode on which oxidation takes place is called the anode and the electrode on which reduction takes place is called the cathode.	The electrode which is connected to the negative terminal of the battery is called cathode, the cations migrate to it which gain electrons and hence reduction takes place here. The other electrode is called the anode.
5. The salt bridge or a porous pot is required in this cell.	No salt bridge is required in this case.

18.3 SCHEMATIC REPRESENTATION OF AN ELECTROCHEMICAL CELL

An electrochemical cell is represented as under for the Daniel cell:

$$Zn \mid Zn^{2+}(C_1) \parallel Cu^{2+}(C_2) \mid Cu$$

Conventionally, the electrode on which oxidation takes place is written on the left-hand side and the other electrode on which reduction takes place is on the right-hand side. The electrode on the left-hand side is written by writing the symbol of the metal (or the gas) first followed by the symbol of the ion with its concentration in brackets. The electrode on the right-hand side is written by first writing the ion along with its concentration in brackets followed by the symbol of the metal (or the gas). Single vertical lines show the phase boundaries of the electrodes and the double line represents the salt bridge. C_1 and C_2 represent the concentration of Zn^{2+} ions and Cu^{2+} ions respectively.

In a similar manner, Cu-$AgNO_3$ cell may be represented as

$$Cu \mid Cu^{2+}(C_1) \parallel Ag^{2+}(C_2) \mid Ag$$

Electrode Potential The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in the solution is called its electrode potential.

The electrode potential is further termed ***oxidation potential*** if the oxidation takes place at the electrode (with respect to normal hydrogen electrode) and is called ***reduction potential*** if reduction takes place at the electrode (with respect to normal hydrogen *electrode).* If in the half cell, the metal rod is suspended in the solution of unit activity and the temperature is kept at 298 K, the electrode potential is called ***standard electrode potential.*** It is represented usually by $E°$. If a gas is involved, the standard conditions chosen are 1 atmosphere pressure.

At each electrode-electrode interface, there is a tendency of the metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode, thus making it negatively charged. At equilibrium, there is separation of charges and depending upon the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called ***electrode potential.***

18.4 EMF OF A CELL

The force which causes the flow of electrons from one electrode to the other and thus results in the flow of the current is called electromotive force, or emf, and is measured in volts.

This force arises because of the different potentials possessed by the two electrodes. Thus, ***electromotive force may also be defined as the difference of potential which causes the current to flow from an electrode at higher potential to an electrode at a lower potential.*** If all the reactants and products are present in their state at 25°C, the emf is called ***standard emf.***

Measurement by Potentiometrie Method This method is based upon compensation principle and is used for the accurate measurement of emf. In this method, the unknown emf is opposed by another known emf until the two are equal. The general principle involved may be

explained with the help of Fig. 18.5 given below.

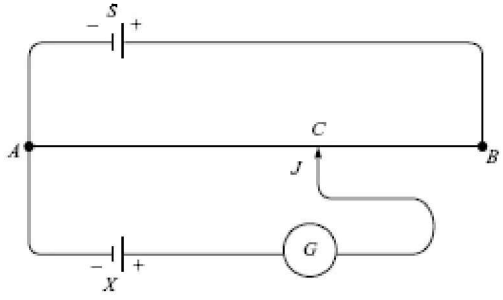


Fig. 18.5 *Compensation method for measuring emf*

AB is a stretched wire of uniform thickness, *S* is standard cell whose emf is known. It is connected to the end *A* and *B*. *X* is a cell whose emf is to be determined. One end of the cell *X* is connected to the end *A* and other to the sliding contact *J* through the galvanometer *G*, in such a manner that it sends emf in a direction opposite to that of the cell *S*. The sliding contact is moving along the wire *AB*. At a particular point, say *C*, no deflection is observed in the galvanometer. If E_s represents emf of the standard cell *S* and E_x that of the experimental cell *X*, then

$$\frac{E_x}{E_s} = \frac{\text{Length } AC}{\text{Length } AB}$$

or

$$E_x = \frac{\text{Length } AC}{\text{Length } AB} \times E_s$$

Thus, knowing E_s, E_x can be calculated.

18.5 WESTON STANDARD CELL

It consists of an H-shaped glass vessel (Fig. 18.6). One of the limbs contains mercury covered with paste of mercurous sulphate and mercury, a crystals of solid $CdSO_4 \cdot 8/3\ H_2O$ and saturated solution of cadmium sulphate. This limb acts as an anode. The other limb which acts as cathode contains cadmium amalgam (containing 12-14% of Cd by weight), covered with crystals of solid $CdSO_4 \cdot 8/3\ H_2O$ and then saturated $CdSO_4$ solution. Platinum wires are sealed into the bottom of the limbs to make contact with the active materials. The limbs are finally closed with corks and sealing wax. The purpose of placing solid crystals of $CdSO_4 \cdot 8/3\ H_2O$ is to keep the $CdSO_4$ saturated at all temperatures.

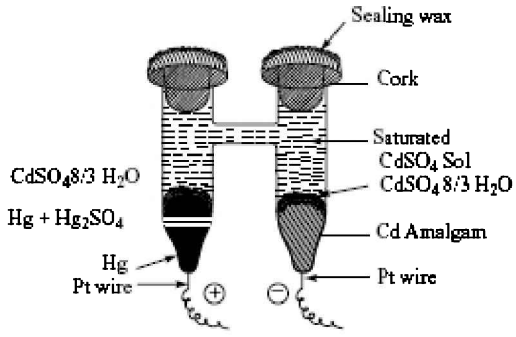


Fig. 18.6 *Weston standard cell*

This cell has a constant reproducible value of emf which does not change with time. Also, the temperature efficient of emf is very low, i.e. variation in emf per degree change of temperature is very small.

The emf of the above cell is 1.0185 volts at 15°C and 1.0181 volts at 25°C.

The reaction taking place in the cell is as follows.

$$Cd + Hg_2SO_4 + aq \longrightarrow CdSO_4 \cdot 8/3\ H_2O + 2Hg$$

18.6 REVERSIBLE CELL

A cell is said to be reversible if it satisfies the following three conditions:

1. If an opposing emf equal to that of the cell is applied to the cell, no current should flow in the circuit and hence no chemical reaction should take place.
2. If an opposing emf slightly (infinitesimally) smaller than that of the cell is applied, an infinitesimally small current should flow from the cell and an infinitesimally small reaction should take place.
3. If an opposing emf infinitesimally greater than that of the cell is applied, an infinitesimally small current should flow in the opposite direction and an infinitesimally small reaction in the reverse direction should occur.

This is illustrated in Fig. 18.7.

A well-known example of a reversible cell is that of Daniel cell, consisting of a zinc electrode dipped in $ZnSO_4$ solution and copper electrode dipped in $CuSO_4$ solution. When it is producing current, the reaction taking place in the cell is

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

The emf of the reversible cell can be measured with the help of a potentiometer.

As no current flows at the time of measurement, the conditions of reversibility are satisfied in the potentiometric method for the determination of emf.

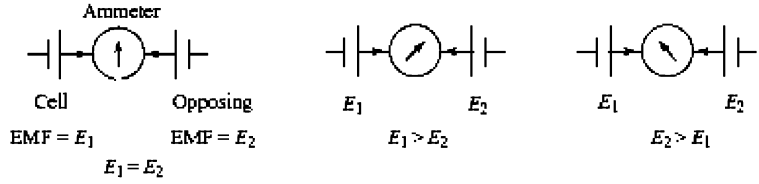


Fig. 18.7 *Concept of reversible cell*

18.7 IRREVERSIBLE CELL

Consider a cell consisting of a zinc rod and silver rod dipped in dilute sulphuric acid. When the two rods are connected with a wire, the following reaction takes place:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

i.e., zinc is oxidised to Zn^{2+} ions and H^+ ions are reduced to H_2 gas. In other words, zinc dissolves at one electrode and H_2 gas is evolved at the other.

If the cell is connected to an external source of emf whose emf is slightly greater than that of the cell and is opposing the cell, silver dissolves at one electrode and H_2 gas is evolved at the other.

$$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2$$

i.e., now oxidation takes place at silver electrode and reduction at the other. Thus, the condition of reversibility is not satisfied or the chemical change is not reversed (i.e. $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$) does not become $Zn^{2+} + H_2 \rightarrow Zn + 2H^+$). Instead, a new chemical reaction takes place. Hence, the above cell is not categorised as reversible but is irreversible.

18.8 TYPES OF ELECTRODES

Different types of electrodes are described as under:

1. Metal-Metal Ion Electrodes Such an electrode consists of a metal dipped in the solution of its ions, e.g. a zinc rod dipped in zinc sulphate solution, copper rod dipped in copper sulphate solution.

Taking the example of copper-copper ion electrode, when ***oxidation*** takes place at the electrode, the reaction may be represented as

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

On the other hand, when ***reduction*** takes place at the electrode, the reaction would be represented as

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

We can say that the electrode is reversible with respect to copper ions.

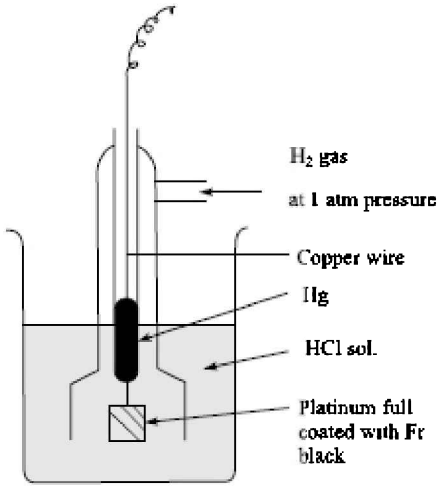


Fig. 18.8 *Hydrogen electrode*

2. Hydrogen Electrode The design of the hydrogen electrode is shown in Fig. 18.8. In the standard or normal hydrogen electrode, hydrogen gas at 1 atmospheric pressure is passed into 1 M HCl acid in which the foil of platinised platinum remains immersed.

If in a cell, the electrode acts as the ***anode*** then ***oxidation*** takes place. The reaction can be written as

$$H_2 \longrightarrow 2H^+ + 2e^-$$

i.e., some hydrogen gas changes into H^+ ions which goes into the solution.

If this electrode acts as ***cathode,*** then, ***reduction*** takes place. The reaction can be written as under:

$$2H^+ + 2e^- \longrightarrow H_2$$

i.e., some H^+ ions from the solution change into H_2 gas. Thus, the electrode is reversible with respect of H^+ ions. This electrode is usually represented as

$$Pt, H_2(g) \mid H^+ (\text{conc.} = C)$$

3. Hg-Hg_2Cl_2-KCl Electrode (Calomel Electrode) It is prepared as follows:

Pure mercury is placed at the bottom of the tube *T* (Fig. 18.9). It is covered with a paste of mercurous chloride (calomel) and then filled with either ***decinormal*** or ***normal*** or ***saturated*** solution of KCl from the side tube *A* such that the side tube *B* is also filled with KCl solution. *A* tube *C* having a piece of platinum wire sealed at its end is fixed into the tube *T* such that the platinum wire remains dipped into the mercury. A little mercury is placed in the tube *C* and a copper wire is put into it, to make an electrical contact.

A more convenient and practical assembly of the calomel electrode used in the laboratory as shown in Fig. 18.10.

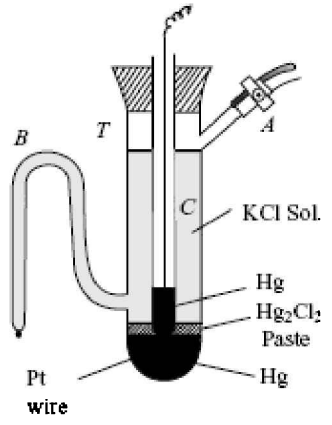


Fig. 18.9 *Calomel electrode.*

Oxidation occurs at this electrode through the following reactions:

$$2\,Hg(l) \rightarrow Hg_2^{2+} + 2e^-$$

$$\underline{Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2(s)}$$

Overall reaction is $2Hg(l) + 2\,Cl^- \rightarrow Hg_2Cl_2(s) + 2e^-$

Reduction occurs at this electrode as follows:

$$Hg_2Cl_2(s) \rightarrow Hg_2^{2+} + 2Cl^-$$

$$\underline{Hg_2^{2+} + 2e^- \rightarrow 2\,Hg(l)}$$

Overall reaction:

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2\,Cl^-$$

This overall reaction is just the reverse of the overall reaction during oxidation. Hence, the calomel is reversible with respect to chloride ions.

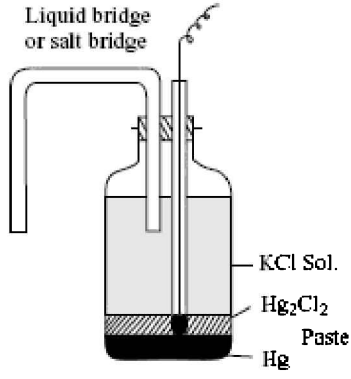


Fig. 18.10 *Another form of calomel electrode*

4. Reduction-oxidation (Redox) Electrodes Such electrodes are constituted by dipping a platinum wire in a mixture of solution of metal salts in different oxidation states (like cuprous and cupric salts, aurous and auric salts, ferrous and ferric salts, etc.) A metal in a particular reaction has a tendency to transform from one oxidation state to another. This gives rise to emf. Platinum serves the purpose of an electrical conductor. The reaction taking place in such electrodes may be represented as

$$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$$
$$Cu+ \rightleftharpoons Cu^{2+} + e^-$$

Example 1 *Devise a cell in which the overall reaction is*

$$Zn + Hg_2SO_4\,(s) \rightarrow ZnSO_4 + 2Hg(l)$$

and write the separate electrode reactions.

Solution: The cell can be represented as under:

$$Zn \mid ZnSO_4\,(aq) \parallel K_2SO_4\,(aq), Hg_2SO_4(s) \mid Hg$$

Thus, the anode (LHS) consists of zinc electrode and the cathode (RHS) consists of calomel electrode. The electrode reactions are as under:

Anode $\quad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$ (i)

Cathode $\quad Hg_2SO_4(s) \longrightarrow Hg_2^{2+} + SO_4^{2-}$

$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg(l)$$

$$Hg_2SO_4(s) + 2e^- \longrightarrow 2Hg(l) + SO_4^{2-} \quad \text{(ii)}$$

The overall cell reaction can be obtained by adding the two electrode reactions (i) and (ii)
Overall reaction: $Zn(s) + HgSO_H(s) \longrightarrow Zn^{2+}(aq) + 2\,Hg\,(l) + SO_4^{2-}$

Example 2 *Write down the reactions taking place separately at the two electrodes and the complete cell reaction.*

$$Pt, H_2(g) \mid HCl(aq) \parallel KCl(aq), AgCl(s) \mid Ag$$

Solution: According to the conventions, anode is written on the LHS and cathode on the RHS. Hence, in this case, hydrogen electrode is the anode, i.e., oxidation takes place here.
Anode Reaction (Hydrogen Electrode)

$$H_2(g) \longrightarrow 2H^+(aq) + 2e \quad \text{(i)}$$

The other electrode (RHS is metal-metal insoluble salt-salt anion electrode. Reduction takes place here.)
Cathode Reaction

$$AgCl(s) \longrightarrow Ag^+ + Cl$$
$$Ag^+ + e^- \longrightarrow Ag(s)$$
$$AgCl(s) + e \longrightarrow Ag(s) + Cl \quad \text{(ii)}$$

The net reaction may be written as under (i) + (ii):

$$H_2(g) \longrightarrow 2H^+ + 2e^-$$
$$2AgCl\,(s) + 2e^- \longrightarrow 2Ag(s) + 2Cl^-$$
$$H_2(g) + 2AgCl\,(s) \longrightarrow 2H^+ + 2Ag(s) + 2Cl^-$$

18.9 RELATIONSHIP BETWEEN ELECTRICAL ENERGY AND CHEMICAL ENERGY

The electrical energy produced in a cell is defined as the product of the quantity of the electricity that passes through the cell and emf of the cell, i.e.,

Electrical energy = Quantity of electricity × emf

For every one mole of electrons transferred in the cell reaction (i.e. for every one gram equivalent of the ions deposited), the quantity of electricity that flows through the cell is one faraday (1F = 96500 coulombs). Thus, if n moles of electrons are transferred in any cell reaction (e.g., for the reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, $n = 2$), the quantity of the electricity passing through the cell will be nF faradays. If E is the emf of the cell then

Electrical energy = nFE

For a large number of reactions, it was noticed that the electrical energy produced was not equal to the chemical energy. It was suggested by Gibbs (1875) and Helmholtz (1882) that the electrical energy produced in a reversible cell is equal to the decrease in the free energy accompanying the cell reaction. Thus, if ΔG represents the change in free energy, we must have,

$$-\Delta G = nFE \qquad \ldots(18.1)$$

According to Gibbs-Helmholtz equation, we have

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad \ldots(18.2)$$

Substituting the value of ΔG from Eq. (18.1) in Eq. (18.2), we get,

$$-nFE = \Delta H + T\frac{\partial(-nFE)}{\partial T}$$

$$nFE = -\Delta H + TnF\left(\frac{\partial E}{\partial T}\right)_P \qquad \ldots(18.3)$$

or

$$E = \frac{-\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P \qquad \ldots(18.4)$$

From Eq. (18.3), it follows that whether electrical energy *(nFE)* produced is equal to, less than or greater than the enthalpy change (ΔH), it depends upon the sign of $\partial E/\partial T$, i.e., the ***temperature coefficient*** of the emf. Thus,

1. If $\partial E/\partial T$ is extremely small (almost equal to zero), as is the case in Daniel cell, the electrical energy produced is equal to the enthalpy change.
2. $\partial E/\partial T$ is positive, the electrical energy produced is greater than the heat of reaction at constant pressure, the additional energy being absorbed from the surroundings.
3. If $\partial E/\partial T$ is negative, the electrical energy produced is less than the heat of reaction at constant pressure, the additional energy being absorbed by the surroundings.

18.10 EXPRESSIONS FOR ΔG, ΔH AND ΔS IN TERMS OF TEMPERATURE COEFFICIENT OF THE EMF

ΔG is related to emf according to the expression,

$$\Delta G = -nFE \qquad \ldots(18.5)$$

Thus, knowing the emf, E, ΔG can be calculated.

Equation (18.3) of section 18.9 can be rearranged as

$$\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right] \qquad \ldots(18.6)$$

Thus, knowing the emf, E and the temperature coefficient of the emf, $\left(\frac{\partial E}{\partial T}\right)_P$, the heat of reaction, ΔH can be calculated.

Having known the values of ΔG and ΔH, the entropy change (ΔS) accompanying the reaction can be calculated using the relationship.

$$\Delta G = \Delta H - T\Delta S \qquad \ldots(18.7)$$

Example 3 *The emf of the cell*

$$Cd/CdCl_2 \cdot 2\frac{1}{2}H_2O \text{ (saturated)} \,//\, AgCl(s) \,/\, Ag$$

is found to be 0.6753 volt at 25°C and 0.6915 volt at 0°C. Calculate ΔG, ΔH and ΔS of the cell reaction at 25°C.

Solution: The cell reaction may be written as

$$Cd + 2AgCl + aq \longrightarrow CdCl_2 \cdot 2\frac{1}{2}H_2O\,(sat.) + 2Ag$$

or
$$Cd + 2Ag^+ \longrightarrow Cd^{2+} + 2Ag$$

$\therefore$
$$n = 2$$

(a) *Calculation of free energy change* (ΔG)

$$\Delta G = -nFE = -2 \times 96500 \times 0.6753$$
$$= -130333 \text{ joules} = -130.33 \text{ kJ mol}^{-1}$$

(b) *Calculation of enthalpy change* (ΔH)

At atmospheric pressure, the temperature coefficient of emf in the range 0°C–25°C will be

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{E_2 - E_1}{T_2 - T_1} = \frac{0.6915 - 0.6753}{0 - 25}$$

$$= \frac{-0.0162}{25} = -0.00065 \text{ volt per degree}$$

Use the following relationship to calculate ΔH,

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_P$$

Using the data at 25°C, we get

$$\Delta H = -2 \times 96500 \times 0.6753 + 298 \times 2 \times 96500 \times (-0.00065)$$
$$= -167717 \text{ joules} \quad = -167.72 \text{ kJ mol}^{-1}$$

(c) *Calculation of entropy change* (ΔS)

Entropy change is related to enthalpy change as under:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-167717 - (-130333)}{298} = -125.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

The negative signs with Δg, ΔH and ΔS indicate the ***decrease*** in these quantities.

18.11 MEASUREMENT OF ELECTRODE POTENTIALS OF ZINC ELECTRODE AND COPPER ELECTRODE

1. Determination of Standard Electrode Potential of Zn/Zn^{2+} Electrode It is not possible to determine the absolute value of potential of a single electrode. It can only be measured relative to a reference electrode. One of the reference electrodes that can be used to measure the potential of an electrode is the standard hydrogen electrode. This reference electrode is shown in Fig. 18.11 (RHS portion, H_2 gas at 1 atm pressure is bubbled through an acid solution of unit molarity (1 M) with platinum as electrical contact. The potential of the electrode is taken as zero).

Standard electrode potential of hydrogen electrode is zero.

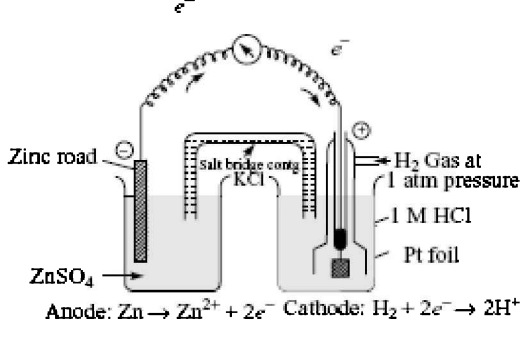


Fig. 18.11 *Measurement of standard electrode potential of Zn/Zn^{2+} electrode, using standard hydrogen electrode as the reference electrode.*

The emf of the above cell comes out to be 0.76 volt. Hence, standard electrode potential (reduction) of Zn/Zn^{2+} electrode = –0.76 volt. Further, the direction of flow of current indicates that oxidation takes place at the zinc electrode.

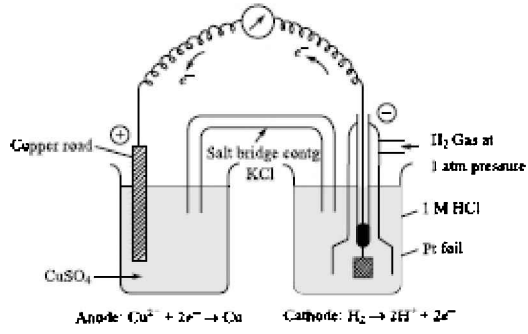


Fig. 18.12 *Measurement of standard electrode potential of Cu/Cu^{2+} electrode, using hydrogen electrode as the reference electrode*

2. Determination of Standard Electrode Potential of Cu/Cu^{2+} Electrode A cell comprising of copper electrode immersed in 1 M $CuSO_4$ solution and a standard hydrogen electrode is set up as shown in Fig. 18.12.

Standard electrode potential of hydrogen electrode is zero.

The emf of the cell comes out to be 0.34 volts. The direction of flow of current indicates that reduction takes place at the copper electrode. Hence, 0.34 volt is the ***standard reduction potential*** of Cu/Cu^{2+} electrode.

18.12 REFERENCE ELECTRODES

The potential of an unknown electrode can be obtained only by combining it with an electrode of known potential to make a cell. The emf of this cell is determined and then the potential of the unknown electrode is calculated. ***The electrode with a known potential used to determine the potential of unknown electrodes is called reference electrode.*** One of the electrodes used as reference electrode is the hydrogen electrode. Its electrode potential is taken as zero.

But the use of hydrogen electrode as a reference electrode is not convenient obviously because it involves the use of H_2 gas. Hence, a number of other electrodes have been used as reference electrodes. The most common out of these is the ***calomel electrode.*** The electrode potential at the calomel electrode at 25°C using 0.1 N KCl, 1.0 N KCl and saturated KCl solution have been determined accurately. These values are given below as ***reduction potentials.***

Table 18.2 *Concentration of KCL and reduction potential*

Conc. of KCl solution	Reduction potential
0.1 N	+0.3338 volt
1.0 N	+0.2800 volt
Saturated	+0.2415 volt

To determine the electrode potential of any electrode, a cell is constituted using this as one of the electrodes and calomel electrode as the second electrode. The emf of the cell is measured and then the following expression is used to calculate the required electrode potential.

emf of the cell = Reduction potential of the cathode – Reduction potential of the anode

Calomel Electrode

This reference electrode is shown in Fig. 18.13 (R.H.S). Standard electrode potentials of Zn/Zn^{2+} and Cu/Cu^{2+} are determined using calomel electrode as under.

1. Determination of Standard Electrode Potential of Zn/Zn^{2+} Electrode A cell comprising zinc electrode immersed in 1 M $ZnSO_4$ solution and the calomel electrode (say, using in KCl solution) is set up as shown in Fig. 18.13.

The emf of the above cell at 25°C comes out to be 1.083 volt. The direction of flow of current shows that oxidation takes place at zinc electrode. Thus, zinc electrode is the anode and calomel is cathode.

emf of the cell = Reduction potential of cath

ode (calomel) – Reduction potential of anode

1.083= 0.280 – Reduction potential of anode

(Zn electrode)

or reduction potential of anode (Zn electrode)

$$= 0.280 - 1.083 = -0.803 \text{ volt}$$

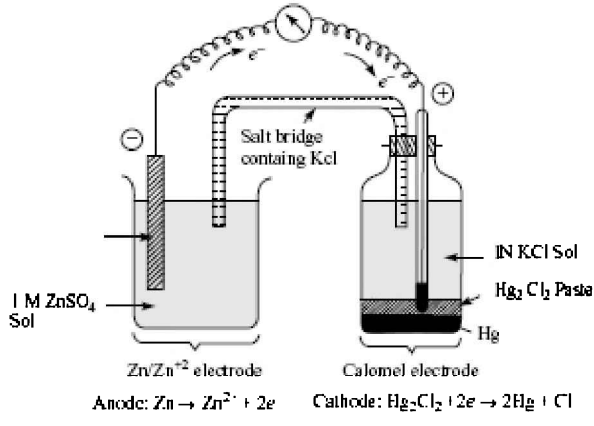


Fig. 18.13 *Measurement of standard electrode potential of Zn/Zn^{2+} electrode using calomel electrode as the reference electrode.*

2. Determination of the Standard Electrode Potential of Cu/Cu^{2+} Electrode A cell comprising of copper electrode immersed in 1 M $CuSO_4$ solution and the calomel electrode (say using in KCl solution) is set up as shown in Fig. 18.14.

The emf of the above cell comes out to be 0.018 volt. The direction of flow of current shows that reduction takes place at the copper electrode. Thus, copper electrode is the cathode and calomel is the anode.

emf of the cell = Reduction potential of cathode (copper) – Reduction potential of anode (calomel)

or 0.018 = Reduction potential of copper cathode – 0.280

or Reduction potential of copper cathode = 0.018 + 0.280 = 0.298 volt

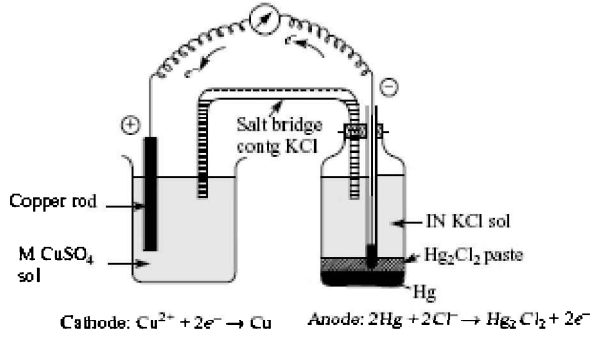


Fig. 18.14 *Measurement of standard electrode potential of Cu/Cu^{2+} electrode using calomel electrode as the reference electrode*

18.13 ELECTROCHEMICAL SERIES

Various electrodes have been arranged in order of their decreasing values of standard reduction potentials. This arrangement is called electrochemical series (Table 18.3)

Applications of the Electrochemical Series

1. To Predict Spontaneity of a Reaction To find out whether a reaction is feasible or not, emf of the cell based upon the given redox reaction is calculated. If the emf of the cell comes out to be positive, the reaction is feasible. If it comes out to be negative, the reaction is not feasible.

2. To Predict Whether a Metal Reacts with Acid to Give Hydrogen Gas In order that a metal (M) may react with an acid to give H_2 gas, the following reaction should take place.

$$M + H^+ \rightarrow M^+ + 1/2\ H_2$$

This reaction can be split into two half reactions as

$$M \rightarrow M^+ + e \qquad \text{(Oxidation half reaction)}$$
$$H^+ + e^- \rightarrow 1/2\ H_2 \qquad \text{(Reduction half reaction)}$$

i.e., the metal should have the tendency to lose electrons, i.e. it undergoes oxidation with respect to hydrogen. In other words, the metal would have a negative reduction potential. Thus, all metals lying below hydrogen (having negative reduction potential) in the electrochemical series (Table 18.3) react with the acid to give hydrogen gas.

Further evidently, lower the reduction potential, higher is the reactivity.

3. To Predict the Relative Ease of Oxidation or Reduction of Various Elements By convention, the positive sign is used to represent the reduction potential. This means greater the reduction potential, more easily is the substance (element or ion) reduced or in other words, the stronger an oxidising agent is. F_2 has the highest reduction potential and Li^+ ion has the lowest reduction potential. This means F_2 is reduced most easily whereas Li^+ ions are reduced

with greatest difficulty. In other words, F_2 is the strongest oxidising agent, whereas Li^+ ions are the weakest oxidising agent. Conversely, writing the reaction in the reverse order, it can be postulated that lithium (Li) will be oxidised most easily and hence is best reducing agent while fluoride ions (F^-) are oxidised with greatest difficulty and hence, are the weakest reducing agents.

4. To Calculate the Standard emf of Any Electrochemical Cell Electrochemical cell is based on a redox reaction which can be split into two half reactions, viz.,

(a) Oxidation half reaction

(b) Reduction half reaction

In the representation of a cell, the electrode on which oxidation takes place is written on the right-hand side:

$$\text{Standard emf of the cell} = \begin{bmatrix}\text{Standard reduction}\\ \text{potential of the}\\ \text{RHS electrode}\end{bmatrix} - \begin{bmatrix}\text{Standard reduction}\\ \text{potential of the}\\ \text{LHS electrode}\end{bmatrix}$$

Table 18.3 *Standard reduction potentials at 25°C (Electrochemical series)*

Reduction half reaction	Standard reduction potential E° (in volts)
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$CO^{3+} + e^- \rightarrow CO^{2+}$	1.82
$Au^{3+} + 3e^- \rightarrow Au$	1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
$Ag^+ + e^- \rightarrow Ag$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$I_2 + 2e^- \rightarrow 2I^-$	0.53
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Cu^{2+} + e^- \rightarrow Cu^+$	0.15
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.13
$2H^+ + 2e^- \rightarrow H_2$	0.00

$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25
$CO^{2+} + 2e^- \rightarrow CO$	–0.28
$PbSO_4 + 2e^- \rightarrow Pb + SO^{2-}_4$	–0.31
$CO^{2+} + 2e^- \rightarrow Cd$	–0.40
$Fe^{2+} + 2e^- \rightarrow Fe^-$	0.44
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18
$Al^{3+} + 3e^- \rightarrow Al$	–1.66
$Mg^{2+} + 2e^- \rightarrow Mg$	–2.37
$Na^+ + e^- \rightarrow Na$	–2.71
$Ca^{2+} + 2e^- \rightarrow Ca$	–2.87
$Ba^{2+}\ 2e^- \rightarrow Ba$	–2.90
$K^+ + 2e^- \rightarrow K$	–2.93
$Li^+ + e^- \rightarrow Li$	–3.05

Example 4 *Arrange the following metals in the order in which they displace each other from the solution of their salt:*

Al, Cu, Fe, Mg and Zn

Solution: After consulting the table of electrochemical series, the metals can be arranged as under:

Mg, Al, Zn, Fe, Cu, Ag

Example 5 *Given the standard electrode potentials*

$$K^+/K = -2.93\ V, Ag^+/Ag = 0.80\ V, Hg^{2+}/Hg = 0.79\ V$$
$$Mg^{2+}/Mg = -2.37\ V, Cr^{3+}/Cr = -0.74\ V$$

Arrange these metals in their increasing order of reducing power

Solution: More negative the reduction potential, more easily it is oxidised and hence, greater is the reducing power

Thus, increasing order of reducing power will be

$$Ag < Hg < Cr < Mg < K$$

Example 6 *Depict the galvanic cell in which the following reaction takes place:*

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

Further, show

(a) which of the electrodes is negatively charged,

(b) carriers of current in the cell, and

(c) individual reaction at each electrode.

Solution: The cell may be depicted as

$$Zn(s) \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

(a) Anode, i.e. Zn electrode, is negatively charged

(b) The current is carried by the ions inside the cell and by electrons outside the cell

(c) *At Anode*: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Example 7 *Calculate the standard emf of a cell which involves the following cell reaction*

$$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$$

Given that, $E^\circ_{Zn, Zn^{2+}} = 0.76$ *volt and* $E^\circ_{Ag, Ag^+} = -0.80$ *volt*

Solution: As oxidation takes place at the zinc electrode, the reduction takes place at the silver electrode. By convention, the cell may be represented as

$$Zn \mid Zn^{2+} \parallel Ag^+ \mid Ag$$

$$\text{Standard emf of the cell } (E^\circ_{cell}) = \begin{bmatrix}\text{Standard reduction}\\ \text{potential of the}\\ \text{RHS electrode}\end{bmatrix} - \begin{bmatrix}\text{Standard reduction}\\ \text{potential of the}\\ \text{LHS electrode}\end{bmatrix}$$

As standard oxidation potentials of zinc electrode and silver electrode are given to be 0.76 volt and –0.80 volt, their standard reduction potentials will be –0.76 volt and +0.80 volt respectively.

Hence, $E^\circ_{cell} = 0.80 - (-0.76) = 1.56$

Example 8 *Predict whether zinc and silver react with 1 N sulphuric acid to give out hydrogen gas or not. Given that the standard reduction potentials of zinc and silver are –0.76 volt and 0.80 volt respectively.*

Solution:

(a) *To predict the reduction of zinc with sulphuric acid:* If it reacts, the following reaction should take place:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

i.e. $$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

The cell will be represented as,

$$Zn \mid Zn^{2+} \parallel H^+ \mid H_2$$

$$\therefore \text{ standard emf of the cell } (E^\circ_{cell}) = \begin{vmatrix}\text{Standard reduction}\\ \text{potential of the}\\ \text{RHS electrode}\end{vmatrix} - \begin{vmatrix}\text{Standard reduction}\\ \text{potential of the}\\ \text{LHS electrode}\end{vmatrix}$$

$$= 0 - [-0.76] = +0.76 \text{ volt}$$

Thus, the emf of the cell comes out to be positive. Hence, the reaction takes place.

(b) *To predict the reaction of silver with sulphuric acid*

Let us suppose that silver reacts with sulphuric acid to give the following reaction:

$$2Ag + H_2SO_4 \rightarrow Ag_2SO_4 + H_2$$

i.e. $$2Ag + 2H^+ \rightarrow 2Ag^+ + H_2$$

The cell may be represented as

$$Ag \mid Ag^+ \parallel H^+ \mid H_2$$

$$E^\circ_{cell} = E^\circ_{H^+, H_2} - E^\circ_{Ag^+, Ag}$$

$$= 0 - 0.80 \text{ volt} = -0.80 \text{ volt}$$

As the emf of the supposed cell comes but to be negative, this reaction does not take place.

Example 9 *A cell is prepared by dipping a copper rod in 1 M $CuSO_4$ solution and a nickel rod in 1 M $NiSO_4$*

The standard reduction potentials of copper electrode and nickel electrode are 0.34 volt and –0.25 volt respectively.

(a) What will be the cell reaction ?

(b) What will be the standard emf of the cell?

(c) Which electrode will be positive?

(d) How will the cell be represented?

Solution:

(a) The cell reaction can be

either $$Ni + CuSO_4 \rightarrow NiSO_4 + Cu$$

i.e. $$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$$

or $$Cu + NiSO_4 \rightarrow CuSO_4 + Ni$$

i.e. $$Cu + Ni^{2+} \rightarrow Cu^{2+} + Ni$$

The correct cell reaction will be the one which gives positive emf.

If the first reaction is the cell reaction,

$$Ni \rightarrow Ni^{2+} + 2e^-$$

Standard reduction potential = –0.25 volt

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Standard potential = +0.34 volt

Overall reaction $Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$

$$\text{Std. emf} = 0.34 - (-0.25) \text{ volt} = 0.59 \text{ volt}$$

The emf is positive for this reaction. Hence, this is the correct cell reaction. (If the other reaction is checked, emf will come out to be –0.59 volts)

(b) Standard emf of the cell is calculated above = 0.59 volt

(c) Since oxidation takes place at the ***nickel electrode,*** therefore it acts as ***anode*** or since electrons are produced at this electrode it acts as ***negative pole.*** Obviously, copper electrode will act as ***cathode*** or a ***positive*** pole.

(b) By convention, the cell will be represented as

$$Ni \mid NiSO_4 \text{ (1 M)} \parallel CuSO_4 \text{ (1 M)} \mid Cu$$

Example 10 *Can a solution of 1 M copper sulphate be stored in a vessel made of nickel metal? Given that* $E°_{Ni,Ni^{2+}} = +0.25$ *volt and* $E°_{Cu,Cu^{2+}} = -0.34$ *volt.*

Solution: In this problem, we want to see whether the following reaction takes place or not:

$$Ni + CuSO_4 \rightarrow NiSO_4 + Cu$$

i.e.

$$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$$

The cell may be represented as

$$Ni \mid Ni^{2+} \parallel Cu^{2+} \mid Cu$$

Oxidation potentials are given as

$$E°_{Ni,\,Ni^{2+}} = 0.25 \text{ volt, and } E°_{Cu,\,Cu^{2+}} = -0.34 \text{ volt}$$

Hence, the reduction potential will be

$$E°_{Ni^{2+},\,Ni} = -E°_{Ni,\,Ni^{2+}} = -0.25 \text{ volt}$$

and

$$E°_{Cu^{2+},\,Cu} = -E°_{Cu,\,Cu^{2+}} = +0.34 \text{ volt}$$

$\therefore$

$$E°_{cell} = E°_{\text{R.H.S. electrode}} - E°_{\text{L.H.S. electrode}}$$

$$= +0.34 - (-0.25) = 0.59 \text{ volt}$$

PROBLEMS FOR PRACTICE

1. Predict the reaction of 1 N sulphuric acid with the following metals:

   (a) Copper

   (b) Lead

   (c) Iron

   Given: $E°_{Cu^{2+},Cu} = 0.34$ volt, $E°_{Pb^2,Pb} = -0.13$ volt and

   $E°_{Fe^{2+},Fe} = -0.44$ volt

   [Ans. (i) No (ii) Yes (iii) Yes]

2. Can a solution of 1 M $ZnSO_4$ be stored in a vessel made of copper?

   Given: $E°_{Zn,Zn^{2+}} = 0.76$ volt, $E°_{Cu^{2+},Cu} = 0.34$ volt

[Ans. Yes]

3. Can we stir copper sulphate solution with a silver spoon? Given standard electrode potentials of copper and silver electrodes are 0.34 volt and 0.80 volt. respectively.

[Ans. No]

4. The standard emf of the cell

$$Ni \mid Ni^{2+} \parallel Cu^{2+} \mid Cu$$

is 0.59 volt. The standard electrode potential (reduction potential) of copper electrode is 0.34 volt. Calculate the standard electrode potential of nickel electrode.

[Ans. $E°_{Ni^{2+},Ni} = -0.25$ volt]

5. Calculate the standard emf of the following cell:

$$Cd \mid Cd^{2+} \parallel Ag^{+} \mid Ag$$

Write the cell reaction, given that

$E°_{Cd^{2+},Cd} = -0.40$ volt, $E°_{Ag^{+},Ag} = 0.80$ volt

[Ans. 1.20 volt, $Cd + 2Ag^{+} \rightarrow Cd^{2+} + Ag$]

6. The emfs of the cells

$$Pt, H_2(1 \text{ atm}) \mid H^{+}(1 \text{ M}) \parallel KCl \text{ (saturated)}, Hg_2Cl_2(s) \mid Hg, Pt$$

$$\text{and } Zn \mid Zn^{++}(0.1 \text{ M}) \parallel KCl \text{ (saturated)}, Hg_2Cl_2(s) \mid Hg, Pt$$

are 0.242 volt and 0.548 volt respectively. What is the value of oxidation potential of $Zn|Zn^{++}$ (0.1 M) electrode?

The activity coefficient of H^{+} ions in the first cell may be taken as unity.

[Ans. 0.306 volt]

18.14 ACTIVITY AND ACTIVITY COEFFICIENT OF ELECTROLYTES

The effective concentration of an ion or the electrolyte in the solution is called its ***activity.***

The activity of an electrolyte in a solution usually represented by a. It is related to the actual concentration, expressed as ***molarity*** m by the equation

$$a = \gamma \times m \qquad (18.8)$$

where, γ is the activity coefficient, i.e.

$$\gamma = \frac{a}{m} \qquad (18.9)$$

Hence, ***activity coefficient may be defined as the ratio of the activity to the actual concentration (molarity) of the solution.***

As $a < m$ for the real solutions, γ is less than 1. For ideal solutions (i.e. for very dilute solutions), $a = m$ and hence $\gamma = 1$

It is observed that as the concentration is increased, the activity coefficient first decreases below unity, passes through a minimum and then begins to increase and then may attain values much greater than one.

Activity of an electrode, in fact, is the product of the activities of its ions for uni-univalent

electrolyte,

i.e., $a = a_+ \cdot a_-$ ...(18.10)

where a_+ and a_- denote the activity coefficients of the cation and the anion.

Since the activities of the individual ions cannot be determined, a term called ***mean ionic activity*** has been introduced. The mean ionic activity (a_Z) for a uni-univalent electrolyte is defined by the expression

$$a_{\pm} = \sqrt{a} = \sqrt{a_+ \cdot a_-} \qquad \ldots(18.11)$$

In a similar manner, the term ***mean activity coefficient*** ($\gamma_\pm$) has been introduced. For a uniunivalent electrolyte, it is defined by the expression,

$$\gamma_\pm = \sqrt{\gamma_+ \cdot \gamma_-} \qquad \ldots(18.12)$$

Also, $a_- = \gamma_- m_+$

and $a = \gamma\ m$

Substituting the values of a_+ and a_- in Eq. (18.12), we get,

$$a_\pm = \sqrt{a} = \sqrt{\gamma_+ m_+ \times \gamma_- m_-}$$

For a uni-univalent electrolyte,

$$m_+ = m_- = m \text{ and } \gamma_+ = \gamma_- = \gamma_\pm$$

$$\therefore \quad \sqrt{a} = \sqrt{m^2 \gamma_\pm^2}$$

or $$a = m^2 \gamma_\pm^2 \qquad \ldots(18.13)$$

18.15 NERNST EQUATION FOR MEASURING EMF OF A CELL

Standard state implies that gases should be at one atmosphere pressure, and the solution should be one molar. Also, the activity of a pure liquid and solid should be unity. For measuring emf of a cell in which the reactants and products are not in standard state, we use an equation, known as Nernst equation.

Suppose the cell reaction involved in any reversible cell is represented by the general equation

$$aA + bB + \ldots \rightarrow xX + yY + \ldots$$

The free-energy change of this reaction is given by the equation,

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_X^x \cdot a_Y^y \ldots}{a_A^a \cdot a_B^b \ldots} \qquad \ldots(18.14)$$

where ΔG° represents the standard free energy and a_A, a_B, a_X, and a_Y represent the activities of A, B, X and Y respectively in any state, other than the standard state at the state of equilibrium.

If the cell reaction involves transference of n moles of the electrons, this corresponds to the flow of nF faradays of electricity. If E is the *emf* of the cell then electrical energy produced in the cell is equal to nFE. Since electrical energy produced is equal to the decrease in free energy of the cell reaction, we have

$$-\Delta G = nFE \qquad \ldots(18.15)$$

For the standard state, we have a similar equation,

$$-\Delta G^\circ = nFE^\circ \qquad \ldots(18.16)$$

where, E° is the standard *emf* of the cell.

Substituting the values of ΔG and ΔG° from equations (18.15) and (18.16) in Eq. (18.14), we get

$$-nFE = -nFE^\circ + RT \ln \frac{a_X^x \cdot a_Y^y \ldots}{a_A^a \cdot a_B^b \ldots}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_X^x \cdot a_Y^y \ldots}{a_A^a \cdot a_B^b \ldots} \qquad \ldots(18.17)$$



Fig. 18.15 *Walther Nernst was born in Briesen, west Prussia in 1864. He founded the Institute of Physical Chemistry and Electrochemistry in Gottingen. He received the Nobel Prize in chemistry in 1920 for his work on photochemistry.*

Thus, knowing the cell reaction, the value of n and the standard emf of the cell, the emf of the cell for known activities of the various reactants and products can be calculated. Equation (18.17) is called

Nernst equation for the calculation of emf of cell.

When the concentrations are not very high, activities can be replaced by concentrations.

Equation (18.17) becomes,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[X]^x \cdot [Y]^y \ldots}{[A]^a \cdot [B]^b \ldots} \qquad \ldots(18.18)$$

Substituting for $R = 8.314$ and $F = 96500$, at 25°C, i.e. $T = 298$ K,

Eqn. (18.18) can be written as

$$E = E^\circ - \frac{0.0591}{n} \ln \frac{[X]^x \cdot [Y]^y \ldots}{[A]^a \cdot [B]^b \ldots}$$

It must be borne in mind that the activities or the concentrations of the pure liquids or pure solids are taken as unity.

Taking a particular case of Daniel cell, the reactions involved are,

$$Zn \rightarrow Zn^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \rightarrow Cu$$
$$n = 2$$

The overall reaction is,

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Hence, we will have

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}} \cdot a_{Cu}}{a_{Zn} \cdot a_{Cu^{2+}}} \quad \ldots(18.19)$$

Putting the activities of solids equal to unity, i.e. $a_{Cu} = 1$, and $a_{Zn} = 1$, Eq. (18.19) reduces to

$$E = E^\circ \quad \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad \ldots(18.20)$$

Writing concentrations in place of activities, Eq. (18.20) becomes,

$$E = E^\circ - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad \ldots(18.21)$$

Substituting the values of R = 8.314 joule deg^{-1} mol^{-1} and F = 96500 coulombs and converting ln into log to the base 10 at 25°C, Eq. (18.21) changes to

$$E = E^\circ - 0.0295 \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad \ldots(18.22)$$

Important If the potential is given for the reaction

$$M \rightarrow M^{n+} + ne$$

it shows that it is oxidation potential. If the value of potential is given as $E_{M/M^{n+}}$, it again expresses oxidation potential. Reduction potential may be obtained by changing the sign.

Example 11 *Represent schematically the cell made up of the following half-cell reactions:*

$$Mg \longrightarrow Mg^{2+}(0.01\ M) + 2e^-,\ E^\circ = +2.34\ volts$$
$$Sn^{2+}(0.1\ M) + 2e^- \longrightarrow Sn,\ E^\circ = -0.136\ volt$$

Calculate the emf of the above cell at 25°C.

Solution: Oxidation potential of the Mg-electrode is 2.34 volts. Its reduction potential will, therefore, be –2.34 volts. The potential of tin electrode is given is reduction potential.

The cell will be represented as

$$Mg \mid Mg^{2+}\ (0.01\ M) \parallel Sn^{2+}(0.1\ M) \mid Sn$$

Standard emf of the cell $(E^\circ) = -0.136 - (-2.34)$

$$= 2.204 \text{ volts}$$

The overall reaction is

$$Mg + Sn^{2+}\ (0.1\ M) \rightarrow Mg^{2+}(0.01\ M) + Sn$$

Here $n = 2$

By Nernst equation, the emf of the cell at 25°C is given by the following equation:

$$E = E^\circ - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Sn^{2+}]} \qquad \text{[as [Mg] = [Sn] = 1]}$$

$$= 2.204 - \frac{0.0591}{2}\log\frac{0.01}{0.1} = 2.204 - 0.02955 \times (-1) = 2.23355 \text{ volts} = 2.234 \text{ volts}$$

Example 12 *Calculate the emf of a zinc-silver cell at 30°C when activity of Zn^{2+} ions is 0.5 and the activity of Ag^+ ions is 10.*

Standard reduction potentials at 30°C are:

(a) Ag^+, Ag electrode = +0.799 volt

(b) Zn^{2+}, Zn electrode = –0.760 volt

Solution: Since reduction potential of silver (0.799 volt) is greater than that of zinc (–0.760 volt), this means that in the cell reaction, reduction takes place at the silver electrode and oxidation at the zinc electrode. Hence, the cell reaction will be

$$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$$

Here, $n = 2$

The cell may represented as

$$Zn \mid Zn^{2+}(a = 0.5) \parallel Ag^+(a = 10) \mid Ag$$

$\therefore$ Standard emf of the cell,

$$E^\circ = E^\circ_{Ag^+,\,Ag} - E^\circ_{Zn^{2+},\,Zn}$$
$$= +0.799 - (-0.760) \text{ volt}$$
$$= 1.559 \text{ volt}$$

By Nernst equation, the emf of the given cell is given by

$$E = E^\circ - \frac{RT}{nF}\ln\frac{a_{Zn^{2+}}}{a^2_{Ag^+}} = 1.599 - \frac{8.314\,(30 + 273)\,2.303}{2 \times 96500}\log\frac{0.5}{(10)^2}$$

$$= 1.559 - 0.03006 \log (5 \times 10^{-3}) = 1.559 + 0.069 = 1.628 \text{ volt}$$

PROBLEMS FOR PRACTICE

1. Calculate the emf of the cell

$$Pb \mid Pb^{2+}(a = 0.200) \parallel Sn^{2+}(a = 0.800) \mid Sn$$

Given that, E° for Sn, Sn^{2+}, $(Sn \rightleftharpoons Sn^{2+} + 2e^-) = +0.140$ volt

E° for Pb, Pb^{2+} $(Pb \rightleftharpoons Pb^{2+} + 2e^-) = +0.126$ volt and $\log 4 = 0.60$

[Ans. 0.00373 volt]

and the reaction of the cell will be $Pb + Sn^{++} \rightarrow Pb^{++} + Sn$]

2. The E° for the reaction

$$Fe(s) + Zn^{2+} \rightarrow Zn(s) + Fe^{2+}$$

is –0.0032 volt. What is the concentration of Fe^{2+} reached when a piece of iron is placed in 1 M Zn^{2+} solution? The value of $\frac{2.303\,RT}{F}$ at 25°C is 0.059.

[Ans. 1.283 M]

3. What will be the emf of the cell

$$Zn, Zn^{2+}\ (a = 0.1) \,||\, Fe^{2+}\ (a = 0.005), Fe \text{ at } 25°C?$$

Given $E° = 0.323$ volts, $\frac{2.303\,RT}{F} = 0.059$

[Ans. 0.314]

18.16 NERNST EQUATION FOR SINGLE ELECTRODE POTENTIAL

1. Metal-Metal Ion Electrode Take an example of a zinc electrode in which the zinc metal is in equilibrium with zinc ions. The electrode reactions written as reduction reaction will be

$$Zn^{2+} + 2e^- \longrightarrow Zn\ (n = 2)$$

Applying the Nernst equation, the electrode potential of zinc electrode is given by,

$$E_{Zn^{2+},\,Zn} = E^\circ_{Zn^{2+},\,Zn} - \frac{RT}{2F} \ln \frac{a_{Zn}}{a_{Zn^{2+}}} \qquad \ldots(18.23)$$

$$= E^\circ_{Zn^{2+},\,Zn} + \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Zn}}$$

where, $E^\circ_{Zn^{2+},\,Zn}$ represents the standard electrode potential of the zinc electrode. In the symbols, $E_{Zn^{2+},\,Zn}$ and $E°_{Zn^{2+},\,Zn}$, the ions have been written first because these represent ***reduction*** potentials.

Putting $a_{Zn} = 1$ (because the activity of pure solid is unity), Eq. (18.23) becomes,

$$E_{Zn^{2+},\,Zn} = E^\circ_{Zn^{2+},\,Zn} + \frac{RT}{2F} \ln a_{Zn^{2+}}$$

Assuming that the solution is dilute, the activity of Zn^{2+} ions may be replaced by molar concentrations.

$$E_{Zn^{2+},\,Zn} = E^\circ_{Zn^{2+},\,Zn} + \frac{RT}{2F} \ln [Zn^{2+}]$$

Similarly, the expression for the silver electrode may be derived.

The electrode reaction, written as reduction reaction, is

$$Ag^+ + e^- \longrightarrow Ag (n = 1)$$

Applying Nernst equation and simplifying the result obtained, we have

$$E_{Ag^+,\,Ag} = E^\circ_{Ag^+,\,Ag} + \frac{RT}{F} \ln [Ag^+]$$

In general, for any metal electrode, consisting of the metal (M) in equilibrium with its ions,

(M^{n+}), the electrode reaction, written as reduction reaction, is

$$M^{n+} + ne^- \longrightarrow M$$

The electrode potential will then be given by the expression

$$E_{M^{n+}, M} = E^{\circ}_{M^{n+}, M} + \frac{RT}{nF} \ln [M^{n+}]$$

Putting R = 8.314 joules, F = 96500 coulombs, ln $[M^{n+}]$ = 2.303 log $[M^{n+}]$ and T = 25 + 273 K (assuming that the measurements are carried out at 25°C), the above equation takes the form

$$E_{M^{n+}, M} = E^{\circ}_{M^{n+}, M} + \frac{0.0591}{n} \log [M^{n+}]$$

This is the *Nernst equation* for the calculation of electrode potential of metal-metal ion electrode.

2. Hydrogen Electrode The hydrogen electrode consists of H_2 gas in equilibrium with H^+ ions. The electrode reaction, written as reduction reaction, is

$$H^+ + e^- \longrightarrow \frac{1}{2} H_2 \ (n = 1)$$

Applying Nernst equation, the electrode potential of the hydrogen electrode is given by

$$E_{H^+, H_2} = E^{\circ}_{H^+, H_2} - \frac{RT}{F} \ln \frac{(aH_2)^{1/2}}{a_{H^+}} \qquad \ldots(18.24)$$

If H_2 gas is at 1 atmospheric pressure, $aH_2 = 1$

Equation (18.24) above takes the form

$$E_{H^+, H_2} = E^{\circ}_{H^+, H_2} - \frac{RT}{F} \ln \frac{1}{a_{H^+}}$$

$$E_{H^+, H_2} = E^{\circ}_{H^+, H_2} + \frac{RT}{F} \ln a_{H^+}$$

Activity of H^+ ions may be replaced by its molar concentration; thus, we have

$$E_{H^+, H_2} = E^{\circ}_{H^+, H_2} + \frac{RT}{F} \ln [H^+]$$

Since the standard electrode potential of hydrogen electrode is taken as zero,

$\therefore$ $$E^{\circ}_{H^+, H_2} = 0$$

Hence, $$E_{H^+, H_2} = \frac{RT}{F} \ln [H^+] = 0.0591 \log [H^+] \text{ at } 25^{\circ}C$$

3. Calomel Electrode The electrode reaction, written as reduction reaction, is

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^- \ (n = 2)$$

By Nernst equation, the electrode potential of this electrode is given by,

$$E_{cal} = E^{\circ}_{cal} - \frac{RT}{2F} \ln \frac{a^2_{Cl^-} \times a^2_{Hg}}{a_{Hg_2Cl_2}} \quad \ldots(18.25)$$

As Hg is a pure liquid and Hg_2Cl_2 is a pure solid, therefore, $a_{Hg} = 1$ and $a_{Hg_2Cl_2} = 1$. Hence, Eq. (18.25) takes the form,

$$E_{cal} = E^{\circ}_{cal} - \frac{RT}{2F} \ln a^2_{Cl^-}$$

$$= E^{\circ}_{cal} - \frac{RT}{F} \ln a_{Cl^-}$$

Taking molar concentration in place of activity, we have

$$E^{\circ}_{cal} = E^{\circ}_{cal} - \frac{RT}{F} \ln [Cl^-]$$

18.17 ELECTRODE POTENTIAL OF REDUCTION–OXIDATION ELECTRODE

Consider the electrode prepared by putting a platinum wire in a solution of a mixture of a ferrous salt and a ferric salt. The electrode reaction, expressed as reduction reaction, is

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (n = 1)$$

Applying Nernst equation, the electrode potential of this electrode is given by,

$$E_{Fe^{3+}, Fe^{2+}} = E^{\circ}_{Fe^{3+}, Fe^{2+}} - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

or

$$E_{Fe^{3+}, Fe^{2+}} = E^{\circ}_{Fe^{3+}, Fe^{2+}} - \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

General Expression for any Reversible Electrode The electrode reaction can be written in a general form as

Oxidized state + *n* electrons = Reduced state

Applying Nernst equation, the expression for the electrode potential will be

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

or

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[\text{Oxidised state}]}{[\text{Reduced state}]}$$

Here, E represents the electrode potential at the given concentrations of the ions and E° represents the standard electrode potential.

Example 13 *A zinc electrode is placed in a 0.1 M solution of zinc sulphate at 25°C. If the degree of dissociation of salt at this concentration is found to be 0.95, calculate the electrode potential of the electrode at 25°C. Given that* $E^{\circ}_{Zn^{2+}, Zn} = -0.76$ *volt.*

Solution: As $\alpha = 0.95$, the salt is 95% dissociated. Concentration of Zn^{2+} ions is given by,

$$[Zn^{2+}] = \frac{95}{100} \times 0.1 = 0.095$$

$$E = E^{\circ} + \frac{0.0591}{2} \log 0.095 = -0.76 + \frac{0.0591}{2} \times (-1.022)$$
$$= -0.76 - 0.03 = -0.79 \text{ V}$$

Example 14 *Calculate the electrode potentials (reduction potentials) of each of the following single electrodes at 25°C.*

(a) Sn/Sn^{++} $(a = 0.01)$ $\quad E^{\circ}_{Sn^{++},\,Sn} = -0.14\ V$

(b) $Ag/AgCl(s), Cl^{-}$ $(a = 0.0001)$ $\quad E^{\circ}_{AgCl,\,Cl^{-}} = 0.22\ V$

Solution:

(a) The electrode reaction expressed as reduction reaction is

$$Sn^{++} + 2e^{-} \rightarrow Sn (n = 2)$$

$$\therefore \qquad E_{Sn^{2+},\,Sn} = E^{\circ}_{Sn^{2+},\,Sn} + \frac{RT}{2F} \ln a_{Sn^{2+}}$$

Substituting the values, we have

$$E_{Sn^{2+},\ Sn} = -0.14 + \frac{0.0591}{2} \log 0.01 = -0.14 - 0.0591 = -0.1991 \text{ V}$$

(b) The electrode potential for the reaction

$$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-} (n = 1)$$

$$\therefore \qquad E_{AgCl,\,Cl^{-}} = E^{\circ}_{AgCl,\,Cl^{-}} - \frac{RT}{F} \ln a_{Cl^{-}}$$

Substituting the values,

$$E_{AgCl,\,Cl^{-}} = 0.22 - 0.0591 \log 0.0001 = 0.22 + 0.2364 = 0.4564 \text{ V}$$

Example 15 *Calculate the electrode potential of a copper wire dipped in 0.1 molar copper sulphate solution at 25°C. At this temperature, the standard electrode potential of copper is 0.34 volt (F = 96500) coulombs, R = 8.314 joules/degree/mol). Assume $CuSO_4$ to be completely ionised and take the activity of copper ions equal to the molar concentration.*

Solution : The electrode reaction as reduction reaction may be written as,

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Here, $n = 2$

By Nernst equation, the electrode potential is given by,

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[Cu^{2+}]}{[Cu]}$$

The concentration of solid is taken as unity; thus [Cu] = 1

Substituting for $[Cu^{2+}]$ and [Cu], we have

$$E = E^\circ + \frac{2.303\,RT}{nF}\log[Cu^{2+}] = 0.34 + \frac{2.303\times 8.314\times 298}{2\times 96500}\log[0.1]$$

or $$E = 0.34 + (-0.0296) = 0.3104 \text{ volt}$$

PROBLEMS FOR PRACTICE

1. Calculate the electrode potential of the following electrodes at 25°C:

$$Zn\,|\,Zn^{2+}\ (a = 0.1)$$

Given that $E^\circ_{Zn,\,Zn^{2+}} = 0.7618$ volt

[Hint: $E^\circ_{Zn^{2+},\,Zn} = -0.7618$ volt]

[Ans. $E_{Zn2+\ Zn} = -0.7914$ volt]

2. A zinc electrode is placed in 0.1 M solution of zinc sulphate at 25°C. If degree of dissociation of the salt at this concentration is found to be 0.95, calculate the electrode potential of the electrode at 25°C. Given that,

$E^\circ_{Zn^{2+},\,Zn} = -0.76$ volt

[Hint: As $\alpha = 0.95$, i.e. the salt is 95% dissociated, $[Zn^{2+}] = \frac{95}{100}\times 0.1 = 0.095$ M]

[Ans. = –0.79 volt]

18.18 CALCULATION OF EQUILIBRIUM CONSTANT (K) FROM NERNST EQUATION

The Nernst equation for a reversible cell in a state of equilibrium can be represented as

$$E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF}\log K \qquad \ldots(18.26)$$

K denotes the equilibrium constant. Consider the Zn-Cu cell as represented below:

$$Zn(s)\ |\ ZnSO_4(aq)\ ||\ CuSO_4(aq)\ |\ Cu(s)$$

Zinc acts as the anode and copper acts as the cathode in the above cell. The cell reaction can be written as

$$Zn(s) \rightarrow Zn^{2+} + 2e \qquad \ldots(18.27a)$$

$$Cu^{2+} + 2e^- \rightarrow Cu(s) \qquad \ldots(18.27b)$$

As the reaction takes place, the concentration of $ZnSO_4$ increases while that of $CuSO_4$ decreases with time. Thus, the potentials of zinc and copper electrodes keep changing in accordance with the Nernst equation. At the point of equilibrium, the two electrode potentials become equal. At this stage, the emf of the cell becomes zero (Fig. 18.16). We observe no flow of electrons from the anode to the cathode in the outer circuit. The cell reaction in state of equilibrium can be written by adding equations (18.27a) and (18.27b)

$$Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

The equilibrium constant for the above reaction can be written as

$$K = \frac{[Zn^{2+}]\,[Cu(s)]}{[Cu^{2+}]\,[Zn(s)]}$$

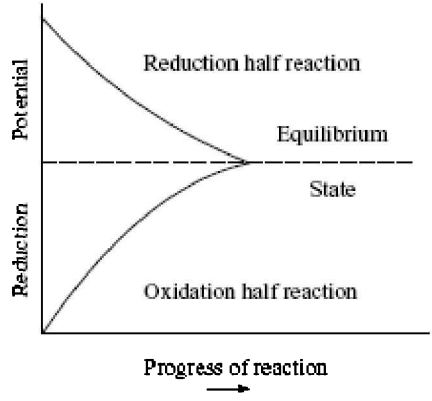


Fig. 18.16 *The cell stops working after some time when the equilibrium is reached*

Taking the values of Cu(s) and Zn(s) as unity each, we have

$$K = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Substituting the values of K in Eq. (18.26) above,

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\,RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (18.28)$$

At equilibrium $E_{cell} = 0$, Eq. (18.28) becomes

$$E^{\circ}_{cell} - \frac{2.303\,RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 0$$

or

$$E^{\circ}_{cell} = \frac{2.303\,RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

In general, we can write

$$E^{\circ}_{cell} = \frac{2.303\,RT}{nF} \log K$$

Knowing the value of E°_{cell}, we can calculate the value of K.

Example 16 *Calculate the value of equilibrium constant for the reaction* $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq.)$ *at 25°C. Standard emf of the cell is 1.10 V*

Solution : Writing the Nernst equation in terms of equilibrium constant,

$$E^{\circ}_{cell} = \frac{0.059}{nF} \log K$$

For the Zn-Cu cell, $n = 2$ and E°_{cell} is given as 1.10 V.

Substituting the values in the equation above, we have

$$1.10 = \frac{0.059}{2} \log K \quad \text{or} \quad \log K = \frac{1.10 \times 2}{0.059} = 37.2 \text{ or } K = 1.6 \times 10^{37}$$

PROBLEMS FOR PRACTICE

1. Calculate at 25°C the equilibrium constant for the reaction

$$Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

Given that $[E^{\circ}_{Fe^{3+}/Fe^{2+}}], Pt = 0.771$ V and $[E^{\circ}_{Sn^{4+}/Sn^{2+}}], Pt = 0.150$ V

[Ans. 1.035×10^{21}**]**

2. Calculate the equilibrium constant for the reaction

$$Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

Given that,

$$E^{\circ}_{Ag^{+}/Ag} = 0.80 \text{ V and } E^{\circ}_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

[Ans. 3.688×10^{15}**]**

3. Calculate the equilibrium constant for the reaction at 298 K:

$4Br^{-} + O_2 + 4H^{+} \rightarrow 2Br_2 + 2H_2O$ Given that, $E^{\circ}_{cell} = 0.16$ V

[Ans. 6.747×10^{10}**]**

4. Calculate the equilibrium constant for the reaction at 298 K:

$$Fe^{3+}\ 2I^{-} \rightarrow 2Fe^{2+}\ I_2 \text{ if } E^{\circ}_{cell} = 0.235 \text{ V}$$

[Ans. 8.967×10^{7}**]**

18.19 IRREVERSIBLE ELECTRODE PROCESSES

So for, we have studied reversible electrodes in which emf measurements are made under the conditions of "no flow of electricity" that we expect from the conditions of a reversible process. Practical applications of cells involve appreciable flow of current. Under these conditions, we come across irreversible electrode processes. Two phenomena are associated with irreversible electrode processes in which there is flow of electric current. These are discussed as under:

1. Polarisation In a reversible galvanic process, the rate of formation and rate of deposition of ions are equal when equilibrium has been established. There is a flow of only infinitesimally small current.

In a situation when there is a flow of appreciable quantity of current, the rate of formation and rate of deposition of ions are no more equal. The disturbance of equilibrium associated with flow of current is called ***polarisation.*** We say that the electrode has been polarised. Polarisation causes change of concentration of ions around the electrode.

Consider an electrode M^{n+}/M. The electrode possesses certain potential depending upon the concentration of ions, which can be obtained from the Nernst equation, other factors remaining constant. We consider two situations.

(a) Suppose the metal is made the cathode and the potential applied is just greater than the reversible potential of the electrode. The metal ions will start getting discharged according to the reaction,

$$M^{n+} + ne^- \rightarrow M$$

This will result in decrease in concentration of metal ions M^{n+}. The electrode potential will decrease according to the Nernst equation

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln [M^{n+}]$$

(b) Likewise, if the metal is made the anode and the potential applied is slightly greater than the reversible electrode potential, the metal will start changing into M^{n+} according to the equation:

$$M \rightarrow M^{n+} + ne^-$$

The concentration of metal ions around the electrode will increase. Hence, the electrode potential will also increase.

Thus, ***we define polarisation (or concentration polarisation) as the increase or decrease in electrode potential caused by increase or decrease in the concentration of metal ions.***

2. Overpotential or Overvoltage During the process of electrolysis, the potential at which metal ions deposit on the cathode is very near the reversible electrode potential for the metal. But when evolution of the gas like hydrogen or oxygen takes place at the anode, a potential is required which is much higher than the reversible potential of hydrogen electrode or oxygen electrode.

The difference between the potential of the electrode when gas evolution is actually observed and the reversible value for the same evolution is called overvoltage

Consider the following electrochemical cell

$$Pt|H_2(1 \text{ atm})|HCl(a = 1)|Pt|O_2(1 \text{ atm})$$

Using the electrode potential data, its emf comes out to be 1.12 V.

Thus, if an emf slightly greater than 1.12 V is applied in the opposing direction, it should reverse the reaction leading to evolution of H_2 and O_2 gases. Actually, a voltage of 1.17 V is needed to evolve these gases.

The difference between the actual emf and the theoretical value (1.17 – 1.12 = 0.58 V) is called overvoltage or overpotential of the cell, sometimes the term ***bubble overvoltage*** is also used for this phenomenon, because it refers to the stage at which the bubbles of the gas are evolved at the electrodes.

18.20 CONCENTRATION CELLS

Cells in which the emf produced is only due to the difference in the concentrations of the electrodes or that of the solutions of the electrolytes with which they are in contact are called concentration cells.

When the difference is in concentration of the electrodes, the cells are called ***electrode concentration cells.*** When the difference is in concentration of electrolytes, the cells are called

electrolyte concentration cells.

Applying Chemistry to Life

Concentration cells have an important applications in biological systems. Biological cells are comparable to concentration cells for the purpose of calculating membrane potential. Membrane potential is the electrical potential that exists across the membrane of muscle cell, nerve cell, etc. This potential is responsible for the propagation of nerve impulses and heartbeat. Just as a potential difference is established when two electrodes of a concentration cell are connected, a membrane potential is established whenever there are unequal concentrations of the same type of metal ion (Na^+ in this case) in the interior and exterior of the biological cell and the ions from each side can cross over to the other side through the membrane. Thus, treating the biological cell as concentration cell and applying the Nernst equation for single ion, we can write

$$E = -\frac{0.059\ \text{V}}{1} \times \log \frac{[\text{Na}^+]_{\text{exterior}}}{[\text{Na}^+]_{\text{interior}}}$$

Concentration of Na^+ ions in the exterior and interior of nerve cell are $1.5 ¥ 10^{-1}$ M and $1.5 ¥ 10^{-2}$ M respectively. Substituting the values in the above equation, we have

$$E = -0.059 \times \log \frac{1.5 \times 10^{-1}}{1.5 \times 10^{-2}} \quad \text{or} \quad E = -0.059\ \text{V or } 59\ \text{mV}$$

Thus, an electric potential of 59 mV exists across the membrane. This potential produces enough current to be detected by electrodes placed on the chest. This is the basis of working of electrocardiology instruments. The amplified signals of can be recorded on a moving chart called electrocardiograph (ECG).



Fig. 18.17 *A child undergoing electrocardiogmphy*

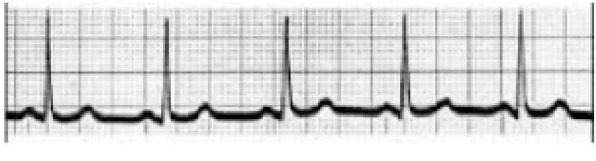


Fig. 18.18 *Electrocardiogram*

Electrocardiology works on the principle of concentration cell.

1. Example of Electrode Concentration Cell

$$H_2(P_{H_2} = P_1)|H^+|H_2(P_{H_2} = P_2)$$

In the above cell, both electrodes are hydrogen electrodes immersed in the same solution of H^+ ions but the H_2 gas passed in the two electrodes is at different pressures (Fig. 18.19).

In the above cell, there is no transference of electrolyte and hence, this is called ***concentration cell without transference.***

2. Examples of Electrolyte Concentration Cells

Type A ***Those cells in which the two electrodes are same, having different concentrations of the electrolytes and connected by a salt bridge.***

(a) $H_2(l\ atm.)\ |\ H^+(a_1)||\ H^+(a_2)|\ H_2(l\ atm)$

Both the electrodes are hydrogen electrodes, and in each electrode, the H_2 gas at 1 atmospheric pressure is passed but the activity of H^+ ions is different in two electrodes. The two electrodes are connected by a salt bridge.

(b) $Zn|Zn^{2+}(a_1)||Zn^{2+}(a_2)|Zn$

Here, both the electrodes are zinc electrodes but in one electrode, the zinc metal is in contact with Zn^{2+} ions having activity a_1, and in the other electrode, the zinc metal is in contact with Zn^{2+} ions having activity a_2. Again the two electrodes are connected by a salt bridge (Fig. 18.20). *Type A cells are concentration cells without transference.*

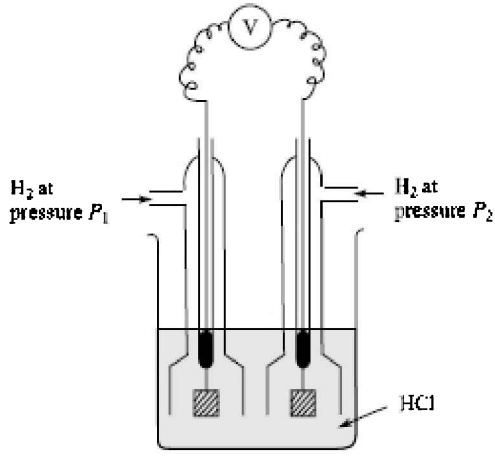


Fig. 18.19 *Electrode concentration cell consisting of hydrogen electrodes*

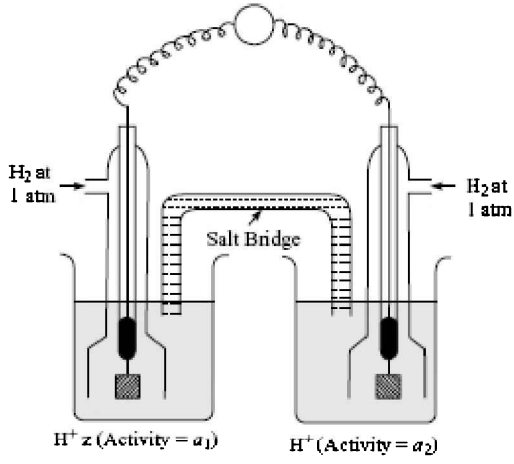


Fig. 18.20 *Electrolyte concentration cells of hydrogen electrode connected by a salt bridge.*

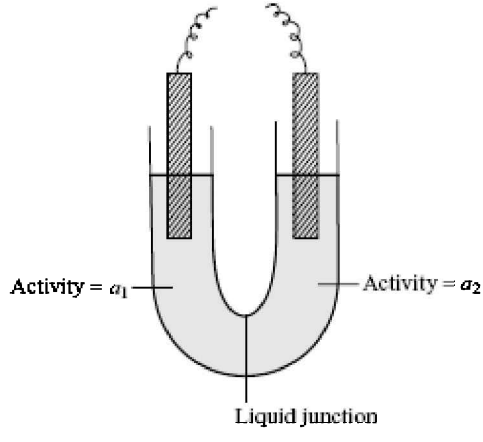


Fig. 18.21 *Electrolyte concentration with a liquid junction*

Type B ***The two electrodes are same having different concentrations of the electrolytes but the two solutions are directly in contact with each other.*** This can be done by putting the two solutions in a tube very carefully so that there is no mixing of the two solutions (Fig. 18.21).

In such a case, the cells are represented as

(a) $H_2(atm) \mid HCl(a_1) : HCl(a_2) \mid H_2$ (1 atm)

(b) $Zn \mid ZnSO_4(a_1) : ZnSO_4(a_2) \mid Zn$, i.e. the double line is replaced by a dotted line. The junction at which the two solutions meet is called the ***liquid junction.*** In this type of concentration cell, there is a direct transference of electrolyte from one solution to the other through the liquid junction. Hence, these cells are called ***concentration cell with transference.***

18.21 EMF OF ELECTRODE CONCENTRATION CELL WITHOUT TRANSFERENCE

It may be mentioned again that transference can take place only in an electrolyte concentration cell and not in an electrode concentration cell.

Let us consider the following two electrode concentration cells.

1. Electrode Concentration Cell Consisting of Gas Electrodes

$$H_2(P_{H_2} = P_1)\,|H^+(a_{H^+})|H_2(P_{H_2} = P_2)$$

Oxidation takes place in the left-hand electrode, i.e. reaction in the left-hand electrode is

$$\frac{1}{2}H_2(P_1) \longrightarrow H^+(a_{H^+}) + e^- \qquad \ldots(18.29a)$$

This reaction may by written as reduction reaction as

$$H(a_H) + e^- \longrightarrow \frac{1}{2}H_2(P_1)\ (n = 1) \qquad \ldots(18.29a)$$

$\therefore$ electrode potential (reduction potential) of this electrode according to the Nernst equation is given by

$$\therefore \qquad E_1 = E^\circ_{H^+,\,H2} - \frac{RT}{F}\ln\frac{P_1^{1/2}}{a_{H^+}}$$

But standard electrode potential of hydrogen electrode, $E°_{H^+,\,H_2} = 0$

$$\therefore \qquad E_1 = -\frac{RT}{F}\ln\frac{P_1^{1/2}}{a_{H^+}} \qquad \ldots(18.30)$$

At the right-hand electrode, reduction takes place, i.e. the reaction is

$$H^+_{(aH^+)} + e^- \longrightarrow \frac{1}{2}H_2(P_2) \quad (n = 1) \qquad \ldots(18.31)$$

Applying Nernst equation, the electrode potential of this electrode, is given by

$$E_2 = -\frac{RT}{F}\ln\frac{P_2^{1/2}}{a_{H^+}} \qquad \ldots(18.32)$$

The overall reaction taking place can be obtained by adding equations (18.29a) and (18.31).

$$\frac{1}{2}H_2(P_1) \longrightarrow \frac{1}{2}H_2(P_2) \qquad \ldots(18.33)$$

The emf (E) of the cell is given by the relation

E = [Electrode potential of the right-hand electrode] – [Electrode potential of the left-hand electrode]

$= E_2 - E_1$

Substituting the values of E_1 and E_2 we have,

$$E = -\frac{RT}{F}\ln\frac{P_2^{1/2}}{a_{H^+}} + \frac{RT}{F}\ln\frac{P_1^{1/2}}{a_{H^+}}$$

$$= \frac{-RT}{F}(\ln P_2^{1/2} - \ln a_{H^+}) + \frac{RT}{F}(\ln P_1^{1/2} - \ln a_{H^+})$$

$$= \frac{-RT}{F}\ln P_2^{1/2} + \frac{RT}{F}\ln P_1^{1/2} = \frac{-RT}{2F}\ln P_2 + \frac{RT}{2F}\ln P_1 = \frac{RT}{2F}(\ln P_1 - \ln P_2)$$

or
$$E = \frac{RT}{2F}\ln\frac{P_1}{P_2} \qquad \ldots(18.34)$$

From Eq. (18.34), we find that there is no net chemical reaction. There is no transference of electrolyte Also, Eq. (18.34) shows that the emf of the cell depends only upon the pressures P_1 and P_2 and is independent of the activity of the H^+ ions.

2. Electrode Concentration Cell Consisting ofAmalgam Electrodes

$$Zn(Hg)(a_{Zn} = a_1)|Zn^{2+}(a_{Zn^{2+}})|Zn(Hg)(a_{Zn} = a_2)$$

For the left-hand electrode, the reaction is

$$Zn(Hg)(a_1) \longrightarrow Zn^{2+}(a_{Zn^{2+}}) + 2e \qquad \ldots(18.35$$

Writing as reduction half reaction, we have

$$Z_n^{2+}(a_{Zn^{2+}}) + 2e^- \longrightarrow Zn(Hg)(a_1) \qquad (n = 2)$$

By Nernst equation, electrode potential is given by

$$E_1 = E^\circ_{Zn^{2+},Zn} - \frac{RT}{2F}\ln\frac{a_1}{a_{Zn^{2+}}} \qquad \ldots(18.36)$$

For the right-hand electrode, the reaction is

$$Zn^{2+}(a_{Zn^{2+}}) + 2e \longrightarrow Zn(Hg)(a_2) \qquad \ldots(18.37)$$

By Nernst equation, electrode potential is given by

$$E_2 = E^\circ_{Zn^{2+},Zn} - \frac{RT}{2F}\ln\frac{a_1}{a_{Zn^{2+}}} \qquad \ldots(18.38)$$

Overall reaction is obtained by adding equations (18.35) and (18.37)

$$Zn(Hg)(a_1) \longrightarrow Zn(Hg)(a_2) \qquad \ldots(18.39)$$

The emf of the cell is obtained by the expression,

$$E = E_2 - E_1$$

Substituting the values of E_1 and E_2, we have

$$E = \frac{-RT}{2F}\ln\frac{a_2}{a_{Zn^{2+}}} + \frac{RT}{2F}\ln\frac{a_1}{a_{Zn^{2+}}}$$

or
$$E = \frac{RT}{2F}\ln\frac{a_1}{a_2} \qquad \ldots(18.40)$$

From Eq. (18.39), it follows that the emf of the cell is obtained due to transfer of zinc from amalgam where its activity is a_1 to the amalgam where its activity is a_2. There is no transference

of the electrolyte (namely Zn^{2+} ions). Also Eq. (18.40) reveals that the emf of the cell depends only upon the activities of zinc in the two amalgams and not at all on the activity of the Zn^{2+} ions, in the solution. There is one more observation, in the final expression for the emf of the cell, $E°$ does not appear. This is true for all the concentration cells. We may, therefore, conclude that $E° = 0$ for concentration cells. Hence, for a concentration cell in which each electrode reaction involves transference of n electrons, the emf will be given by the general expression

$$E_{cell} = \frac{RT}{nF} \ln \frac{a_1}{a_2} \qquad \ldots(18.41)$$

18.22 EMF OF ELECTROLYTE CONCENTRATION CELLS WITHOUT TRANSFERENCE

We shall explain it by taking three different concentration cells. Let us first take hydrogen concentration cell having different concentration of electrolytes.

1. H_2(l atm)| $H^+(a_1)$ || $H^+(a_2)$| H_2(1 atm) On the left-hand electrode, by convention, oxidation takes place.

Therefore, the electrode reaction is

$$\frac{1}{2} H_2(1 \text{ atm}) \longrightarrow H^+(a_1) + e^- \qquad \ldots(18.42)$$

This reaction may be written as reduction half reaction as

$$H^+(a_1) + e^- \longrightarrow \frac{1}{2} H_2(1 \text{ atm}) \quad (n = 1)$$

$\therefore$ electrode potential of the left-hand electrode by Nernst equation will be

$$E_1 = E^\circ_{H^+, H_2} - \frac{RT}{F} \ln \frac{1}{a_1} \qquad [\because a_{H_2} = 1]$$

$$= E^\circ_{H^+, H_2} + \frac{RT}{F} \ln a_1$$

$$= \frac{RT}{F} \ln a_1 \qquad [\because E^\circ_{H^+, H_2} = 0] \ldots(18.43)$$

On the right-hand electrode, by convention, reduction takes place. Therefore, the electrode reaction is

$$H^+(a_2) + e^- \longrightarrow \frac{1}{2} H_2(1 \text{ atm}) \qquad \ldots(18.44)$$

By Nernst equation, the emf of this electrode is given by (as deduced for left hand electrode),

$$E_2 = \frac{RT}{F} \ln a_2 \qquad \ldots(18.45)$$

The overall reaction is obtained by adding the reactions (18.42) and (18.44),

$$H^+(a_2) \longrightarrow H^+(a_1) \qquad \ldots(18.46)$$

The emf of the cell is given by the expression,

$$E = E_2 - E_1$$

Substituting the values of E_1 and E_2, we get

$$E = \frac{RT}{F} \ln a_2 - \frac{RT}{F} \ln a_1$$

or

$$E = \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \ldots(18.47)$$

From Eq. (18.46), it follows that for 1 faraday of electricity to be produced, there is a transfer of 1 mole of H^+ ions from solution having activity a_2 to the solution having activity a_1. The transfer takes place through the salt bridge. Secondly, from Eq. (18.47), it is evident that for emf to be positive, a_2 must be greater than a_1.

2. For the Zinc Concentration Cell

$$Zn \mid Zn^{2+}(a_1) \parallel Zn^{2+}(a_2) \mid Zn$$

Following the same steps as in the hydrogen concentration cell, it can be seen that the overall reaction is

$$Zn^{2+}(a_2) \longrightarrow Zn^{2+}(a_1) \quad \ldots(18.48)$$

and the emf of the cell is

$$E = \frac{RT}{2F} \ln \frac{a_2}{a_1} \text{ (as } n = 2) \quad \ldots(18.49)$$

In general, for any such cell, involving n faradays of electricity, the emf is given by,

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1} \quad \ldots(18.50)$$

On replacing the activities of the ions by the products of their molarities and activity coefficients, i.e. putting $a_1 = m_1\gamma_1$ and $a_2 = m_2\gamma_2$, we get

$$E = \frac{RT}{nF} \ln \frac{M_2\gamma_2}{M_1\gamma_1} \quad \ldots(18.51)$$

3. Cells Obtained by Combination of Two Chemical Cells

Consider the Following Chemical Cell

$$H_2(1 \text{ atm}) \mid HCl(a_1), AgCl(s) \mid Ag$$

i.e. the hydrogen electrode and the silver-silver chloride electrode are dipped in the same solution of HCl (of activity = a_1)

For this cell, the reaction may be expressed as,

$$\frac{1}{2} H_2(1 \text{ atm}) + AgCl(s) \longrightarrow Ag(s) + HCl(a_1) \quad \ldots(18.52)$$

By Nernst equation, the emf of this cell is given by

$$E_1 = E^\circ - \frac{RT}{F} \ln a_1 \quad \ldots(18.53)$$

$n = 1$ and the activities of solids Ag and AgCl and that of H_2 at 1 atm are taken as unity.

Now suppose we have the same cell but with different activity of HCl acid (say a_2).

$$H_2 \text{ (1 atm)} \mid HCl(a_2), AgCl(s) \mid Ag$$

The cell reaction will be

$$\frac{1}{2}H_2(1\text{ atm}) + AgCl(s) \longrightarrow Ag(s) + HCl(a_2) \quad \ldots(18.54)$$

By Nernst equation, the emf of this cell is given by

$$E_2 = E^\circ - \frac{RT}{F}\ln a_2 \quad \ldots(18.55)$$

If the above two cells are connected to oppose each other, we have the following cell:

$$H_2(1\text{ atm})\, HCl(a_1), AgCl(s)\, Ag\text{–}Ag \mid AgCl(s), HCl(a_2) \mid H_2\,(1\text{ atm})$$

The overall reaction of this cell (a combination of two cells) will be the difference between equations (18.52) and (18.54).

$$\frac{1}{2}H_2(1\text{ atm}) + AgCl(s) - \frac{1}{2}H_2(1\text{ atm}) - AgCl(s) = Ag(s) + HCl(a_1) - Ag(s) - HCl(a_2)$$

or
$$HCl(a_2) = HCl(a_1) \quad \ldots(18.56)$$

Similarly, the emf (E) of combination will be the difference between equations (18.53) and (18.55), i.e.

$$E = E_1 - E_2 = \left[E^\circ - \frac{RT}{F}\ln a_1\right] - \left[E^\circ - \frac{RT}{F}\ln a_2\right]$$

or
$$E = \frac{RT}{F}\ln\frac{a_2}{a_1} \quad \ldots(18.57)$$

From Eq. (18.56), it is obvious that for 1 faraday of electricity passing through the cell, the overall change taking place is simply the transfer of 1 mol of HCl acid from the solution where its activity is a_2 to the solution where the activity is a_1. Hence, it constitutes at an electrolyte concentration cell. However, there is no direct transference of the electrolyte, HCl, from one solution to the other. Hence, strictly speaking, it is an ***electrolyte concentration cell without transference.***

The cells of the above type are useful in the determination of the ***activity coefficient of the electrolytes involved.*** For the purpose, the concentration of the electrolyte in one of the cells is kept constant and the concentration of the electrolyte in the second cell is varied. For each concentration, the emf is measured.

Putting $a_1 = m_1^2\,\gamma_1^2$ and $a_2 = m_2^2\,\gamma_2^2$ in Eq. (18.57), we get (Refer Eq. 8.13)

$$E = \frac{RT}{F}\ln\frac{m_2^2\gamma_2^2}{m_1^2\gamma_1^2} = \frac{2RT}{F}\ln\frac{m_2\gamma_2}{m_1\gamma_1}$$

or
$$E = \frac{2RT}{F}\ln\frac{m_2}{m_1} + \frac{2RT}{F}\ln\frac{\gamma_2}{\gamma_1} \quad \ldots(18.58)$$

Knowing γ_2 corresponding to m_1 (which has been kept constant), the values of γ_2 can be calculated for different values of m_2.

18.23 EMF OF AN ELECTROLYTE CONCENTRATION CELL WITH TRANSFERENCE

Consider the cell (Fig. 18.22):

$$H_2(1\text{ atm}) \mid HCl\,(a_1) : HCl\,(a_2) \mid H_2\,(1\text{ atm})$$

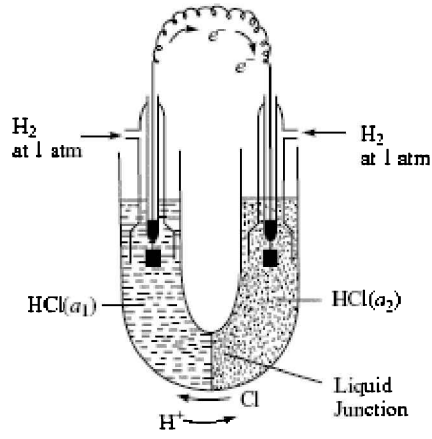


Fig. 18.22 *Concentration cell with transference.*

1. Processes Taking Place at the Electrodes By convention, oxidation takes place at the left-hand electrode. Therefore, the electrode reaction on the left-hand electrode may be written as

$$1/2\ H_2(1\ atm) \rightarrow H^+(a_1) + e^-$$

Reduction takes place at the right-hand electrode. Therefore, the electrode reaction on the right hand electrode may be written as

$$H^+(a_2) + e^- \rightarrow 1/2\ H_2(1\ atm)$$

The sum of the two electrode reaction gives

$$H^+(a_2) \rightarrow H^+(a_1) \qquad \ldots(18.59)$$

2. Processes Taking Place at the Liquid Junction Electrons flow in the external circuit from left to right. As H^+ ions are produced in the left electrode and Cl^- ions are left in the right electrode, the inner circuit is completed by the transference of Cl^- ions from right to left and the transference of H^+ ions from left to right across the liquid junction. If the transport number of Cl^- ions is represented by t_- then for one faraday of electricity passing through the cell, t_- gram equivalents of the Cl^- ions will be transferred from right to left (i.e. from solution of activity a_2 to the solution of activity a_1)

$$t_- Cl^-(a_2) \rightarrow t_- Cl^-(a_1) \qquad \ldots(18.60)$$

Transport number of H^+ ions = $1 - t_-$. Therefore, during the same time, $(1 - t_-)$ gram equivalent of H^+ will be transferred from left to right, i.e. from solution activity a_1 to the solution of activity a_2, i.e.

$$(1 - t_-)\ H^+(a_1) \rightarrow (1 - t_-)\ H^+(a_2) \qquad \ldots(18.61)$$

Overall Process To calculate the net transfer of the material, equations (18.59), (18.60) and (18.61) may be added.

$$H^+(a_2) + t_- Cl^-(a_2) + (1 - t_-) H^+(a_1) = H^+(a_1) + t_- Cl^-(a_1) + (1 - t_-) H^+(a_2)$$

or $$t_- H^+(a_2) + t_- Cl^-(a_2) = t_- H^+(a_1) + t_- Cl^-(a_1)$$

or $$t_- HCl(a_2) = t_- HCl(a_1) \quad \ldots(18.62)$$

This equation tells that for one faraday of electricity passing through the cell, t_- gram equivalents of HCl from the solution of activity a_2 are transferred to HCl solution of activity a_1. For the passage of one faraday of electricity through the cell, one **full gram equivalent** of HCl is transferred.

Applying Nernst equation to the process (18.62), the emf of the cell is given by,

$$E = \frac{-RT}{F} \ln \frac{a_1^{t_-}}{a_2^{t_-}}$$

$$- \frac{t_- RT}{F} \ln \frac{a_2}{a_1} \quad \ldots(18.63)$$

For emf to be positive, a_2 must be greater than a_1.

Replacing the activities of electrolytes by the molarities and activity coefficients of the ions, we have

$$E = \frac{t_- RT}{F} \ln \frac{m_2^2 \gamma_2^2}{m_1^2 \gamma_1^2}$$

$$- \frac{2t_- RT}{F} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} \quad \ldots(18.64)$$

Thus, the emf of such a cell can be calculated be calculated if we know molarities, activity coefficients and transport number of ions.

NUMERICAL PROBLEM ON CONCENTRATION CELLS

Example 17 *What is the EMF of a concentration cell consisting of zinc electrodes, one immersed in a solution of 0.05 molar concentration and the other in a solution of 0.5 molar concentration of ions at 25°C. The two solutions are connected by a salt bridge.*

Solution : Given that, $C_2 = 0.5$ M, $C_1 = 0.05$ M As the cell involves Zn, Zn^{2+} ions, $n = 2$

At 25°C,

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1} = \frac{0.0591}{2} \log \frac{0.5}{0.05} = 0.02955 \text{ volt}$$

PROBLEMS FOR PRACTICE

1. Calculate the emf of the concentration cell consisting of zinc electrodes, one immersed in a solution of 0.01 M concentration and the other in a solution of 0.1 M concentration of its ions at 25°C.

[Ans. 0.02955 volt]

2. Calculate the emf of the following concentration cell at 25°C.

$$Cd \mid CdSO_4(m = 0.01, \gamma = 0.383) \parallel CdSO_4\ (m = 1.00, \gamma = 0.042) \mid Cd$$

[Ans. 0.0307 volt]

3. Calculate the voltage generated in a cell at 25°C in which one half consists of a 1 M $AgNO_3$ solution and a silver wire electrode. In the other half, a silver wire dips into 0.01 M $AgNO_3$ solution.

[Ans. 0.1182 volt]

18.24 LIQUID JUNCTION POTENTIAL

The potential set up at the junction of the two solutions because of the difference in the speeds of the ions moving across the boundary is called liquid junction potential.

The emf of the cell is thus not only the sum of the oxidation potential (E_1) of the electrode where oxidation occurs and reduction potential (E_2) of the electrode where reduction occurs, but also includes the junction potential (E_1).

In other words, the emf of the cell is

$$E = E_1 + E_2 + E_j$$

However, the type of junction employed most commonly is the salt bridge containing an electrolyte such as KCl. If we assume that the K^+ ions and Cl^- move almost with equal speed, the junction potential is almost reduced to zero. In such a case, the emf of the cell can be simply taken as

$$E_1 + E_2$$

Expression for Liquid Junction Potential Consider the following concentration cell with transference:

$$H_2(1 \text{ atm}) \mid HCl\ (a_1) : HCl(a_2) \mid H_2(1 \text{ atm})$$

Sum of the two electrode reactions gives

$$H^+(a_2) \longrightarrow H^+(a_1)$$

And the sum of the two electrode potentials, i.e. $E_1 + E_2$ is given by,

$$E_1 + E_2 = \frac{-RT}{F} \ln \frac{(a_{H^+})_1}{(a_{H^+})_2} = \frac{RT}{F} \ln \frac{(a_{H^+})_2}{(a_{H^+})_1}$$

$$= \frac{RT}{F} \ln \frac{(m_{H^+} \gamma_{H^+})_2}{(m_{H^+} \gamma_{H^+})_1} \quad \ldots(18.65)$$

The emf of the cell considered above is given by

$$E = \frac{2t_- RT}{F} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} \text{ [Refer Eq. (18.64)]} \quad \ldots(18.66)$$

Subtracting Eq. (18.65) from Eq. (18.66), we get

$$E_j - E - (E_1 + E_2)$$

$$= \frac{2t_- RT}{F} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} - \frac{RT}{F} \ln \frac{(m_{H^+} \gamma_{H^+})_2}{(m_{H^+} + \gamma_{H^+})_1} \quad \ldots(18.67)$$

But $(m_{H^+})_2 = m_2$ and $(m_{H^+})_1 = m_1$

If the activity coefficient of an ion is taken to be equal to the mean activity coefficient of the electrolyte then

$$(\gamma_{H^+})_1 = \gamma_2 \text{ and } (\gamma_{H^+})_2 = \gamma_2.$$

Hence, Eq. (18.67) becomes,

$$E_j = \frac{2t_- RT}{F} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} - \frac{RT}{F} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1}$$

$$= (2t_- - 1) \frac{RT}{F} \ln \frac{m_2 \gamma_2}{m_1 \gamma_2} \qquad \ldots(18.68)$$

Also, we know

$$t_+ + t_- = 1$$

$$\therefore \quad 2t_- - 1 = t_- + (t_- - 1) = t_- + (-t_+)$$

$$= t_- - t_+$$

Hence, Eq. (18.68) may be written in the form

$$E_j = (t_- - t_+) \frac{RT}{F} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1}$$

Thus, we find that the liquid junction potential depends not only can the activities of the two solutions constituting the junction but also depends upon the difference between the two transport numbers of the electrolyte. When $t_- = t_+$ then $E_j = 0$. In case of an electrolyte for which $t_- > t_+$, E_j will be positive and thus E will be greater than $E_1 + E_2$ by E_j. In case of an electrolyte for which $t_- < t_+$, E_j will be negative and hence, E will be less than $E_1 + E_2$ by E_j.

18.25 DETERMINATION OF ACTIVITY AND ACTIVITY COEFFICIENT FROM EMF MEASUREMENT

In order to know the activity of a solution corresponding to the given molarity, we must measure the activity coefficient of the electrolyte in the given solution. To understand the method for this determination, consider the example of the ***determination of activity coefficient of hydrochloric acid.*** For this purpose, consider the following chemical cell without transference:

$$H_2(1 \text{ atm}) \mid HCl(\text{activity} = a), AgCl(s) \mid Ag$$

It consists of hydrogen and silver-silver chloride electrodes in hydrochloric acid as the electrolyte. As the two electrodes are reversible with respect to the ions of the electrolyte, they may be immersed directly in the acid to give a cell with no liquid junction. The cell reaction is given by the equation

$$\frac{1}{2} H_2(1 \text{ atm}) + AgCl(s) \rightarrow Ag(s) + H^+(a_{H^+}) + Cl^-(a_{Cl^-})$$

and the emf of the cell is given by

$$E_{cell} = E^\circ_{Ag,AgCl} - \frac{RT}{F} \ln a_{H^+} a_{Cl^-}$$

$$- E^\circ_{Ag,AgCl} \quad \frac{RT}{F} \ln a \qquad \ldots(18.69)$$

where a is the activity of HCl as a whole.

As the activity (a) of HCl at any molarity m is related to the mean activity coefficient $\gamma_\pm$ by the expression $a = m^2\gamma^2_\pm$, substituting this value in Eq. (18.69), we get,

$$E_{cell} = E^\circ_{Ag/AgCl} - \frac{RT}{F} \ln m^2\gamma_\pm^2$$

$$E_{cell} = E^\circ_{Ag/AgCl} - \frac{2RT}{F} \ln m - \frac{2RT}{F} \ln \gamma_\pm$$

$$E_{cell} + \frac{2RT}{F} \ln m = E^\circ_{Ag/AgCl} - \frac{2RT}{F} \ln \gamma_\pm \qquad \ldots(18.70)$$

All the quantities on the left-hand side of this equation are determined experimentally. To calculate $\gamma_\pm$, the value of $E°_{Ag/AgCl}$ is needed. To determine $E°_{Ag/AgCl}$, the quantity $E_{cell} + \frac{2RT}{F} \ln m$ is plotted against m and the result is extrapolated to $m = 0$. When $m = 0$, $\gamma_\pm = 1$, therefore, from Eq. (18.70) $E°_{Ag/AgCl} = E_{cell} + \frac{2RT}{F} \ln m$ i.e. equal to the value of the ordinate.

Example 18 *Calculate the mean ionic activity coefficient of 0.1 molar hydrochloric acid at 25°C given that the emf of the cell*

$$H_2(1\ atm)\,|HCl(a),\ AgCl(s)\,|Ag$$

is 0.3524 V at 25°C and that the standard electrode potential of Ag-AgCl is 0.2224 V at 25°C.

Solution : For the given cell,

$$E_{cell} + \frac{2RT}{F} \ln m = E^\circ_{Ag/AgCl} - \frac{2RT}{F} \ln \gamma_2$$

or
$$E_{cell} + \frac{2 \times 2.303\, RT}{F} \log m = E^\circ_{Ag/AgCl} - \frac{2 \times 2.303\, RT}{F} \log \gamma_\pm$$

Putting $T = 298$ K, $R = 8.314$ JK^{-1} mol^{-1} and $F = 96500$ C, this equation becomes

$$E_{cell} + 0.01183 \log m = E^\circ_{Ag/AgCl} - 0.1183 \log \gamma_\pm$$

Substituting $E_{cell} = 0.3524$ V, $E^\circ_{Ag/AgCl} = 0.2224$ V

and $m = 0.1$ mol kg^{-1}

we obtain

$$0.3524 + 0.1183 \log 0.1 = 0.2224 - 0.1183 \log \gamma_\pm$$

$$\log \gamma_\pm = \frac{-0.3524 + 0.2224 + 0.1183}{0.1183} = -0.0989$$

or $\gamma_2 = 0.796$

18.26 APPLICATIONS OF EMF MEASUREMENTS

1. To Determine the Transport Number of Ions For a cell with transference

$$H_2(1\text{ atm})\,|HCl(a_1) : HCl(a_2)\,|\,H_2(1\text{ atm})$$

the emf is given by,

$$E = \frac{t_- RT}{F} \ln \frac{a_2}{a_1} \qquad \ldots(18.71)$$

By measuring the emf of the cell and knowing the activities of the two solutions, the transport number of the anion (t_-) can be calculated.

2. Determine the Solubility and Solubility Product of Sparingly Soluble Salts The emf of a concentration cell is given by

$$E = \frac{RT}{nF} \ln \frac{C_2}{C_1} \qquad \ldots(18.72)$$

Thus, knowing the emf of the cell and the concentration of ions in one of the solutions, that in the order can be calculated. If the second solution in another beaker is that of the sparingly soluble salt, its ionic concentration is equal to its solubility assuming that the substance is completed dissociated.

Suppose it is required to find the solubility of the sparingly soluble salt, AgCl. The following cell is set up and its emf is measured.

$$Ag\,\Big|\,N/10\ AgNO_3\text{ solution}\,\Big\|\,\text{Saturated } NH_4NO_3\,\Big|\begin{matrix}N/10\text{ KCl solution}\\ \text{Saturated with AgCl}\end{matrix}\Big|\,Ag$$

This cell is prepared by dipping a silver electrode in N/100 $AgNO_3$ solution taken in one beaker and dipping another silver electrode in N/10 KCl solution in another beaker to which 1 or 2 drops of $AgNO_3$ solution are added, forming AgCl which is enough to make the solution saturated with AgCl. The two beakers are then connected by a salt bridge containing saturated NH_4NO_3 solution.

Calculations The cell, as described above, is a concentration cell having higher concentration of Ag^+ ions in the left-hand electrode and lower concentration of Ag^+ ions in the right-hand electrode (produced by dissociation of AgCl). By convention, we write the electrode with higher concentration of ions on the right-hand side.

$$Ag\,\Big|\begin{matrix}N/10\text{ KCl solution}\\ \text{saturated with AgCl}\\ [Ag^+] = C\text{ (say)}\end{matrix}\Big\|\begin{matrix}\text{saturated}\\ NH_4NO_3\end{matrix}\Big\|\begin{matrix}N/10\ AgNO_3\text{ solution}\\ [Ag^+] = 0.01\end{matrix}\Big|\,Ag$$

The emf of this cell at 25°C is given by

$$E = 0.0597 \log \frac{0.01}{C}$$

From this equation, the value of C can be calculated. Thus, in the solution of AgCl in N/10 KCl,

$[Ag^+] = C$ gram equivalents/litre

As AgCl dissolves to a very small extent, the Cl^- ions produced from AgCl are negligible as compared to that produced from KCl. Therefore, in the solution of AgCl in N/10 KCl,

$$[Cl^-] = [KCl] = 0.1$$

The solubility product (K_s) of AgCl is, therefore, be given by the equation,

$$K_s = [Ag^+]\,[Cl^-]$$
$$= C \times 0.1$$

If the solubility of AgCl is s moles/litre then

$$[Ag^+] = [Cl^-] = s \text{ gram equivalents/litre}$$
$$K_s = [Ag^+]\,[Cl^-] = s \times s = s^2$$

or
$$s = \sqrt{K_s}$$

Knowing the value of K_s, the value of s can be calculated.

Example 19 *Consider the cell*

$$Ag\,|\,0.005\ M\ AgNO_3\,||\,KNO_3(salt)\,||\,AgCl(salt)\,|\,Ag$$
$$\text{salt bridge}$$

If the emf of the cell at 25°C is 0.1585 volt, calculate the solubility of AgCl at this temperature.

Solution: Solubility of AgCl in water is very small; therefore, the concentration of Ag^+ ions in AgCl solution will be very small as compared to that of Ag^+ ions in 0.005 $AgNO_3$ solution. On writing the electrode with higher concentration of Ag^+ ions on the right-hand side, we have

$$Ag\,|\,AgCl\ (salt)\,||\,KNO_3(salt)\,||\,0.005\ M\ AgNO_3\,|\,Ag$$

Let C be the concentration of Ag^+ ions in the left-hand electrode of the above concentration cell. Substituting the values in the equation of emf of concentration cell, we have

$$0.1585 = \frac{0.591}{1} \log \frac{0.005}{C}$$

which gives

$$\log C = \log 0.0005 - 2.6819$$
$$= -3.301 - 2.6819 = -5.9829 = \bar{6}.0171$$
$$C = 1.040 \times 10^{-6} \text{ g eq/litre} = 1.040 \times 10^{-6} \times 143.5 \text{ g/litre}$$

or
$$C = 1.49 \times 10^{-4} \text{ g/litre}$$

3. To Calculate Standard Free–Energy Change and Equilibrium Constant of a Given Reaction Electrical energy produced in the cell is equal to the decrease in free energy accompanying the cell reaction,

i.e.
$$-\Delta G = nFE \qquad \ldots(18.73)$$

where ΔG is the change in free energy accompanying the reaction, n is the number of the moles of electrons transferred in the cell reaction, F is one faraday (= 96500 columns), E is the emf of the cell.

If the reactants and products are taken in the standard state, we can write

$$-\Delta G^\circ = nFE^\circ \qquad \ldots(18.74)$$

Knowing the values of E° the value of ΔG° can be calculated.

For a reversible reaction in equilibrium, ΔG° is related to the equilibrium constant K according to the equation

$$\Delta G^\circ = -RT \ln K = -2.303\, RT \log K \qquad \ldots(18.75)$$

Thus, knowing ΔG°, K can be calculated at the given temperature T.

Example 20 *Calculate the free energy change of the following cell at 25°C.*

$$Sn|Sn^{2+}(a = 0.6)||Pb^{2+}(a = 0.3)|Pb$$

Standard emf of the cell is 0.014 volt.

Solution: The cell reaction can be written as

$$Sn + Pb^{2+} \rightarrow Sn^{2+} + Pb$$

Here, $n = 2$

By Nernst equation, the emf of this cell at 25°C is given by

$$E = E^\circ - \frac{0.0591}{n} \ln \frac{a_{Sn^{2+}}}{a_{Pb^{2+}}} = E^\circ - \frac{0.0591}{n} \log \frac{a_{Sn^{2+}}}{a_{Pb^{2+}}}$$

$$= 0.014 - \frac{0.0591}{n} \log \frac{0.6}{0.3} = 0.0051 \text{ volt}$$

ΔG can be obtained as follows:

$$\Delta G = -nFE = -2 \times 96500 \times 0.0051 \text{ joules}$$
$$= -984.3 \text{ joules}$$

4. To Determine the Valency of the Ions The emf of a concentration cell without transference is given by

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1} \simeq \frac{RT}{nF} \ln \frac{C_2}{C_1} \qquad \ldots(18.76)$$

In this expression, n is the valency of the ion involved. Thus, knowing all other quantities, n can be calculated.

For example, the valency of mercurous ions, which remained doubtful for a very long time, was determined by this method, by setting up the following cell:

Hg | N/20 mercurous nitrate solution || N/2 mercurous nitrate solution |Hg

Here,

$$\frac{C_2}{C_1} = \frac{1/2}{1/20} = 10$$

Writing the values of the various constants in Eq. (18.75) at 25°C, we get

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Putting $\frac{C_2}{C_1} = 10$ i.e., $\log \frac{C_2}{C_1} = \log 10 = 1$, we get

$$E = \frac{0.0591}{n}$$

The emf of the above cell was found to be 0.0295 volt

Hence, $$n = \frac{0.0591}{E} = \frac{0.0591}{0.0295} = 2$$

Thus, the valency of mercurous ion is 2 and it is represented as Hg^{2+}_2 and its salts, such as nitrate, by $Hg_2(NO_3)_2$.

18.27 DIFFERENT TYPES OF ELECTRODES IN PRACTICAL USE

1. Dipping Calomel Electrode The calomel electrode is now commercially available as a self-contained unit. It is used by simply dipping the tip of the electrode in the solution of another electrode whose emf is to be determined.

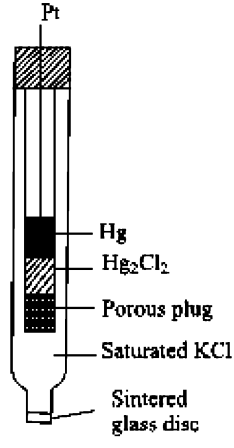
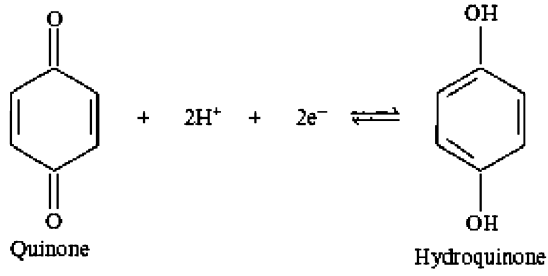


Fig. 18.23 *A dipping calomel electrode*

This type of electrode is often referred as the dipping calomel electrode (Fig. 18.23). This saves us from the cumbersome method of preparing the calomel.

The mercury and the calomel (Hg_2Cl_2) are held in a narrow central tube by a porous cottonwool plug. A platinum wire dips into the mercury. The KCl saturated solution contained in the electrode makes contact with the other electrode solution through a sintered glass disc. This disc functions as a 'salt bridge' between the two electrode solutions. Thus, a galvanic cell is set up and its emf is measured with the help of a voltmeter.

2. Quinhydrone Electrode It is a widely used secondary standard electrode. It involves the redox reaction between quinone (Q) and hydroquinone (QH_2).



Or Simply

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

The hydroquinone half-cell consists of a platinum strip immersed in a saturated solution of quinhydrone at a definite H^+ ion concentration (Fig. 18.24). Quinhydrone is a molecular compound which gives equimolar amounts of quinone and hydroquinone in solution. The quinhydrone half-cell may be represented as $Pt/QH_2, Q.H^+$

The potential developed is measured against a hydrogen electrode or calomel electrode. The emf with respect to a standard hydrogen electrode is 0.6996 V at 25°C.

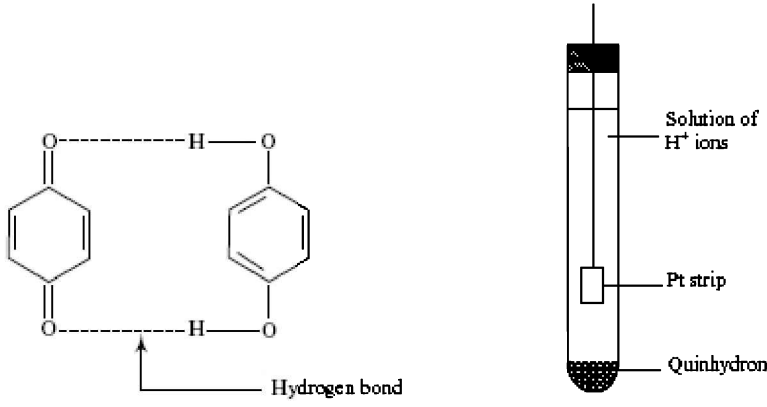


Fig. 18.24 *Quinhydrone electrode*

3. Glass The Electrode A commonly used secondary standard electrode is the glass electrode. Its emf is determined by coupling with a Standard Calomel Electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution.

A glass electrode (Fig. 18.25) consists of a glass tube having a thin-walled bulb at the lower end. The bulb contains 1 M HCl solution. A silver wire coated with silver chloride (or a simple Pt wire) is sealed into the glass tube at its lower end. The lower end of the silver wire dips into the hydrochloric acid, forming silver-silver chloride electrode. The glass electrode may be represented as,

$$Ag, AgCl|1M\ HCl|H^+\ (Test\ solution)$$

When placed in a solution, the potential of the glass electrode depends on the H^+ ion concentration of the solution. The potential develops across the glass membrane as a result of a concentration difference of H^+ ions on the two sides of the membrane. This happens much in the same way as the emf of a concentration cell develops.

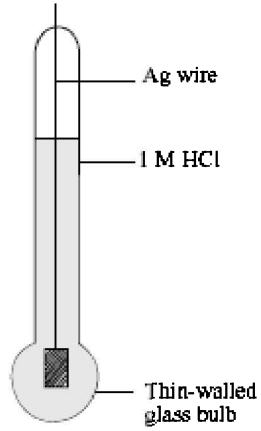


Fig. 18.25 *Glass electrode*

The potential of a glass electrode can be determined against a standard calomel electrode (SCE).

18.28 DETERMINATION OF pH OR H^+ CONCENTRATION OF A SOLUTION BY EMF MEASUREMENT

The basic principle of the method is to set up a cell in which one of the electrodes is such that its potential depends upon the H^+ ion concentration in the solution under examination and the other electrode is a reference electrode. Knowing the emf of the constituted cell and the potential of reference electrode, we can calculate the potential of the electrode containing the solution under examination and then the H^+ ion concentration using the Nernst equation. The various electrodes whose potentials depend upon the H^+ ion concentration are ***hydrogen electrode, quinhydrone electrode, and glass electrode.*** Using these electrodes against the reference calomel electrode, the various methods of determination of pH are briefly described below:

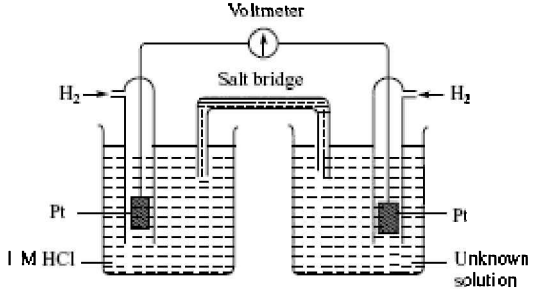


Fig. 18.26 *Determination of pH with hydrogen electrode*

1. Using Hydrogen Electrode The electrode reaction, written as reduction reaction, is

$$H^+ + e^- \longrightarrow \frac{1}{2} H_2 \quad (1 \text{ atm})$$

Potential of this electrode is given by,

$$E_{H^+, H_2} = E^\circ_{H^+, H_2} + \frac{RT}{F} \ln [H^+] \text{ (Nernst equation)}$$

$$= E^\circ_{H^+, H_2} + 0.0591 \log [H^+] \text{ at } 25°C$$

$$= 0.0591 \log [H^+] \qquad [\text{as } E^\circ_{H^+, H_2} = 0]$$

$$= -0.0591 \text{ pH} \qquad [\text{as } -\log [H^+] = \text{pH}]$$

A standard hydrogen electrode is coupled with another hydrogen electrode which contains the solution of unknown pH (Fig. 18.26). In both half-cells, hydrogen gas is used at 1 atm pressure and 25°C. The emf of the cell

$$Pt|H_2(1 \text{ atm})|H^+(1 \text{ M})||H^+(\text{unknown})|H_2(1 \text{ atm})|Pt.$$

is found out from experiment.

The emf of the cell, E_{cell}, is given by,

$$E_{cell} = E_{R.H.S} - E_{L.H.S.}$$

The left-hand electrode is the standard hydrogen electrode and its emf is zero. Thus,

$$E_{cell} = E_{R.H.S} - E_{L.H.S} = -0.0591 \text{ pH}$$

or

$$\text{pH} = \frac{-E_{cell}}{0.0591}$$

2. Using the Quinhydrone Electrode Quinhydrone is a compound which contains equimolar amounts of quinone ($C_6H_4O_2$) and hydroquinone ($C_6H_6O_2$). The working of the quinhydrone electrode is based upon the fact that quinone is reduced to hydroquinone ions.

i.e.

$$\underset{\text{Quinone}}{C_6H_4O_2} + 2e^- \longrightarrow \underset{\text{Hydroquinone ion}}{C_6H_4O_2^{2-}}$$

The hydroquinone ions combine reversibly with the H^+ ions to form hydroquinone.

$$C_6H_4O_2^{2-} + 2H^+ \rightleftharpoons C_6H_6O_2$$

The overall reaction is

$$\underset{\text{Quinone}}{C_6H_4O_2} + 2H^+ + 2e^- \rightleftharpoons \underset{\text{Hydroquinone}}{C_6H_6O_2}$$

If quinone is represented by Q then hydroquinone can be represented by QH_2. Therefore, the above reaction may be written as

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

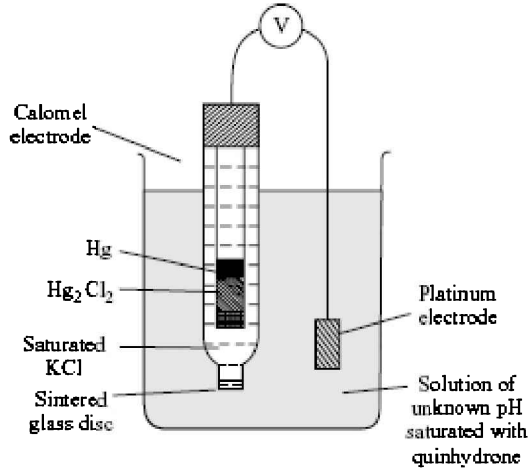


Fig. 18.27 *Quinhydrone electrode coupled with standard calomel electrode*

If a platinum wire is dipped into a solution containing H^+ ions and a pinch of a quinhydrone (i.e. Q + QH_2) is added, it acts as a reversible electrode. (Fig. 18.27). The reaction, as written above, is a reduction reaction. Applying the Nernst equation, the electrode potential of the above electrode is given by

$$E_Q = E_Q^\circ - \frac{RT}{2F} \ln \frac{[QH_2]}{[Q][H^+]^2}$$

[$n = 2$ for the above reaction]

Quinhydrone is an equimolar mixture of Q and QH_2. Taking [Q] = [QH_2] and putting $\frac{[QH_2]}{[Q]} = 1$ in the above equation, we get

$$E_Q = E_Q^\circ - \frac{RT}{2F} \ln \frac{1}{[H^+]^2} = E_Q^\circ + \frac{RT}{F} \ln [H^+]$$

$$= E_Q^\circ + \frac{2.303 \times RT}{F} \log [H^+] = E_Q^\circ + 0.0591 \log [H^+] \text{ at } 25^\circ C$$

$$= E_Q^\circ - 0.0591 \text{ pH}$$

The standard electrode potential (E°_Q) of the quinhydrone electrode has been found to be 0.6996 volt. Hence, we may write

$$E_Q = 0.6996 - 0.0591 \text{ pH}$$

When the quinhydrone is combined with calomel electrode, oxidation takes place at the calomel electrode and reduction at the quinhydrone electrode. Hence, by convention, the cell may be written as,

$$Hg \mid Hg_2Cl_2(s) \mid KCl(\text{saturated}) \parallel H^+(\text{unknown conc.}) \mid Q \mid QH_2 \mid Pt$$

The emf of this cell is given by,

E = [Electrode potential of RHS electrode] – [Electrode potential of the LHS electrode]
= (0.6996 – 0.0591 pH) – 0.2415 = 0.4581 – 0.0591 pH

$$\text{pH} = \frac{0.4581 - E}{0.0591}$$

The emf *(E)* of the cell is measured potentiometrically, from which the pH of the solution can be calculated.

3. Using Glass Electrode If two solutions of different pH are present on the two sides of the glass surface, a potential is established across the glass membrane whose magnitude depends upon the difference in the pH of the two solutions. For a particular variety of a glass, if on one side of the glass surface, a solution of fixed pH value is placed, the potential developed across the glass membrane will depend only upon the pH of the other solution, placed in contact with the other side of the glass surface. The assembly thus obtained is called glass electrode (Fig. 18.28)

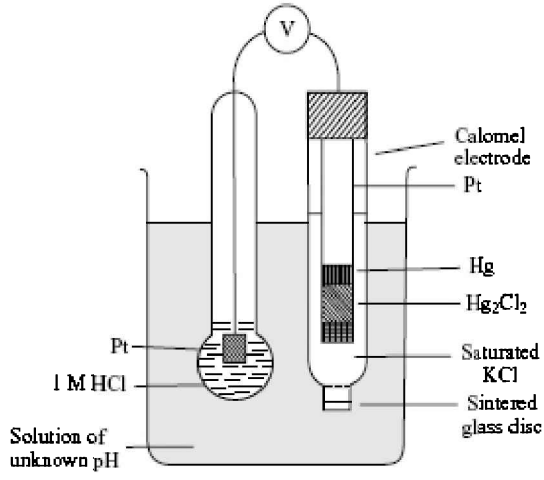


Fig. 18.28 *A glass electrode coupled with standard calomel electrode*

A tube of special variety of glass (usually soda glass) is taken which has low melting point and high electrical conductivity. At the end of this tube is blown a glass bulb having a very thin wall. This is filled with a solution of constant pH. To make the electrical contact with this solution, a platinum wire is dipped into the solution, the other end of which is attached to a terminal. The electrode potential of the glass electrode, as prepared above, is given by the equation

$$E_G = E_G^\circ + 0.0591 \log [H^+] \text{ at } 25^\circ C$$
$$= E_G^\circ - 0.0591 \text{ pH} \qquad \ldots(18.77)$$

where, E°_G is a constant depending upon the nature of the glass and the pH of the solution taken inside the glass bulb. To determine the value of E°_G for a particular glass electrode, the value of E_G is determined for a solution of known pH value.

To determine the value of pH of an unknown solution, the glass electrode is combined with the calomel electrode as usual and the emf of the resulting cell is measured. The cell may represented as

Glass electrode | Experimental solution | Calomel electrode

The emf of this cell will be

$$E = E_C - E_G \qquad \ldots(18.78)$$

where E_C is the electrode potential of the calomel electrode whose value depends upon the concentration of KCl solution used.

From Eq. (18.78),

$$E_G = E_C - E$$

Combining this result with Eq. (18.77), we get

$$E_C - E = E_G^\circ - 0.0591 \text{ pH}$$

$$\text{pH} = \frac{E_G^\circ - E_C + E}{0.0591} \qquad \ldots(18.79)$$

Advantages of Using Glass Electrodes The advantages of glass electrodes over other electrodes are as mentioned below:

(a) They are easy to use.

(b) They are not poisoned easily.

(c) They are not affected by oxidising or reducing agents.

(d) They can be used for very small quantities of the solutions.

Fig. 18.29 *A calomel electrode coupled with unknown hydrogen electrode*

4. Using Calomel Electrode When a hydrogen electrode is coupled with a calomel electrode, oxi- solution dation takes place at the hydrogen electrode and reduction at the calomel electrode. Hence, by convention, the cell may be written as

$$\text{Pt, } H_2 \text{ (1 atm) | } H^+\text{(unknown conc.) symbol || KCl (saturated) | } Hg_2Cl_2(s) \text{ | Hg}$$

The emf of this cell is given by the relation

Thus, measuring the emf *(E)* of the cell potentiometrically, the pH of the solution can be calculated (Fig. 18.29).

Example 21 *Consider the cell*

$$Pt/H_2(g, 1 \text{ atm})/H^+(x \text{ molar})// KCl\ (0.1\ M)/Hg_2Cl_2/Hg$$

If the emf of this cell is 0.50 volt at 25°C, what would be the pH of the x molar acid solution? (Electrode potential of the calomel electrode is 0.281 volt at 25°C.)

Solution: The emf of the given cell is given by,

But by the Nernst equation, we have

PROBLEMS FOR PRACTICE

1. The emf of the cell

Pt, H_2 (1 atm)|solution of unknown pH||Hg_2Cl_2(s) KCl(s)|Hg is 0.366 volt. Ignoring the junction potential, determine the pH of the given solution, electrode potential of SCE being +0.242 volt.

[Ans. 2.098]

2. Determine the pH of the solution at 25°C from the following data:

Pt, H_2(1 atm)|H^+(a = x)|| Normal calomel electrode

$$E_{cell} = 0.6346 \text{ V}$$

Oxidation potential of normal calomel electrode = –0.2800 V

[Ans. 6.0]

3. The emf of the cell

Pt, H_2(g)(1 atm)|H^+(a = ?)||H^+(a = 0.01)|H_2(1 atm), Pt at 25°C is 0.861 volt

What is the pH of the solution around the left-hand electrode? The value of 2.303 RT/F at 25°C os 0.0591.

[Ans. 12.568]

18.29 POTENTIOMETRIC TITRATIONS

In all types of titrations like acid-base titrations, redox titrations, precipitation titrations, etc., one of the solutions is taken in the titration flask and the other solution is added to it from the burette. As a result, the concentration of some ion in the titration flask keeps on changing. If an electrode reversible with respect to this ion is set up in the titration flask, its electrode potential will keep on changing. If the electrode, thus set up in the titration flask, (or beaker) is coupled with a calomel electrode, the emf of the cell will keep on changing or show a sudden change in value when the end point is reached or the reaction is complete. Titrations carried out using this principle are called potentiometric titrations.

Each type of titration is discussed separately as under:

Fig. 18.30 *Potentiometric titration of HCl vs NaOH*

1. Acid-Base Titrations Suppose a solution of HCl acid is to be titrated against NaOH solution. The acid solution is taken in a beaker and a hydrogen electrode (quinhydrone or glass or hydrogen gas) is set up in it. This electrode is then combined with the calomel electrode. A burette containing the NaOH solution is fitted over the beaker (Fig. 18.30). NaOH solution is added to the beaker first in the larger amounts (say 1 ml or 0.5 ml at a time) and then in very small amounts (say 0.1 ml or even less) near the end point. The emf of the cell is noted after each addition. The emf is then plotted against the volume of NaOH added. A curve of the type shown in Fig. 18.31 is obtained. From this curve, the volume of NaOH solution used corresponding to the equivalence point can be found. However, when the solutions are very dilute, or weak acids or bases are involved, the steepness of the curve is less marked and it is difficult to locate the end point. In such a case, we plot the slope of the curve $\Delta E/\Delta V$ against the volume of the alkali used. The maximum of the curve indicates the end point (Fig. 18.32).

Fig. 18.31 *Volume of NaOH solution added*

Fig. 18.32 *Titration curve of a weak acid and weak base*

Fig. 18.33 *Apparatus for potentiometric titration of* Fe^{2+} *with* $K_2Cr_2O_7$

2. Redox Titrations Suppose a solution of ferrous sulphate is to be titrated against K_2Cr_2O7 solution. The ferrous sulphate solution along with dilute H_2SO_4 is taken into a beaker and a platinum wire is inserted into it. The electrode thus formed is combined with calomel electrode (Fig. 18.33). A burette containing $K_2Cr_2O_7$ solution is fixed over the beaker and after every addition of $K_2Cr_2O_7$ solution, the emf of the cell is noted. The end point is then determined in a manner similar to that of acid-base titrations.

Similarly, Fe^{2+} can be estimated potentiometrically using a standard solution of KMnO4. We shall take KMnO4 solution in place of $K_2Cr_2O_7$ solution (Fig. 18.34). Rest of the procedure remains the same. The equivalence point will be determined as in the case of $Fe^{2+} - K_2Cr_2O_7$ titration.

3. Precipitation Titrations Suppose a solution of $AgNO_3$ is to be titrated against NaCl solution. The silver nitrate solution is taken in a beaker and a silver wire is inserted into it (Fig. 18.35). The electrode, thus formed, is then combined with the calomel electrode. A burette containing the NaCl solution is fixed over the beaker and after every addition of NaCl solution, the emf of the cell is noted. The end point is then determined as in the case of acid-base titrations (Fig. 18.36).

Fig. 18.34 *Potentiometrie titration curve of* Fe^{2+} *ions with* $K_2Cr_2O_7$

Fig. 18.35 *Potentiometrie titration of sodium chloride against silver nitrate solution*

Fig. 18.36 *Potentiometrie titration curve for NaCl and* $AgNO_3$

We get a similar curve as in acid-base titration because the electrode potential of the silver electrode depends upon the concentration of Ag^+ ions in the solution. The addition of NaCl solution results into the precipitation of Ag^+ ions to form AgCl (which is sparingly soluble). The concentration of Ag^+ ions in the solution thus keeps on decreasing with the addition of NaCl solution till the end point, when all the Ag^+ ions are precipitated. At this stage, a very small amount of Ag^+ ions are still present which are obtained due to the ionisation of the AgCl that has gone into the solution. Further addition of NaCl solution has no effect on the Ag^+ ion concentration except that it suppresses the ionisation of AgCl due of common-ion effect and as a result the Ag^+ ion concentration, decreases very slightly.

Advantages of potentiometric titrations:

(a) These titrations are very useful in case of coloured solutions where internal indicators fail.

(b) For acid-base titration, no prior knowledge of the pH range in which the indicator changes colour, is required.

18.30 CORROSION

The process of slow eating away of the metal due to the attack of atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, and carbonates, etc., is called corrosion.

Rusting of ion is the most common example of corrosion. Rust is hydrated ferric oxide, $Fe_2O_3 \cdot xH_2O$. Other examples include tarnishing of silver, green coating on copper, bronze, etc.

Types of Corrosion

1. Galvanic Corrosion This is the most common form of corrosion and can be dry or wet, chemical or electrochemical. When two different metals (e.g. zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in the electrochemical series undergoes corrosion. Such type of corrosion is called ***galvanic corrosion.*** In the corrosion, a uniform decrease in the volume of a metal takes place as a result of chemical action and soluble corrosion products are formed (Fig. 18.38).

Fig. 18.37 *Corrosion of metals has proved to be one of the biggest enemies of humans.*

Fig. 18.38 *Volatile oxide layer*

2. Erosion Corrosion It is caused by the combined effect of turbulent flow of gases, vapour and liquids and the mechanical rubbing action of solids over a metal surface. The major cause for its corrosion is the removal of the protective surface film.

3. Intergranular Corrosion Intergranular corrosion occurs along grain boundaries and only where the material, especially sensitive to corrosion attack, exists and corrosive liquid possesses a selective character of attacking only at grain boundaries, but leaving the grain interiors untouched or only slightly attacked. This type of corrosion is due to the fact that grain boundaries contain material, which shows electrode potential more anodic than that of the grain centre in the particular corroding medium. This may be due to the precipitation of certain compounds at the grain boundaries.

4. Exfoliation and Selective Leaching Exfoliation and selective leaching is a subsurface corrosion which starts on a clean surface and spreads below it. If differs from pitting in that the attack has a rather laminated appearance and whole layers of material are corroded. The attack is usually recognised from a flaky or blistered surface. This type of corrosion is known to take place in aluminum alloys and can be avoided by heat treatment and proper alloying.

Selective leaching (parting) is the removal of one of the elements in an alloy. Dezincification from copper-zinc alloys is the most common example. This type of corrosion is highly undesirable as it yields a porous metal with poor mechanical properties. This can be remedied by the use of nonsusceptible alloys.

This type of corrosion involves in a localised electrochemical corrosion, occurring along narrow paths, forming anodic areas with respect to the more cathodic areas at the metal surface.

5. Soil Corrosion Corrosion by soils is very important in case of water mains, electric cables and other underground structures, which are embedded in the soil. The various factors that are responsible for soil corrosion include the following:

(a) Acidity of the soil

(b) Moisture content

(c) Content of electrolytes

(d) Microorganisms present

(e) Content of organic matter

(f) Physical properties of the soil

Soil corrosion is purely electrochemical in character. The texture of the soil is determined by the percentage of particles of various sizes.

6. Microbiological Corrosion Corrosion caused by the metabolic activity of various micro-organisms is called ***microbiological corrosion.*** The microorganisms can develop in an environment with or without oxygen and are classed as aerobic or anaerobic respectively.

Bacteria, fungi, algae, diatoms, etc., are capable of forming microorganisms. Such a film maintains concentration gradients of dissolved salts, gases, acids, etc., on the surface of ions and as a result, local biological concentration cells are developed on the surface leading to microbiological corrosion.

7. Crevice Corrosion It is a local corrosion and is usually caused by dirt deposits, corrosion products, crack in paint coatings, etc. It is usually attributed to changes in acidity in the crevice and lack of O_2 in the species in the crevice.

8. Pitting Corrosion Pitting corrosion is usually due to the breakdown of cracking of the protective film on a metal at specific points. It is a localised accelerated attack, resulting in the formation of cavities around which the metal is relatively unattached and this corrosion results in the formation of pinholes, pits and cavities in the metal. Pitting corrosion gives rise to the formation of small anodic and larger cathodic areas.

9. Stress-corrosion Cracking Stress corrosion is due to the combined effect of static tensile stresses and the corrosive environmental stresses on the metal that cause cracking resulting from residual cold working and quenching, welding, thermal treatment or due to applied loads during service.

In such cases, the metal under stress becomes more anodic and tends to increase the rate of corrosion. For stress corrosion to occur, presence of tensile stress and a specific corrosive environment are necessary. The corrosive agents are highly specific and selective.

10. Waterline Corrosion Waterline corrosion results from differential aeration leading to the formation of oxygen concentration cells. It has generally been observed that maximum corrosion takes place in a steel tank containing water along a line just beneath a level of water, because access of oxygen is much less there (Fig. 18.39). The area above the waterline is highly oxygenated and hence, acts as a cathodic area.

Fig. 18.39 *Waterline corrosion occurs just underneath the meniscus and the water level.*

Consequently, it is not corroded. However, little corrosion takes place when the water is relatively free form acidity.

Waterline corrosion is also caused in marine ships and is accelerated by marine plants which are attached to the sides of ships.

18.31 ELECTROCHEMICAL THEORY OF CORROSION

The theory of corrosion can be explained by taking the example of rusting of iron. This theory explains the formation of rust on the basis of the formation of electrochemical cells on the surface of the metal.

Fig. 18.40 *Corrosion cell*

The following steps are involved in the formation of rust:

1. The water vapours on the surface of the metal dissolve CO_2 and O_2 from the air. Thus, the surface of the metal is covered with the solution of CO_2 in water, i.e. carbonic acid (H_2CO_3).

   This acts as an electrolyte solution of the cell. The carbonic acid and water ionise to small extent as

2. In contact with the dissolved CO_2 and oxygen, iron undergoes oxidation as follows:

   Thus, the sites where the above reaction takes place act as ***anodes.*** As a result of the above reaction, iron is converted into ferrous (Fe^{2+}) ions.

3. The electrons lost by iron are taken up by the H^+ ions produced by the dissociation of H_2CO_3 and H_2O present on the surface of the metal. Thus, H^+ ions are converted into H-atoms.

   These H-atoms react with oxygen to form water.

   Multiplying Eq. (18.81) by 4 and adding to Eq. (18.82), the complete reduction reaction may be written as

   The dissolved oxygen may take up electrons directly to form OH^- ions as follows:

$$O_2 + H_2O + 4e^- \longrightarrow 4OH^-$$

   The sites where the above reactions take place act as ***cathodes.***

   Adding equations (18.80) and (18.83), the overall reaction of the miniature cell will be

   It may be mentioned here that if water contains some dissolved salts, it helps in the flow of current in the miniature cell and, hence, enhances the process of corrosion. This explains

why there is a faster and greater corrosion by the sea side.

4. The ferrous ions formed react with the dissolved oxygen or oxygen from the air to form ferric oxide

$$4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+ (aq)$$

Ferric oxide then undergoes hydration to form rust,

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3\,xH_2O$$

Fig. 18.41 *Corrosion of iron*

It may be noted that the rust does not stick to the surface. It peels off exposing fresh iron surface for further rusting. It, thus, reduces the life of an article.

The rusting phenomenon may be represented diagrammatically as shown in Fig. 18.41.

Factors Responsible for Corrosion

(a) Reactivity of the Metal More active metals having high oxidation potential values are readily corroded.

(b) Presence of Air and Moisture Air and moisture accelerate the corrosion phenomenon. Presence of gases like SO_2 and CO_2 in air enhance the process of corrosion. Iron does not rust when placed in vacuum.

(c) Presence of Electrolyte Electrolytes increase the rate of corrosion. For example, iron rusts faster in saline water than in pure water.

(d) Strains in Metals Corrosion takes place rapidly at bends, scratches and cuts in the metal.

(e) Presence of Impurities Presence of impurities in metals enhance the chances of corrosion. Pure metals do not corrode.

18.32 METHODS OF PREVENTION OF CORROSION

Some of the methods for prevention of corrosion are explained below:

1. Sacrificial Protection Sacrificial protection implies covering the iron surface with a layer of metal which is more active (electropositive) than iron. It, thus, prevents the iron form losing electrons and getting oxidised. The more active metal loses electrons in preference to iron and converts itself into ionic state. With the passage of time, the more active metal gets consumed into ions but so long as it is present there, it will protect the ions from rusting. It does not allow even the nearly exposed surface of iron to react. The metal often used for protecting iron with a more active metal is zinc and the process is called galvanisation. The layer of zinc on the surface of iron, on coming in contact with moisture, oxygen and carbon dioxide, forms a protective invisible thin layer of basic zinc carbonate, $ZnCO_3$. $Zn(OH)_2$, which causes the galvanised iron sheets to lose their lustre but to protect it from further corrosion.

Fig. 18.42 *The Delhi iron pillar has withstood corrosion for the last 1600 years. It speaks of the high level of skill achieved by ancient Indian ironsmiths in the extraction and processing of iron. If is believed that the iron used in the pillar contains phosphorus and is free from sulphur/magnesium.*

2. Using Anti-rust Solutions These are alkaline phosphate and alkaline chromate solutions. The alkaline medium prevents availability of hydrogen ions. Phosphate deposits an insoluble protective film of iron phosphate on the iron. These solutions are used to prevent rusting of iron parts of the automobile engines and radiators.

3. By External Coating

(a) By applying a film of oil or grease on the surface of the iron tools and machinery, the rusting of the iron can be prevented. It keeps the iron surface protected form moisture, oxygen and carbon dioxide.

(b) The metal surface is coated with a point which prevents the action of air, moisture, etc., till the point layer develops cracks.

(c) The iron surface is coated with a phosphate give a tough adherent insoluble film which does not allow air and moisture to react with iron surface.

(d) The iron surface is coated with noncorroding metals such as nickel, chromium, aluminium, etc., by electroplating with tin, zinc, etc., or by dipping the iron article in the molten metal. This again cuts off the supply of oxygen and water to the iron surface.

4. Electrical or Cathodic Protection The iron object to be protected from corrosion is connected to a more active metal (greater oxidation potential) either directly or through a wire. The iron object acts as cathode and the more active metal acts as anode. The anode gradually disappears due to the oxidation of its metal ions. The iron object remains protected form rusting as long as the active metal is present. The metal used for protecting iron objects from rusting is out of magnesium, zinc and aluminium which are called sacrificial anodes.

Fig. 18.43 *Electrical protection of underground iron pipes*

Cathodic protection is often employed in the protection of iron pipes buried in moist soil, canals, storage tanks, etc. Pieces of magnesium are buried along the pipeline and connected to it by the wire as illustrated in Fig. 18.43. Electrode reactions are given alongside in the figure.

Example 22 *Write down the reactions taking place at the separate electrodes and in the complete reversible cell given below:*

$$Pt, H_2(g)/HCl(aq)//KCl(aq), AgCl(s)\ Ag.$$

Solution: At anode

Example 23 *Taking the example of Daniel cell, explain why the emf of the cell drops to zero after some time.*

Solution: At the zinc electrode, concentration of Zn^{2+} keeps on increasing while at the copper electrode, concentration of Cu^{2+} ion keeps on decreasing. As a result, electrode potential of zinc electrode keeps on increasing while that of copper electrode keeps on decreasing till

ultimately the two electrode potentials become equal. Hence, E_{cell} becomes equal to zero.

Example 24 *Why cannot a voltmeter be used to measure the emf of a cell?*

Solution: The voltmeter draws current from the cell, thereby changing the emf of the cell.

Example 25 *Write down the cell reaction and expression for the emf of the following reversible cells:*

(a) $Cd(s)/Cd^{2+}//H^{+}/H_2(g)/Pt$

(b) $Zn(s)/Zn^{2+}//Fe^{3+}, Fe^{2+}/Pt$

Solution:

Example 26 *Why is a calomel electrode preferred over a hydrogen electrode as a reference electrode? Give the reactions occurring on the calomel electrode.*

Solution: Use of hydrogen electrode is not conveninent because it involves the use of hydrogen gas.

Reactions occurring in calomel electrodes are

(a) When oxidation occurs: $2Hg(l) + 2Cl^{-} \rightarrow Hg_2Cl_2(s) + 2e^{-}$

(b) When reduction occurs: $Hg_2Cl_2(s) + 2e^{-} \rightarrow 2Hg(l) + 2Cl^{-}(aq)$

Example 27 *Explain the meaning of an electrode potential being positive or negative with respect to hydrogen electrodes.*

Solution: Positive electrode potential with respect to hydrogen electrode means that reduction takes place on this electrode and oxidation on the hydrogen electrode. Negative electrode potential with respect to hydrogen electrode means just the opposite.

Example 28 *Write down the reaction taking place at the separate electrode and in the complete cell in the following reversible cell*

$$Pb/PbCl_2(s), KCl(aq)//K_2SO_4(aq), PbSO_4/Pb.$$

Solution: At anode:

Example 29 *Iron does not rust even if the zinc coating is broken in a galvanised iron pipe but rusting occurs much faster if the tin coating over iron is broken. Explain.*

Solution: This is because the standard electrode of zinc is more negative than that of iron but that of tin is less negative than that of iron

SUMMARY

1. A device used to convert chemical energy of reaction into electrical energy is called

electrochemical cell or *galvanic cell.*

2. The electrode where the oxidation takes place is called *anode,* and the electrode where reduction takes place is called *cathode.* Anode is the *negative pole* and cathode is the *positive pole.*
3. Electrons flow from negative pole to the positive pole in the external circuit. Conventionally, the current is said to flow in the *opposite* direction
4. An arrangement in which electrical energy is supplied to bring about the redox reaction which was otherwise non-spontaneous, i.e. to bring about the decomposition of an electrolyte, is called an *electrolytic cell.*
5. The cell representing the reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ is formulated as $Zn|\ Zn^{2+}\ (aq)\ ||\ Cu^{2+}\ (aq)\ |\ Cu(s)$.
6. The tendency of an electrolyte to lose or gain electrons when it is in contact with its own ions in the solution is called *electrode potential.*
7. The force which causes the flow of electrons from one electrode to the other and thus results in the flow of current is called *electromotive force* or emf and is measured in volts.
8. Different types of electrodes are metal-metal ion electrodes, hydrogen electrode, calomel electrode, redox electrode.
9. Electrode potential of an electrode can be measured by combining it with hydrogen electrode or any other standard electrode. From the emf of the cell so constructed, we can determine the potential of the electrode.
10. Different electrodes have been arranged in order of their decreasing values of standard reduction potentials. This arrangement is called *electrochemical series.*
11. With the help of electrochemical series, we can predict spontaneity of a reaction, whether a metal reacts with an acid to give hydrogen gas or not, ease of oxidation or reduction. We can calculate the standard emf of any cell.
12. The effective concentration of an ion or the electrolyte in the solution is called its *activity.* It is represented by the letter a. It is related to the actual concentration expressed as molarity M by the equation $a = \gamma \times M$ where γ is activity coefficient.
13. *Polarisation* and *overpotential* are two phenomena associated with an irreversible electrode process in which there is a flow of electric current.
14. Polarisation is defined as increase or decrease in electrode potential caused by increase or decrease in the concentration of metal ions.
15. The difference between the potential of the electrode when gas evolution is actually observed and the reversible value for the same evolution is called overvoltage or overpotential.
16. Cells in which the emf produced is only due to the difference in the concentrations of the electrodes or that of the solutions of electrolytes with which they are in contact, are called *concentration electrodes.*
17. We can determine the transport number of ions, solubility and solubility product of sparingly soluble salts, standard free-energy change, equilibrium constant of a given reaction and valency of an ion with the help of emf measurements.
18. The process of slow eating away of the metal due to the attack of atmospheric gases on the surface of the metal resulting into the formation of compounds like oxides, sulphides and carbonates, etc., is called corrosion.
19. Different types of corrosion are galvanic corrosion, erosion corrosion, intergranular corrosion, exfoliation, soil corrosion, microbiological erosion, crevice corrosion, pitting

corrosion, stress corrosion and waterline corrosion.

20. Corrosion can be prevented by the following methods: by sacrificial protection, using anti-rust solutions, by external coating and by cathodic protection.

KEY RELATIONS

1. Electrical energy = nFE
2.
3. $a = \gamma \times M$
4.
5. Nernst equation

   Nernst equation for single electrode

6.
7.
8.
9.

EXERCISES

Based on Different University Papers

Multiple-choice Questions

1. In an electrochemical cell,
   (a) potential energy decreases
   (b) kinetic energy decreases
   (c) potential energy changes into electrical energy
   (d) chemical energy changes into electrical energy.
2. If the standard electrode potential of Cu^{2}+/Cu electrode is 0.34 V, what is the electrode potential of 0.01 M concentration of Cu^{2+} (T = 298 K)?
   (a) 0.399 V
   (b) 0.281 V
   (c) 0.222 V
   (d) 0.176 V
3. Three elements *A*, *B* and *C*have reduction potentials –1.5, –0.05, and +1.50. Then the correct order of their reducing power is
   (a) $A > B > C$
   (b) $B > A > C$
   (c) $C > B > A$
   (d) $B > C > A$

4. Cell reaction is spontaneous when
   (a) $E°_{red}$ is +ve
   (b) $\Delta G°$ is –ve
   (c) $\Delta G°$ is +ve
   (d) $E°_{red}$ is +ve
5. For the overall reaction
   $$Cu^{2+}\ (C_1\ aq) + Zn(s) \rightarrow Zn^{2+}\ (C_2\ aq) + Cu(s)$$
   of an electrochemical cell, the change in the free energy ΔG at a given temperature is a function of
   (a) $\ln C_1$
   (b) $\ln (C_2/C_1)$
   (c) $\ln C_2$
   (d) $\ln (C_1 + C_2)$
6. In the electrochemical cell, flow of electrons is from
   (a) cathode to anode in the solution
   (b) cathode to anode through external supply
   (c) cathode to anode through internal supply
   (d) anode to cathode through internal supply
7. The hydrogen electrode is dipped in a solution of pH = 3 at 25°C. The potential of the cell would be
   (a) 0.177 V
   (b) 0.087 V
   (c) –0.177 V
   (d) 0.059 V
8. The oxidation potential of Mg and Al are +2.37 and +1.66 volts respectively. The Mg in the chemical reaction
   (a) will be replaced by Al
   (b) will replace Al
   (c) will not be able to replace Al
   (d) none of the above
9. For a cell reaction involving $2e^-$ change, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction will be
   (a) 2.95×10^2
   (b) 10
   (c) 1×10^{10}
   (d) 1×10^{-10}
10. Saturated solution of KNO_3 is used to make a ‘salt bridge’ because

(a) velocity of K^+ is greater than that of NO^-_3

(b) velocity of NO^-_3 is greater than that of K^+

(c) velocities of K^+ and NO^-_3 both are nearly the same

(d) none of the above

Answers

1. (d)
2. (b)
3. (a)
4. (a)
5. (b)
6. (c)
7. (c)
8. (b)
9. (c)
10. (c)

SHORT-ANSWER QUESTIONS

1. Explain the term polarisation.
2. Discuss the role of calomel electrode as a reference electrode for determination of electrode potential of any electrode.
3. Define galvanic cell or electrochemical cell. Give one example.
4. Write a short note on corrosion.
5. What is an electrochemical series? Discuss its important uses.
6. Define reversible and irreversible cells giving example
7. What is the important condition for a redox reaction to be spontaneous?
8. What is an electrolytic cell?
9. What are concentration cells? What are their different types?
10. Define electrode potential.
11. What do you understand by liquid junction potential?
12. Define emf of a cell. How do you measure it experimentally?
13. How do you represent an electrochemical cell?
14. Derive a relationship between emf of the cell and ΔG, ΔH and ΔS.
15. What is a salt bridge? Give its importance.

GENERAL QUESTIONS

1. What do you understand by emf of a cell? How can it be measured experimentally?

2. Derive Nernst equation for measuring emf of a cell.
3. What is corrosion? Give theory of rusting of iron. Briefly explain differents methods of preventing corrosion.
4. Describe how pH of the solution can be determined by using (a) Quinhydrone electrode, and (b) Glass electrode,
5. What are concentration cells? How are they classified into different types? Give one example of each. Taking a suitable example of concentration cell, derive expression for the emf of concentration cell.
6. Describe the important applications of emf measurements.
7. Briefly explain the terms (a) polarisation, (b) decomposition potential, and (c) discharge potential.
8. Derive the relationship between electrical energy and chemical energy produced in the redox reaction. Explain the effect of temperature coefficient of emf on the enthalpy change.
9. What are 'reversible electrodes'? Explain the different types of reversible electrodes with suitable examples.
10. How is the standard electrode potential of an electrode measured using (a) standard hydrogen electrode, and (b) calomel electrode, as reference electrode? Explain with suitable examples.
11. Taking the example of a suitable concentration cell with transference, derive the expression for the emf of the cell.
12. Explain the terms activity and activity coefficient. How are these determined using emf measurement?
13. Define an electrochemical cell. Taking a typical electrochemical cell, explain its working.
14. What are reversible and irreversible cells? Explain each of them with suitable examples.
15. What do you understand by overvoltage or overpotential? What is hydrogen overvoltage? Briefly explain the factors on which it depends. Give some of its important applications.
16. What is the principle of potentiometric titrations? Briefly explain how the following titrations are carried out potentiometrically.

    (a) Acid-base titrations

    (b) Redox titrations

    (c) Precipitation titrations
17. What are different types of reversible electrodes? Taking a suitable example of each of them, derive the Nernst equation for each case.
18. What is 'liquid junction potential'? Derive expression for the liquid junction potential. How can it be minimised or eliminated?



Atomic Structure and Quantum Mechanics

19

LEARNING OBJECTIVES

- Understand the limitations of classical mechanics
- Learn black body and black-body radiations
- Derive Kirchhoff's law and understand its importance
- Learn Stefan's fourth power law
- Learn spectral distribution of black-body radiations
- Understand Boltzmann's law
- Derive Planck's radiation law and appreciate its importance
- Learn photoelectric effect
- Understand heat capacity of solids
- Learn Bohr model of atom and know its shortcomings
- Learn dual nature of matter and de Broglie equation
- Understand the Heisenberg uncertainty principle
- Learn Compton effect
- Derive the Schrodingerwave equation and understand its importance
- Define eigen values and eigen functions
- Interpret wave function as per the Born concept
- Understand normalised and orthogonal wave functions
- Learn the algebra of operators
- Understand postulates of quantum mechanics
- Derive the Schrodinger equation based on postulates of quantum mechanics
- Learn the meaning of particle in one-dimensional box and three-dimensional box
- Calculate expectation values using wave functions
- Learn the concept of degeneracy
- Derive Schrodinger wave equation in terms of polar coordinates
- Learn how to separate the variables
- Derive expressions for angular spherical wave functions and radial wave functions
- Obtain quantum number from Schrodinger wave equation
- Draw radial probability distribution curves and obtain the shapes of orbitals

19.1 INTRODUCTION

John Dalton conceptualised the atom as hard, dense and the smallest indivisible particle of matter. Later investigations proved that an atom is made up of electrons, protons and neutrons. The British physicist J.J. Thomson determined the ratio *e/m* (charge to mass) of electrons by subjecting the beam of electrons produced in a discharge tube to magnetic as well as electric fields. The magnetic field is applied at right angles to the electric field. Thomson determined the value of *e/m* as 1.75875×10^{11} *C*

kg^{-1} irrespective of the nature of the gas taken.

Robert Millikan determined the charge on an electron by using his famous ***oil-drop*** technique. Millikan found that charge e was equal to 1.6022×10^{-19} C. The value has now been revised to 1.60206×10^{-19} C. The American physicist Robert Millikan was awarded the Physics Nobel Prize in 1923 for determining the charge on an electron. Since we know the values of e/m and e separately, it is possible to calculate the mass of an electron as follows:



Fig. 19.1 *Sir J J Thomson was a British physicist. In 1897, Thomson showed that cathode rays were composed of previously unknown negatively charged particles.*

$$\text{Mass of electron } (m) = \frac{e}{e/m} = \frac{1.60206 \times 10^{-19}\,\text{C}}{1.75875 \times 10^{11}\,\text{C kg}^{-1}} = 9.1091 \times 10^{-31}\,\text{kg}$$

19.2 CLASSICAL MECHANICS

The branch of science based on Newton's laws of Motion and Maxwell's electromagnetic wave theory to explain phenomenon related to motion and energy is known as classical mechanics or Newtonian mechanics. According to classical mechanics, it should be possible to determine simultaneously the position and velocity of a moving particle but the Heisenberg uncertainty principle contradicts it. Classical mechanics assumes that energy is emitted or absorbed in a continuous manner but Planck's quantum theory dictates that emission or absorption of energy takes place in an uncontinuous manner in the form of packets of energy called ***quanta.***

Limitations of Classical Mechanics

Classical mechanics does not provide satisfactory explanation for the following phenomena:

1. Black-body radiation
2. Photoelectric effect
3. Atomic and molecular spectra
4. Heat capacities of solids

The classical point of view is adequate for objects of appreciable size but is quite unsatisfactory for describing the behaviour of particles of atomic dimensions. It has been necessary, therefore, to devise a new mechanics for the treatment of electrons and atomic nuclei. In this new mechanics, which takes into account the de Broglie's dual nature of matter and Heisenberg's uncertainty principle, the exact position of the moving object such as the orbit of an electron around the nucleus of an atom, is replaced by a function which determines the probability of the object being in the particular position. These

probability functions satisfy differential equations which are analogous to those representing the variation of the amplitude of a wave. This new atomic mechanics has been referred to as the ***wave mechanics.*** This new approach to the study of small particles provides a satisfactory basis for many of the quantum postulates and the term ***quantum mechanics*** is generally used for this new approach.

19.3 BLACK BODY AND BLACK-BODY RADIATIONS

If the radiant energy is allowed to fall on a blackened metallic surface or carbon black, it is found that the energy is almost completely absorbed. A ***body which completely absorbs radiant energy falling on it is called a perfect black body.*** The absorption is found to be more perfect if we take a hollow sphere blackened on the inside and having a small hole for the entry of radiation. This is so because any radiation that enters through the hole is reflected over and again by the walls of the sphere till finally it is completely absorbed.

The most commonly used black body is the one shown in Fig. 19.2.

It is a hollow double-walled metallic sphere having a conical projection *P* opposite to the hole *H* and is coated on the inside with lampblack. The projection helps avoid any direct reflection.

A black body is not only a perfect absorber of radiant energy, but also a perfect radiator. In fact, of all bodies, the black body radiates the maximum amount of energy for the given temperature. The radiations thus emitted are called ***black-body radiations.***

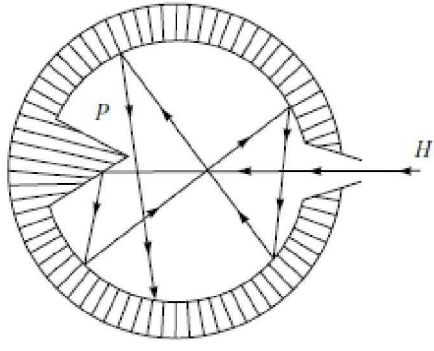


Fig. 19.2 *Black body due to Fermi*

19.4 KIRCHHOFF'S LAW OF BLACK-BODY RADIATIONS

The quantitative relationship between the energy absorbed and the energy emitted by a body was put forward by Kirchhoff in 1859. It is called Kirchhoff's law and it is stated as follows:

At any temperature, the ratio of the emissive power (or emit-tance) of a body to the absorptive power (or absorbance or absorptivity) is constant, independent of the nature of the surface and is equal to the emissive power (emittance) of a perfectly black body.

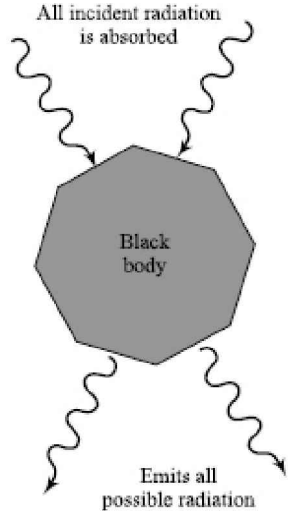


Fig. 19.3 *Black body*

The term ***emissive power*** or *emittance* means the energy emitted by the surface per unit area-whereas the term *absorptive power* or *absorbance* or *absorptivity* is the fraction of the incident energy absorbed by the surface per unit time per unit area.

If E_S and A_S represent the emissive power and absorptive power of any substance and E_B represents the emissive power of a perfectly black body then according to Kirchhoff's law,

$$\frac{E_S}{A_S} = E_B$$

1. Derivation of Kirchhoff's Law Kirchhoff's law can be derived in a simple manner as follows:



Fig. 19.4 *Gustav Kirchhoff was a German physicist who contributed to the understanding of electrical circuits, spectroscopy and emission of black-body radiations by heated objects.*

Suppose Q is the amount of radiation incident per unit area per unit second on a body. If $A$is the absorptive power of the surface then the amount of radiation absorbed by the per unit area per second = $A_S \times Q$.

If E_S represents the emissive power of the surface then the amount of radiation emitted by the surface per unit area per second = E_S

When the body and the enclosure are in ***thermal equilibrium,*** Amount of radiation emitted by the surface per unit area per second = Amount of radiation absorbed by the body per unit area per second

Thus, $E_S = A_S \times Q$ ... (19.1)

For a perfectly black body, $A_S = A_B = 1$ and E_S may be replaced by E_B where A_B and E_B the absorptive power and the emissive power of a perfectly black body.

Thus, we have

$E_B = Q$ ... (19.2)

From equations (19.1) and (19.2), we have

$$E_S = A_S \times E_B$$

or

$$\boxed{\frac{E_S}{A_S} = E_B} \qquad \ldots(19.3)$$

As E_B is constant, the equation gives the expression for Kirch-hoff's law.

2. Stefan's Fourth Power Law

On the basis of experimental studies, Stefan in 1879 showed that the total amount of energy E radiated by a perfectly black body per unit area per unit time is directly proportional to the fourth power of its absolute temperature, T, i.e.



Fig. 19.5 *Joseph Stefan was a Carinthian Slovene physicist, mathematician and poet of Austrian citizenship.*

$$E \propto T^4 \text{ or } E = \sigma T^4$$

where σ is a universal constant called ***Stefan's constant.*** It's value is 5.6697×10^{-5} if energy is expressed in ergs, time in seconds and area in square centimetres. The above statement is called ***Stefan's fourth power law or Stefan-Boltzmann fourth power law***. The theoretical proof of this law was given by Boltzmann using the laws of thermodynamics.

19.5 | SPECTRAL DISTRIBUTION OF BLACK-BODY RADIATION

The energy emitted by a black body at any temperature does not consist of a single frequency and is also not uniformly distributed along the spectrum. Lummer and Pringheim in 1899 studied the distribution of energy amongst different wavelengths of the black-body spectrum as described below.

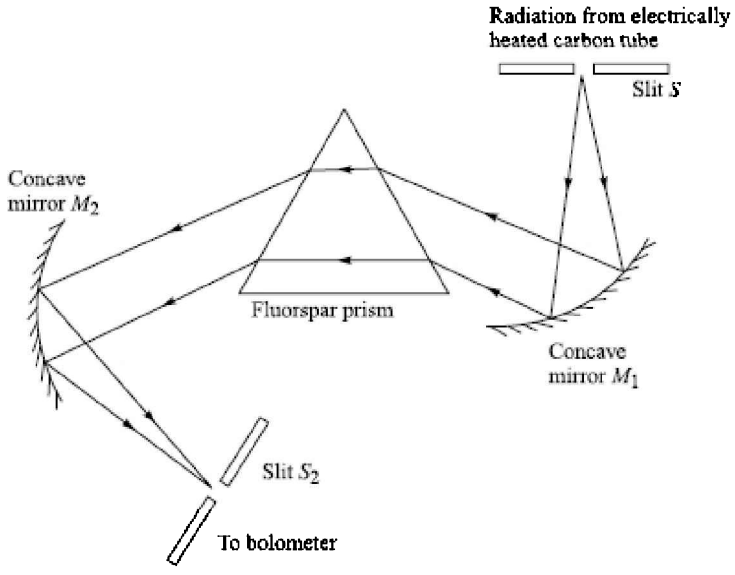


Fig. 19.6 *Lummer and Pringsheim experiment for the study of spectral distribution of black-body radiation*

The black-body radiations were obtained by heating a carbon tube electrically. After passing through the slit S_1, these were made parallel with the help of a concave reflector mirror M_1 and then allowed to fall on a fluorspar prism to get the spectrum. The radiation after reflection through the prism were focussed by another concave mirror M_2 and slit S_2 on to a linear bolometer as shown in Fig. 19.6.

The ***bolometer*** is a sensitive instrument for measuring heat radiations. It consists of two very thin blackened platinum gratings, forming two arms of a Wheatstone bridge circuit. Radiant heat falling on one of the gratings raises its electrical resistance, thus indicating a deflection of the needle of a galvanometer in the circuit.

By gradually rotating the prism, the radiations corresponding to different wavelengths are obtained and focussed on to the bolometer one by one and their intensities measured. By keeping the carbon tube (black body) at different temperatures, a number of observations were made between 621 K to 1646 K. The curves were then plotted between the monochromatic emittance E_λ along the *Y*-axis and the wavelengths along the X-axis for each of the temperatures. These curves are shown in Fig. 19.7. The following observations can be made in respect of these curves.

1. At a particular temperature, the distribution of energy is not uniform along the various wavelengths of the radiations emitted by the black body.
2. For each temperature, there is a wavelength (λ_m) at which the energy radiated is maximum (= E_m).
3. With increase in temperature, the maximum shifts higher but towards lower wavelengths. This means that with increase in temperature, E_m increases but the corresponding λ_m decreases.
4. Higher the temperature, more pronounced is the maximum.
5. The area under the curve for a particular temperature gives the total energy emitted by a black body per unit area per second for the complete spectrum, i.e. corresponding to all the wavelengths at that particular temperature (from $\lambda = 0$ to $\lambda = \infty$).
6. The area under the curve increases with increase of temperature and it is found that the area is proportional to the fourth power of the absolute temperature. As the area under the curve represents the total energy emitted by the black body per unit area per second hence $E_B \propto T^4$. This is ***Stefan boltzmann's law.***

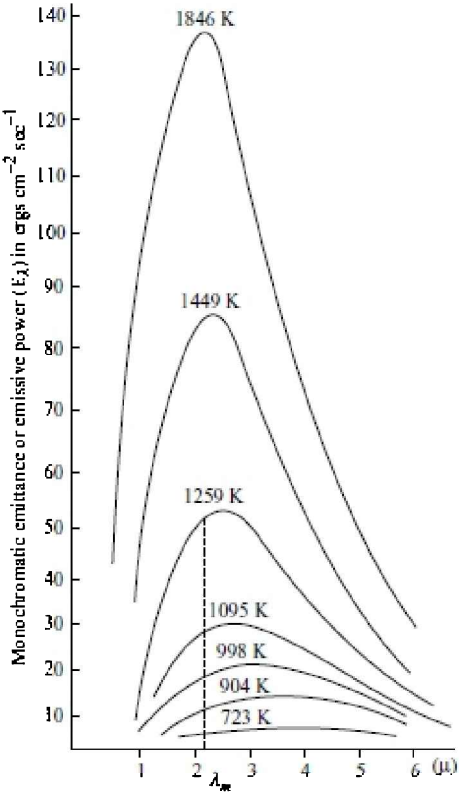


Fig. 19.7 *Distribution of energy in the spectrum or a black body.*

7. From the curves, it is also found that

$$\lambda_{m_1} T_1 = \lambda_{m_2} T_2 = \lambda_{m_3} T_3 \ldots$$

i.e.

$$\lambda_m T = \text{constant}$$

This implies that

$$\lambda_m \propto \frac{1}{T}$$

19.5.1 Wien's Displacement Law

The ***wavelength*** λ_m for ***which the emittance of a black body is maximum is inversely proportional to its absolute temperature.*** This is called Wien's displacement law. Mathematically, the law may be represented as

$$\lambda_m \propto \frac{1}{T}$$

where λ_m = Wavelength corresponding to maximum radiation of energy and T = Temperature on Kelvin Scale.

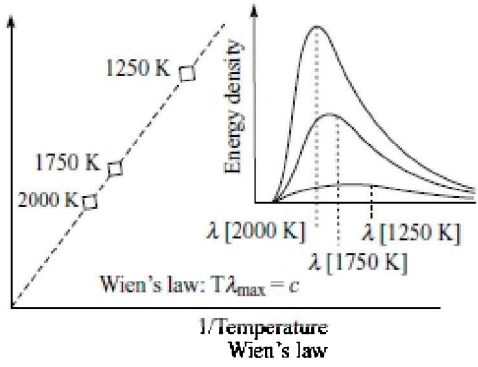


Fig. 19.8 *Wien's law*

This law is able to explain why the colour of the visible light radiation changes from red to yellow as the temperature of hot body is increased.

19.5.2 Failure of Classical Mechanics to Explain the Spectral Distribution of Black-body Radiation

According to Maxwell electromagnetic wave theory of classical mechanics, the sources of radiant energy are the vibrating particles called oscillators and these oscillators can radiate or absorb any amount of energy. The frequency of the energy (or the wave) emitted is equal to the frequency of the oscillator. Based on these classical concepts, Wien in 1896, and Rayleigh and Jeans in 1900 explained the distribution of black-body radiation using the classical concepts of continuous emission of radiation. Wien's equation was able to explain the distribution only at lower wavelengths whereas Rayleigh-Jeans equation was able to do so only at higher wavelengths. However, neither was able to explain the complete distribution of black-body radiation. Later, Planck in 1900 was able to provide explanation for the complete distribution of black-body radiation by propounding his theory of emission and absorption of energy in quantas.

Wien's radiation law equation is,

$$E_\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/kT\lambda}$$

Rayleigh-Jeans radiation law equation is,

$$E_\lambda = \frac{8\pi}{\lambda^4} kT$$

where E_λ is the emissive power of the black body corresponding to the wavelength λ, c is the velocity of light, h is Planck's constant, k is Boltzmann's constant and T is the absolute temperature.

19.6 PLANCK'S RADIATION LAW

Max Planck, in 1900, put forward a theory that the oscillations of a black body cannot have ***just any amount*** of energy but can have only a ***discrete*** amount of energy depending upon the frequency of the oscillator. Planck summed up his result as under:

Energy is emitted or absorbed not continuously but discontinuous-ly in the form of packets of energy called quanta. The energy of each quantum is given by the relation, E = hv, where v is the frequency of the radiation and h is called Planck's constant. Thus, the total energy emitted or absorbed is either unit quantum, i.e. hn, or a whole number multiple of hv, i.e., equal to nhn.

Based upon these concepts, Planck deduced expression for the energy E_λ radiated by a black body at wavelength λ, which is as under:

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/kT\lambda} - 1} \quad \ldots(19.4)$$

This expression is called ***Planck's radiation law.*** Different symbols have usual meanings.



Fig. 19.9 *Max Planck was a German theoretical physicist who originated the quantum theory which won him the Nobel Prize in 1918.*

1. If λT is small, $e^{hc/kT\lambda} >> 1$ so that 1 in the denominator in the above equation can be neglected.

This gives

$$E_\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/kT\lambda}$$

which is Wien's law.

2. If λT is large, $e^{hc/kT\lambda}$ may be expanded by the exponential theorem

$$e^x = 1 + x + x^2 + \ldots$$

We get,

$$e^{hc/kT\lambda} = 1 + \frac{hc}{kT\lambda} + \ldots$$

so that Eq. (19.4) reduces to the form

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{kT\lambda}{hc} = \frac{8\pi}{\lambda^4} kT$$

which is Rayleigh-Jeans law.

Derivation of Planck's Radiation Law Planck considered the black-body radiations to consist of linear oscillators of molecular dimensions and that the energy of linear oscillator can assume only the discrete values,

$$0, h\nu, 2h\nu, 3h\nu \ldots nh\nu$$

If N_0, N_1, N_2, ... are the number of oscillators per unit volume possessing energies 0, $h\nu$, $2h\nu$, ... respectively then the total number of oscillations N per unit volume will be

$$N = N_0 + N_1 + N_2 + \ldots \quad \ldots(19.5)$$

Number of oscillators, N_r having energy E_r is given by (Maxwell's formula)

$$N_r = N_0 e^{-E_r/kT} \quad \ldots(19.6)$$

Substituting these values in the equation of planck's radiation law we get

$$N_r = N_0 + N_0 e^{-h\nu/kT} + N_0 e^{-2h\nu/kT} + \ldots + N_0 e^{-nh\nu/kT}$$
$$= N_0(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots)$$
$$= \frac{N_0}{1 - e^{-h\nu/kT}} \quad [\because \quad (1 - e^{-x})^{-1} = 1 + e^{-x} + e^{-2x} + \ldots] \qquad \ldots(19.7)$$

The total energy of N oscillators will be given by,

$$E = N_1 \cdot h\nu + N_2 \cdot 2h\nu + N_3 \cdot 3h\nu + \ldots$$
$$= h\nu(N_1 + 2N_2 + 3N_3 + \ldots)$$
$$= h\nu(N_0 e^{-h\nu/kT} + 2N_0 e^{-2h\nu/kT} + 3N_0 e^{-3h\nu/kT} + \ldots)$$
$$= N_0 h\nu(e^{-h\nu/kT} + 2e^{-2h\nu/kT} + 3e^{-3h\nu/kT} + \ldots)$$
$$= N_0 h\nu\, e^{-h\nu/kT}(1 + 2e^{-h\nu/kT} + 3e^{-2h\nu/kT} + \ldots)$$
$$= N_0 h\nu\, e^{-h\nu/kT}(1 + 2x + 3x^2 + \ldots) \quad (\text{Putting } e^{-h\nu/kT} = x)$$
$$= N_0 h\nu\, e^{-h\nu/kT}(1 - x)^{-2}$$
$$= \frac{N_0 h\nu e^{-h\nu/kT}}{(1 - x)^2}$$
$$= N_0 h\nu \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2} \qquad \ldots(19.8)$$

Hence, the average energy per oscillator is given by,

$$\bar{E} = \frac{E}{N} = N_0 h\nu \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2} \times \frac{1 - e^{-h\nu/kT}}{N_0}$$

$$\frac{h\nu e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad [\text{Dividing numerator and denominator by } e^{-h\nu/kT}] \qquad \ldots(19.9)$$

Thus, we find that the average energy of the oscillator is not kT (as given by classical theory) but equal to $(e^{h\nu/kT} - 1)$ according to Planck's quantum theory.

Further, it can be deduced that the number of oscillators per unit volume having frequency in the range of ν and $\nu + d\nu$ is equal to

$$\frac{8\pi\nu^2 d\nu}{c^3} \qquad \ldots(19.10)$$

The average energy per unit volume (i.e. energy density) inside the enclosure can be obtained by multiplying (19.9) with (19.10).

$$E_\nu d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \times \frac{h\nu}{e^{h\nu/kT} - 1} \qquad \ldots(19.11)$$

Putting $\nu = \frac{c}{\lambda}$ and $d\nu = -\frac{c}{\lambda^2} d\lambda$, the average energy per unit volume in the enclosure for the wavelengths between λ and $\lambda + d\lambda$ is given by

$$E_\nu d\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{1}{e^{hc/\lambda kT} - 1} d\lambda \qquad \ldots(19.12)$$

or the energy radiated by the black body corresponding to the wavelength λ is

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \qquad \ldots(19.13)$$

which is Planck's radiation law or Planck's distribution law.

Planck's radiation law is able to explain the spectral distribution curves of black-body radiations. This proves the validity of Planck's distribution law.

19.7 PHOTOELECTRIC EFFECT

When a beam of light with frequency equal to or greater than a particular value (called threshold frequency) is allowed to strike the surface of a metal, electrons are ejected instantaneously from the surface of the metal. This effect is called 'photoelectric effect.'

Some characteristics of the photoelectric effect are given below:

1. The electrons are ejected only if the frequency of the incident light is equal to or greater than a minimum value, called ***threshold frequency*** (ν_0) (Fig. 19.10).
2. The electrons are ejected ***instantaneously.*** There is no time lag between striking of the metal surface by the light and emission of electrons.
3. The kinetic energy of the emitted electrons depends upon the **frequency** of the incident light.
4. Einstein explained different observations about photoelectric effect by applying Planck's quantum theory. According to this theory, each quantum of light called ***photon*** has energy ***hν***. When the photon hits the metal atom, it transfers its energy to the electron. Energy equal to the threshold value is used up in the release of the electrons and the remaining energy is stored as the kinetic energy of the electron. (The quantity $h\nu_0$ is called ***work function*** and is equal to the ionisation energy of the metal atom, i.e. $h\nu_0 = IE$.) Thus,

$$h\nu = h\nu_0 + 1/2mv^2 \qquad \ldots(19.14)$$

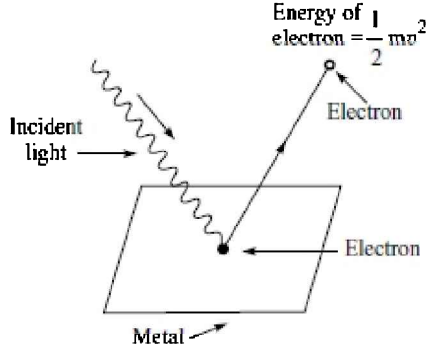


Fig. 19.10 *Photoelectric effect*

Thus, if the frequency of the incident light is equal to the threshold value, electrons emitted will not possess any kinetic energy. Further, intensity of light means the number of photons hitting the metal surface per unit time. An increase in intensity can increase the number of electrons emitted but will have no effect on their kinetic energy.

Equation (19.14) can be rewritten in the form,

$$KE = h\nu - h\nu_0 \qquad \ldots(19.15)$$

This equation shows that kinetic energy of the electrons emitted varies linearly with frequency of the incident radiation. A plot of kinetic energy of the emitted electrons versus frequency of the incident radiation will be a straight line with slope equal to Planck's constant '*h*' (Fig. 19.11). This provides a

method to find the value of Planck's constant.

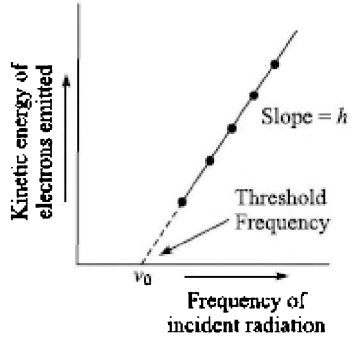


Fig. 19.11 *Variation of kinetic energy of photoelectrons emitted with the frequency of incident radiation*

Applying Chemistry to Life

One of the manifestations of wave theory of matter is photoelectric effect. You might have observed that a mall door stops closing or opens when you move towards it. Similarly, an alarm may sound or light may turn on when there is some movement (motion detection). Such devices work by responding to an interruption in the beam of light. A beam of light is made to shine on a photocathode which emits photo-electrons and a current is constituted. When the beam of light is interrupted, the flow of electrons stops and the current is cut off. When the current stops, the movement of the door stops. In motion-detection devices, a light may turn on (at night, for example) or an alarm might be set.



Fig. 19.12 *Automatic door opening and closing system*

Another application of wave theory of matter or radiation is the use of lasers. They find extensive use in surgery, in drilling holes in precious metals, welding, etc. A laser is an emission that may involve electronic transitions in atoms or molecules. The first laser developed was the ruby laser. Ruby is a deep red mineral consisting of Al_2O_3 in which some Al^{3+} ions have been replaced by Cr^{3+} ions. A cylinder of ruby crystal is placed between two parallel mirrors, one of which is partially reflective. A light source is used to excite the Cr atoms to higher level. Some of the excited Cr atoms return to the ground state and photons in the red region are emitted. Photons are emitted in all directions but those emitted directly at the mirrors will be reflected back. The reflected photons on passing through the ruby crystal stimulate the emission of more photons in the

same direction. This process of reflection and emission continues increasing their power with each emission. When the light gains certain intensity, it emerges from the partially reflective mirror as a laser beam. Laser systems can be used to produce stunning displays of spatial and beam effects and animated graphic sequences.



Fig. 19.13 *Use of lasers in dentistry*



Fig. 19.14 *Lasers in entertainment*

19.8 HEAT CAPACITY OF SOLIDS

Normally, it is expected that the heat capacity of all monoatomic solids (metals) should be constant and equal to $3R$ **(*Dulong and Petit's law*)**. However, experimentally, it is true only at high temperature. At low temperature, the value is found to be less than $3R$ and the values approach zero as T tends to zero degree.

The variation of molar heat capacity of few elements with temperature is shown in Fig. 19.15. Einstein (in 1905) explained the variation of heat capacity with temperature again by using Planck's theory of quantisation.

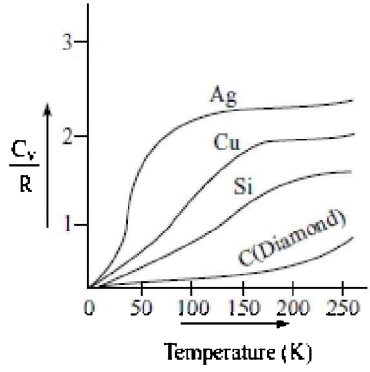


Fig. 19.15 *Variation of molar heat capacity with temperature for Ag, Cu, Si and diamond*

Explanation A monoatomic solid can be considered as a collection of oscillators each having three vibrational degree of freedom. According to the law of equipartition of energy, each atom (oscillator) in the solid has a mean vibrational energy = 3 kT. Therefore, one mole of monoatomic solid (having Avogadro's number of atoms, N_A), will have total vibrational energy, i.e. molar internal energy, equal to

$$E = N_A(3\,kT) = 3RT \quad (N_A k = R, \text{ the gas constant})$$

or
$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3R \qquad (19.16)$$

Using the concepts of Planck's quantum theory, Einstein explained that all the oscillators do not vibrate with the same frequency v, i.e., they do not have the same vibrational energy (hv) but may have energies which are integral multiples of some minimum value, hv_0 (= nhv_0). The mean energy of the oscillator is then given by

$$\bar{E} = \frac{hv_0}{e^{hv_0/kT} - 1} \qquad \ldots(19.17)$$

Molar energy of the solid will be

$$E = N_A \times 3\ \bar{E} = \frac{3N_A hv_0}{e^{hv_0/kT} - 1} \quad \text{(in place of classical value of } 3RT\text{)}$$

$\therefore$
$$C_V = \left(\frac{\partial U}{\partial T}\right)_v = 3N_A k \left(\frac{hv_0}{kT}\right)^2 \frac{e^{hv_0/kT}}{(e^{hv_0/kT} - 1)^2} \qquad \ldots(19.18)$$

Stepwise Detailed Solution of Eq. (19.18) (Optional for Medical Students)

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3N_A h\nu_0 \frac{\partial}{\partial T}(e^{h\nu_0/kT} - 1)^{-1} = 3N_A h\nu_0(-1)(e^{h\nu_0/kT} - 1)^{-2} \frac{\partial}{\partial T}(e^{h\nu_0/kT} - 1)$$

$$= 3N_A h\nu_0(-1)(e^{h\nu_0/kT} - 1)^{-2} e^{h\nu_0/kT} \frac{\partial}{\partial T}\left(\frac{h\nu_0}{kT}\right)$$

$$= 3N_A h\nu_0(-1) \times \frac{e^{h\nu_0/kT}}{(e^{h\nu_0/kT} - 1)^2} \times \frac{h\nu_0}{k} \frac{\partial}{\partial T}(T^{-1})$$

$$= 3N_A h\nu_0(-1) \times \frac{e^{h\nu_0/kT}}{(e^{h\nu_0/kT} - 1)^2} \times \frac{h\nu_0}{k}(-1)T^{-2}$$

$$= 3N_A h\nu_0 \frac{h\nu_0}{kT^2} \times \frac{e^{h\nu_0/kT}}{(e^{h\nu_0/kT} - 1)^2}$$

$$= 3N_A k \left(\frac{h\nu_0}{kT}\right)^2 \frac{e^{h\nu_0/kT}}{(e^{h\nu_0/kT} - 1)^2}$$

At low temperature, $h\nu_0/kT >> 1$ and hence, $e^{h\nu_0/kT} >> 1$.

The Equation (19.18) then reduces to

$$C_v = 3N_A k \left(\frac{h\nu_0}{kT}\right)^2 e^{-h\nu_0/kT} \quad \ldots(19.19)$$

On decreasing the temperature, the exponential factor decreases much more rapidly than the corresponding increase in the factor $(h\nu_0/kT)^2$. Hence, C_v decreases with decrease in temperature.

At ***high temperature,*** it can be seen from Eq. (19.18) that the value of C_v reduces to the classical value of $3R$. This is because at high temperature, $h\nu_0/kT << 1$. Applying expansion series $e^x = 1 + x + x^2 +$ Eq. (19.18) becomes,

$$C_v = 3N_A k \left(\frac{h\nu_0}{kT}\right)^2 \frac{1 + (h\nu_0 + kT) + \ldots}{\left\{1 + (h\nu_0/kT) + \frac{1}{2}(h\nu_0/kT)^2 + \ldots - 1\right\}^2}$$

$$= 3N_A k \left(\frac{h\nu_0}{kT}\right)^2 \frac{1 + (h\nu_0/kT) + \ldots}{\left\{(h\nu_0/kT) + \frac{1}{2}(h\nu_0/kT)^2 + \ldots\right\}^2}$$

$$= 3N_A k \frac{(h\nu_0/kT)^2 + (h\nu_0/kT)^3 + \ldots}{\left\{(h\nu_0/kT) + \frac{1}{2}(h\nu_0/kT)^2 + \ldots\right\}^2}$$

At high temperatures, $h\nu_0/kT$ is very small and hence, the terms with powers 2 and above can be neglected. Thus, the above equation reduces to the form

$$C_v = 3N_A k = 3R \text{ (classical value)}$$

19.9 QUANTUM MECHANICS

The ***wave mechanics*** put forward by Schrodinger in 1926 is based upon de Broglie concepts of dual character of matter and thus takes into account the particle as well as wave nature of the material particles. It is also called ***Particle mechanics*** or ***quantum mechanics*** because it deals with the problem that arises when particles such as electrons, nuclei, atoms, molecules, etc., are subjected to a force.

The branch of science which takes into consideration de Broglie concept of dual nature of matter and Planck's quantum theory and is able to explain the phenomena related to small particles is known as quantum mechanics.

The heart of quantum mechanics is an equation called ***Schrodinger wave equation.*** It can be derived directly or on the basis of certain postulates of quantum mechanics. We shall study certain results that follow from the Schrodinger wave equation and some applications of the Schrodinger wave equation.

Table 19.1 *Comparison of classical mechanics with quantum mechanics*

Classical Mechanics	Quantum Mechanics
(i) It deals with macroscopic (big) particles.	It deals with microscopic (small) particles.
(ii) It is based upon Newton's laws of motion.	It takes into account Heisenberg's uncertainty principle and de Broglie concept of dual nature of matter.
(iii) It is based on Maxwell's electromagnetic wave theory according to which any amount of energy may be emitted or absorbed continuously.	It is based on Planck's quantum theory according to which only discrete values of energy are emitted or absorbed.
(iv) The state of the system is defined by specifying all the forces acting on the particles as well as their positions and velocities (momenta).	It gives probabilities of finding particles at various locations in space.

19.10 BOHR'S MODEL OF ATOM

Neils Bohr, a Danish physicist, in 1913, proposed a model of the atom based upon Planck's quantum theory. This new model is called Bohr's model of the atom.

The main postulates of Bohr's model of the atom are as follows:

1. An atom consists of a small, heavy positively charged nucleus in the centre and the electrons revolving around in circular orbits.
2. Out of a large number of circular orbits theoretically possible around the nucleus, the electrons revolve only in those orbits which have a ***fixed*** value of ***energy***. Hence, these orbits are called ***energy levels*** or ***stationary states***. The word ***stationary*** means that the energy of the electron revolving in a particular orbit is fixed and does not change with time. The different energy levels are numbered as 1, 2, 3, 4, ... etc., or designated as *K, L, M, N, O, P*, ... etc., starting from the nucleus side (Fig. 19.16).

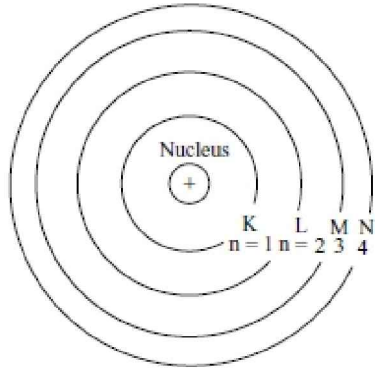


Fig. 19.16 *Circular orbits (energy levels/ stationary states) around the nucleus*

The energies of the different stationary states in case of the hydrogen atom are given by the expression.

$$E_n = -\frac{2\pi^2 me^4}{n^2 h^2}$$

Substituting the values of m (mass of the electron), c (charge on the electron) and h (Planck's constant), we obtain the equation for energy associated with the nth orbit.

$$E_n = \frac{-21.8 \times 10^{-19}}{n^2} \text{ J/atom}$$

$$= \frac{-1312}{n^2} \text{ kJ mol}^{-1}$$

$$= \frac{13.6}{n^2} \text{ eV/atom} \qquad (\because 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$$

where, n = 1, 2, 3, … etc., stand for 1st, 2nd, 3rd, … etc., levels respectively. We find that the first energy level (n = 1) which is closest to the nucleus has lowest energy. The energy of the level increases as we move outwards starting from the first level (K level). For H-like particles, e.g. He^+, Li^{2+}, etc. (containing one electron only),

$$E_n = \frac{-2\pi^2 mZ^2 e^4}{n^2 h^2} = -\frac{1312 Z^2}{n^2} \text{ kJ mol}^{-1}$$

where Z is the atomic number of the element (for $He,^+$, Z = 2, for Li^{2+}, Z = 3)

3. As the electrons revolve only in those orbits which have fixed values of energy, electrons in an atom can have only certain definite or discrete values of energy and not just any value. This is expressed by saying that the energy of an electron is ***quantised.***

(iv) Also, the angular momentum of an electron in an atom can have certain definite or discrete values and not just any value. The permissible values of angular momentum are given by the expression

$$mvr = \frac{nh}{2\pi}$$

This is expressed by saying that angular momentum of the electron is an integral multiple of $h/2\pi$ Here, n is the mass of the electron, υ is the tangential velocity of the revolving electron, r is the

radius of the orbit, h is Planck's constant and n is any integer. Thus, the angular momentum of the electron can be out of $h/2\pi$, $2h/2\pi$, $3h/3\pi$, ... etc. This means that like energy, ***the angular momentum of an electron in an atom is also quantised.***

5. In their lowest (normal) energy state, electrons keep on revolving in their respective orbits without losing energy because energy can neither be lost nor gained continuously. This state of atom is called ***normal or ground state***.
6. Energy is emitted or absorbed only when the electrons jump from one orbit to the other. When energy supplied to an atom in a reaction, etc., an electron in the atom may jump from its normal energy level (ground state) to some higher energy level by absorbing a definite amount of energy. This state of atom is called ***excited state***. Since the lifetime of the electron in the excited state is short, it starts jumping back to the lower energy level by emitting energy in the form of light of suitable frequency or wavelength. The amount of energy emitted or absorbed is given by the difference of energies (ΔE) of the two energy levels concerned, i.e.,

$$\Delta E = E_2 - E_1$$

where E_2 and E_1 are energies of the electron in the higher and lower energy levels respectively.

We can state that for a change of the electronic energy, the electron has to jump and not to flow from one energy to the other.

Shortcomings of Bohr's Model of the Atom

Bohr's model of the atom suffers from the following limitations:

1. ***Inability to explain line spectra of multi-electron atoms***. Bohr's theory could explain the line spectra of hydrogen atom and hydrogen-like particles containing a single electron only. However, it failed to explain the line spectra of multi-electron atoms.
2. ***Inability to explain splitting of lines in the magnetic field (Zeeman effect) and in the electric field (Stark effect)***. If the source emitting the radiation is placed in a magnetic field or in an electric field, it is observed that each spectral line splits up into a number of lines. The splitting of a spectral line in the magnetic field is called ***Zeeman effect,*** while splitting of spectral lines in an electric field is called ***Stark effect***. Bohr's model of the atom could not explain splitting.
3. ***Inability to explain the three dimensional model of atom***. According to Bohr's model of the atom, the electrons move along certain circular paths in one plane. Thus, it ***envisages a flat model of the atom***. But now it is well established that the atom is three dimensional and not flat as suggested by Bohr.
5. ***Inability to explain the shapes of molecules***. We know that in covalent molecules, the bonds have directional characteristics (i.e. atoms are linked to each other in particular directions) and hence, they possess definite shapes. Bohr's model is not able to explain it.

19.11 | DE BROGLIE HYPOTHESIS (DUAL NATURE OF MATTER AND RADIATIONS)

Earlier, it was thought that light is a stream of particles which are photons (or called corpuscles). However, this concept failed to explain the phenomena of interference and diffraction which could be explained only if light is considered to have wave nature. But at the same time, it was observed that the phenomena of black-body radiation and photoelectric effect could be explained only if light is considered to have particle character. Therefore, it was concluded that light has a particle nature as well as wave nature, i.e. it has a dual nature.

Louis de Broglie, a French physicist, in 1924, advanced ***the idea that like photons, all materialparticles such as electrons, protons, atoms, molecules, a piece of chalk, a piece of stone or an iron ball (i.e. microscopic as well as macroscopic objects) also possessed dual character. The wave associated with the particle is called a matter wave or de Broglie wave***

1. The de Broglie Relation The wavelength of a wave associated with any material particle was calculated by analogy with a photon as follows:

In case of photons, if it is assumed to have wave character, its energy is given by

$$E = h\nu \qquad \ldots(19.20)$$

(according to ***Planck's quantum theory)***

where ν is frequency of the wave and h is Planck's constant.

If a photon is supposed to have a particle character, its energy is given by

$$E = mc^2 \qquad \ldots(19.21)$$

(according to ***Einstein equation)***

where m is the mass of photon and c is the velocity of light.

From equations (19.20) and (19.21), we get

$$h\nu = mc^2$$

But $\quad \nu = c/\lambda$

$\therefore \quad h \cdot c/\lambda = mc^2 \qquad \ldots(19.22)$

or $\quad \lambda = h/mc$

de Broglie pointed out that the above equation is applicable to any material particle, big or small. The mass of the photon is replaced by the mass of a material particle and the velocity c of the photon is replaced by the velocity υ of the moving particle. Thus, for any material particle like an electron, we may write,

$$\lambda = h/m\upsilon$$

or $\quad \lambda = h/p \qquad \ldots(19.23)$

where p is the momentum of the particle. The above equation is called de Broglie equation.

2. Significance of de Broglie Equation Although the de Broglie equation is applicable to all material objects, it has significance only in case of microscopic particles. This is because the wavelength produced by a bigger particle (say a ball) using Eq. (19.23) comes out to be too small to be observed. Only particles like electrons, atoms, etc, give an observable value of λ according to Eq. (19.23).

19.12 | HEISENBERG'S UNCERTAINTY PRINCIPLE

Werner Heisenberg, a German physicist, in 1927, gave a principle about the uncertainties in simultaneous measurements of position and momentum of small particles. It is known as Heisenberg's uncertainty principle and it is stated as follows:

It is impossible to measure simultaneously the position and momentum of a small particle with absolute accuracy or certainty. If an attempt is made to measure any one of these two quantities with greater accuracy, the other becomes less accurate. The product of the uncertainty in the position (Δx) and the uncertainty in momentum ($\Delta p = m \cdot \Delta \upsilon$) where m is the mass of the particle and $\Delta \upsilon$ is the uncertainty in the velocity) is always constant and is equal to $h/4\pi$, where h is Planck's constant, i.e.

$$\Delta x \cdot \Delta p = \frac{h}{4\pi} \qquad (19.24)$$

Putting $\Delta p = m \times \Delta \upsilon$, Eq. (19.24) becomes

$$\Delta x \cdot (m\Delta \upsilon) = \frac{h}{4\pi} \qquad \ldots(19.25)$$

$$\Delta x \cdot \Delta \upsilon = \frac{h}{4\pi m} \qquad \ldots(19.26)$$

This implies that the ***position and velocity of a particle cannot be measured simultaneously with certainty.***

1. Explanation of Heisenbergs Uncertainty Principle Suppose we try to measure both the position and momentum of the electron. To locate the position of the electron, we have to use light, so

the photon of light strikes the electron and the reflected photon is seen in the microscope (Fig. 19.17). As a result, of the hitting by the photon, the position as well as the velocity of the electron is altered.

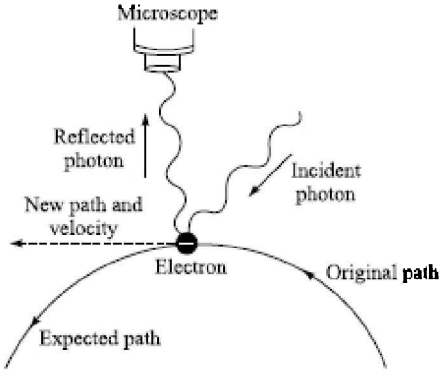


Fig. 19.17 *Change of momentum and position of electron on impact with a photon*

2. Significance of Heisenbergs Uncertainty Principle Although Heisenberg's uncertainty principle holds good for all objects but ***it is of significance only for microscopic particles***. Obviously, the energy of the photon is insufficient to change the position and velocity of bigger bodies when it collides with them. For example, the light from a torch falling on a running ball in a dark room neither changes the speed of the ball nor its direction, i.e. position. This may be further illustrated by comparing $\Delta x \cdot \Delta v$ values for a particle of 1 g mass and a microscopic particle.

For a particle of 1 g mass, we have

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times 3.416 \times (10^{-3}\ \text{kg})} \simeq 10^{-25}\ \text{m}^2 s^{-1}$$

Thus, the product of Δx and Δv is extremely small. Hence, these values are negligible.

For a microscopic particle like an electron, we have

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times 3.1416 \times (9.11 \times 10^{-31}\ \text{kg})} \simeq 10^{-4}\ \text{m}^2 s^{-1}$$

Thus, it uncertainty in position is 10^{-8} m, uncertainty in velocity will be = 10^4 ms^{-1} which is quite significant.

19.13 THE COMPTON EFFECT

AH Compton in 1923 performed experiments to establish the particle nature of the radiation. He found that if ***monochromatic X-rays (i.e. X-rays consisting of a single wavelength) are allowed to hit a material of low atomic weight, e.g. graphite, the scattered radiations contained not only wavelengths of that of the incident X-rays but also contained radiations of higher wavelength (or lower frequency or hence, lower energy)***. This effect is called ***Compton effect***.

As the scattering is produced by electrons, it was thought that it must be due to collision between the *X*-rays, photons and the individual electron of the target that must have resulted in the increase of the wavelength of the scattered *X*-rays.

Suppose λ is the wavelength of the *X*-rays or $h\nu$ is the energy of the incident *X*-ray photon. By de Broglie relation, its momentum will be h/λ or $h\nu/c$ where c is the velocity of light. Suppose λ' is the wavelength of the scattered *X*-ray or $h\nu'$ is the energy of the scattered *X*-ray photon then its momentum

will be h/λ' or $h\nu'/c$.

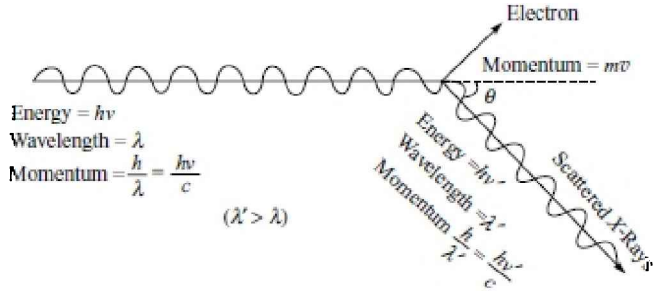


Fig. 19.18 *Compton effect*

If mv is the momentum of the electron after collision (m is the rest mass of the electron and v is its velocity) then by applying the laws of conservation of energy and momentum, we can say that the increase in wavelength ($\Delta\lambda = \lambda' - \lambda$) is given by

$$\Delta\lambda = \lambda' - \lambda = \frac{2h}{mc}\sin^2\frac{\theta}{2} \qquad \ldots(19.27)$$

where θ is the angle between the incident and the scattered X-rays (Fig. 19.18). $\Delta\lambda$ is called ***Compton shift***.

Equation (19.27), indicates that the Compton shift of wavelength is independent of the wavelength of the incident X-rays. This has been confirmed by comparing the experimental value of $\Delta\lambda$ with the theoretically calculated value by substituting the values of m, c, h, and θ in the term on the right-hand side of Eq. (19.27). The two values are found to be in reasonable agreement.



Fig. 19.19 *A H Compton (1892-1962) was an American physicist at the University of Chicago, USA. He received the Nobel Prize in 1927 for his discovery of Compton effect.*

Compton effect also supports the uncertainty principle. If X-rays are used to determine the position and momentum of the electron, after the collision, the wavelength of scattered X-ray photons is found to be more. That is, the scattered X-ray photon has lower energy. Thus, some energy of the X-ray photon might have been transferred to the electron whose energy will, therefore, change and so the momentum will also change. Consequently, the momentum of the electron cannot be determined with certainty, which is the uncertainty principle.

The Compton shift does not depend upon the nature of the material used as target. It depends only

on the angle θ (refer Eq. (19.27)). To interpret results for different values of θ, we write Eq. (19.27) in the form,

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta) \qquad \ldots(19.28)$$

$[\because \quad 2\sin^2 x = 1 - \cos 2x]$

1. When $\theta = 0$, so that $\cos\theta = 1$, $\Delta\lambda = 0$, i.e. no change in Compton shift takes place.
2. When $\theta = 90°$, so that $\cos\theta = 0$, $\Delta\lambda = \frac{h}{mc} = 2.42$ pm (on substituting the values of h, m and c)
3. When $\theta = 180°$, so that $\cos\theta = -1$, $\Delta\lambda = \frac{2h}{mc} = 4.84$ pm, i.e. double the value when $\theta = 90°$.

19.14 SINUSOIDAL WAVE EQUATION

Consider the motion of a wave (say ocean wave) in a particular direction, say x-axis. At any time t, the upward displacement of the wave, represented by y, is the function of position x and time t, i.e. $y = f(x, t)$.

Waves of many shapes occur in nature. One of the simplest and most common is the ***sine wave***. The electric and magnetic fields associated with electromagnetic waves are sine waves. The Schrondinger wave equation is closely connected to sine waves.

A sine wave travelling in the x-direction with velocity v, wavelength λ, frequency ν and amplitude A is described mathematically by a sine function as follows:

$$y = A\sin\left[\frac{2\pi}{\lambda}(x - vt)\right] = A\sin\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right] \quad \{\because v = \nu\lambda\}$$

Here, y is the ***wave function***. The equation tells about the displacement y at any point x and at any time t.

Any equation having the characteristics of the sine function is called a *sinusoidal wave function.*

Stationary or Standing Waves A stationary or standing wave can be explained by taking the example of a string stretched between two fixed points. Suppose a string is stretched between two fixed points and a wave is allowed to travel along the string in one direction. When the wave reaches the other end, it is diverted in the opposite direction with the same wavelength, speed and amplitude. In this process, the string is divided into a number of vibrating segments. Such a vibrating motion is called stationary or standing wave as shown in Fig. 19.20.

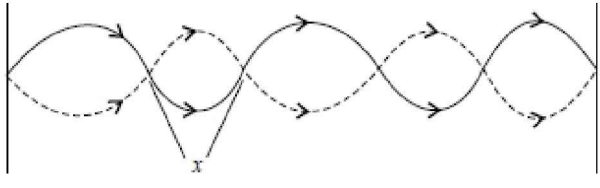


Fig. 19.20 *Stationary waves in a string*

Points x which represent zero amplitude are called **nodes**.

19.15 SCHRODINGER WAVE EQUATION

Consider the simplest type of wave motion like that of the vibration of a stretched string travelling

along the *x*-axis with velocity ∪ (Fig. 19.21). If ω is the amplitude of the wave at any point whose coordinate is *x*, at any time *t* then the equation for such a wave motion is

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \omega}{\partial t^2} \qquad \ldots(19.29)$$

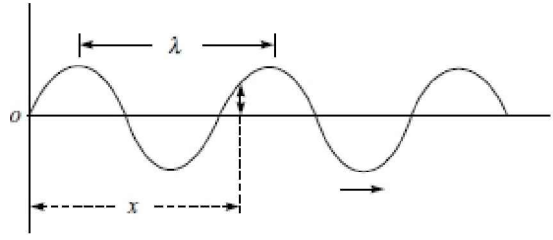


Fig. 19.21 *Vibration in a stretched string.*

The differential equation indicates that the amplitude ω of the wave at any time travelling with a particular velocity depends upon the displacement *x* and the time *t*. In other words, ω is the function of *x* and *t*.

Hence, we may write

$$\omega = f(x) f''(t) \qquad \ldots(19.30)$$

where $f(x)$ is a function of the coordinate *x* only and $f'(t)$ is a function of the time *t* only.

But for the stationary waves, we have

$$F'(t) = A \sin 2\pi vt \qquad \ldots(19.31)$$

where, *v* is the frequency of vibration and *A* is a constant, equal to the maximum amplitude of the wave.

Substituting the value of $f'(t)$ from Eq. (19.31), in Eq. (19.30), we get,

$$\omega = f(x) A \sin 2\pi vt \qquad \ldots(19.32)$$

Differentiating this equation twice w.r.t. *t*, we get

$$\frac{\partial^2 \omega}{\partial t^2} = -f(x) 4\pi^2 v^2 (A \sin 2\pi vt)$$

$$= -4\pi^2 v^2 f(x) f''(t) \qquad \ldots(19.33)$$

Differentiating Eq. (19.30) twice w.r.t. *x*, we get,

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2} f'(t) \qquad \ldots(19.34)$$



Fig. 19.22 *Erwin Schrodinger was an Austrian physicist who developed a number of results which formed the basis of wave mechanics*

Substituting the values of $\partial^2\omega/\partial t^2$ and $\partial^2 w/\partial x^2$ from Eq. (19.33) and (19.34) into Eq. (19.29), we get

or

$$\frac{\partial^2 f(x)}{\partial x^2} f''(t) = \frac{-1}{v^2} 4\pi^2 \nu^2 f(x) f''(t)$$

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{4\pi^2 \nu^2}{v^2} f(x) \qquad \ldots(19.35)$$

This equation has become ***time-independent*** and hence represents the variation of the amplitude function $f(x)$ with x only.

The velocity υ is related to the frequency ν and the wavelength λ of the wave by the expansion,

$$v = \nu\lambda \qquad \ldots(19.36)$$

Substituting this value in Eq. (19.36), we obtain the result,

$$\frac{\partial^2 f(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} f(x) \qquad \ldots(19.37)$$

This equation has been derived for the motion in one direction only. For extending this equation to the wave motion in three dimensions, the amplitude function $f(x)$ for one coordinate may be replaced by $\psi(x, y, z)$ or simply written as ψ for the sake of brevity which represents the ***amplitude function*** for three coordinates. Thus, the equation for wave motion in three dimensions becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi \qquad \ldots(19.38)$$

This equation is applicable to all particles like electrons, nuclei, atoms, molecules, photons, etc. Further, applying the de Broglie equation, according to which $\lambda = h/m\upsilon$ where m is the mass of the particle, υ is the velocity and h is the Planck's constant. Eq. (19.38) becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{-4\pi^2 m^2 v^2}{h^2} \psi \qquad \ldots(19.39)$$

Also,

Total energy *(E)* of the particle = Kinetic energy + Potential energy

i.e. $$E = \frac{1}{2}mv^2 + V \qquad \ldots(19.40)$$

where V represents the potential energy of the particle.

Substituting the value of mv^2 from Eq. (19.40) in Eq. (19.39), we have,

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m(E-V)}{h^2}\psi = 0 \qquad \ldots(19.41)$$

This equation which represents the wave motion of the particle in three dimensions is called ***Schrodinger wave equation***.

Eigen Values and Eigen Functions (Wave Functions)

For a stationary (or standing) wave in a stretched string, the amplitude function $f(x)$ can have significance only for certain definite values of λ. These functions will be those which must satisfy the following conditions:

1. $f(x)$ must be equal to zero at each end of the string as the string is fixed at these points and the amplitude of the vibration is zero.
2. $f(x)$ must be single valued and finite, i.e. at every point on the vibrating string, the amplitude has a definite value at any given instant.

Similarly, the Schrodinger wave equation, being a second-order differential equation can have a number of solutions for the amplitude function ψ but only those values of ψ are acceptable and have significance which correspond to some definite values of the total energy E. Such values of the total energy E are called ***eigen values***. These values are also called ***proper values*** or ***characteristic values***. The corresponding values of the function ψ are called ***eigen functions*** or ***wave functions***. In the case of a stretched string, the eigen functions of the Schrodinger equation will be those which must satisfy the following conditions.

1. ψ must be single valued and finite, i.e. for each value of the variable x, y, z, there is only one definite value of the function ψ.
2. ψ must be continuous, i.e. there must not exist any sudden changes in ψ as its variables are changed.
3. ψ must become zero at infinity.

We define a class of functions as all those functions which obey certain specified conditions. It may happen that in a given class, ***there are functions which when operated on by an operator, α are merely multiplied by some constant, or in symbols,***

$$\alpha f(x) = af(x) \qquad \ldots(i)$$

Those members of the class which obey such a relation are known as characteristic or eigen functions of the operator α. The various possible values of α are called the characteristic values or eigen values of the operator.

For example, when function $\psi = \sin kx$ on which the operator

$$\delta = \frac{d}{dx} \text{ operates, we get}$$

$$\frac{d\psi}{dx} = \frac{d}{dx}(\sin kx) = k\cos kx$$

Since $\cos kx \neq \psi$, $\frac{d}{dx}$ is not an eigen operator for the function $\psi = \sin kx$. Now, let us consider $\frac{d^2}{dx^2}$ as the operator for the same functions $\psi = \sin kx$. Then upon operating, we get

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left[\frac{d}{dx}\sin kx\right]$$

$$= \frac{d}{dx}[k\cos kx]$$

$$= -k^2 \sin kx = -k^2\psi$$

Here, $\frac{d^2}{dx^2}$ is an eigen operator for $\psi = \sin kx$. Thus for $\psi = \sin kx$ is an eigen function for operator $\frac{d^2}{dx^2}$ having eigen value $-k^2$.

Let us take another example when function $\psi = e^{imx}$; operators are $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$.

Then $$\frac{d}{dx}(\psi) = ime^{imx} = im\psi$$

Here, $\frac{d}{dx}$ is an eigen operator, im is the eigen value for the eigen function $\psi = e^{imx}$

Also, $$\frac{d^2\psi}{dx^2} = imime^{imx} = -m^2\psi.$$

Here, $\frac{d^2}{dx^2}$ is an eigen operator with eigen value $-m^2$ for the given function $\psi = e^{imx}$.

As is clear, different eigen operators have different eigen values for the same function.

19.16 BORN'S INTERPRETATION AND SIGNIFICANCE OF WAVE FUNCTION (Ψ)

For a particle like an electron, the wave function ψ represents the amplitude of the electron wave at any instant of time when the coordinates of the electron are x, y, z. However, it was suggested by Max Born that just as in the case of light or sound, the square of the amplitude of the wave at any point gives the intensity of light or sound at that point, the square of the amplitude of the electron wave, i.e. ψ^2 at any point gives the intensity of the electron wave at that point. However, keeping in view the Heisenberg's uncertainty principle, the intensity of the electron at any point may be interpreted as the probability of finding the particle electron at that point (Fig. 19.23). ***Thus, ψ^2 at any point gives the probability of finding the electron at that point***. That is why the wave function ψ^2 is also called ***probability amplitude***. But the probability is directly related to the density (concentration) of the electron cloud. Thus, ψ^2 gives the electron density at any given point. Since the region around the nucleus which represents the electron density at different points is called an orbital, the wave function for an electron in an atom is called ***orbital wave function*** or simply atomic orbital.

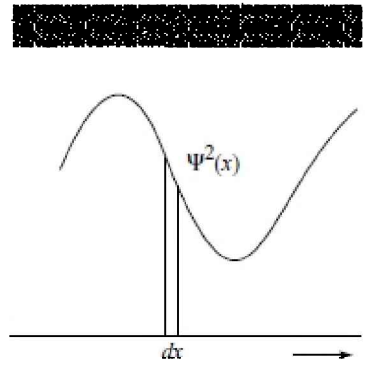


Fig. 19.23 *Born interpretation of wave function in one dimensional system. Probability of finding the particle at points along x-axis. $\psi^2(x)$ is represented by the density of shading in the upper half of the diagram.*



Fig. 19.24 *Max Born was a German-British physicist and mathematician who was instrumental in the development of wave mechanics*

Further, it may be noted that ψ may not always come out to be real. In some cases, it may come out to be imaginary, i.e. it may include the imaginary quantity $i(=\sqrt{-1})$. Then ψ^2 may be real or imaginary depending upon the nature of the expression for ψ. However, since the probability of finding a material particle at any point in space must always be real, the value taken is $\psi\psi^*$ in place of ψ^2, where ψ^* is called ***complex conjugate*** of ψ and is obtained by replacing i by $-i$. This product (i.e. $\psi\psi^*$) is always real irrespective of whether ψ is real or imaginary. For example, suppose $\psi = a + ib$. Then the complex conjugate will be $\psi^* = a - ib$. The product $\psi\psi^* = (a + ib)\,(a - ib) = a^2 + b^2$ which is real. The product $\psi\psi^*$ is usually represented by $|\psi|^2$ where, $|\psi|$ represents ***modulus or absolute*** value of ψ.$|\psi|^2$ is called the square modulus of ψ. If ψ is real then $\psi = \psi^*$ and the product will automatically be equal to ψ^2.

The Born interpretation of a wave function may be summed up as follows:

1. ***For a one-dimensional system,*** if the amplitude of the wave function of a particle is ψ at some point x then the probability of finding the particle between x and $x + d_x$ is proportional to $\psi(x)\psi^*(x)\,d_x$ or

in short, it is written as $\psi\psi^* dx$. Fig. 19.25

2. ***For a particle free to move in three dimensions*** (i.e. an electron near the nucleus of an atom), if ψ is the amplitude of the wave function at some point at a distance r then the probability of finding the particle in a small volume element $dx\ dy\ dz$ at that point whose coordinates are x, y, z, is proportional to $\psi(x, y, z,)\ \psi^*(x, y, z)\ dx, dy, dz$ or in short, it is written as $\psi\psi^*\ d\tau$ where $d\tau = dx, dy, dz$ represents the small volume element of the space at some distance r (Fig. 19.25). For this reason, the product $\psi\psi^*$ is called ***probability distribution function***.

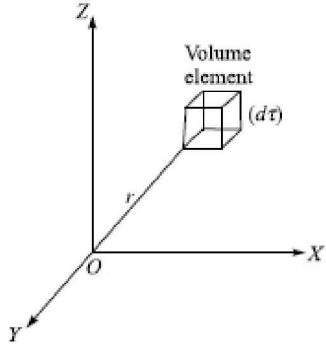


Fig. 19.25 *Born interpretation of the wave function in three-dimensional space*

19.17 NORMALISED AND ORTHOGONAL WAVE FUNCTIONS

$\psi\psi^*\partial\tau$ is proportional to the probability of finding the particular system in the small volume element $\partial\tau$. For most of the purposes it is taken as equal to rather than proportional to the probability. In such a case, the integration of $\psi\psi^*\partial\tau$ over the whole of the configuration space, which gives the total probability, must be equal to unity, i.e.

$$\oint \psi\psi^* d\tau = 1 \qquad \ldots(19.42)$$

where $\oint$ represents the integration over the whole space. In place of $\oint$, we can also use the symbol $\int_{-\infty}^{+\infty}$.

A wave function which satisfies the above equation is said to be normalised.

In some cases, the result of integration is found to be equal to some constant, say N. Then we have

$$\oint \psi\psi^* d\tau = N \qquad \ldots(19.43)$$

To make the result equal to unity, we have

$$\frac{1}{N} \oint \psi\psi^* d\tau = 1 \qquad \ldots(19.44)$$

or

$$\oint \left(\frac{1}{N^{1/2}}\psi\right)\left(\frac{1}{N^{1/2}}\psi^*\right) d\tau = 1 \qquad \ldots(19.45)$$

The factor $1/N^{1/2}$ is called ***normalisation constant*** and the function $\left(\frac{1}{N^{1/2}}\psi\right)$ is called the ***normalised function.***

If ψ_i and ψ_j are two different eigen functions obtained as satisfactory solutions of the wave

equation then these functions will be normalised if

$$\oint \psi_i \psi_j^* d\tau = 1 \quad \text{and} \quad \oint \psi_j \psi_j^* d\tau = 1 \qquad \ldots(19.46)$$

Further, if they satisfy the following conditions

$$\oint \psi_i \psi_j^* d\tau = 0 \quad \text{and} \quad \oint \psi_i^* \psi_j d\tau = 0 \qquad \ldots(19.47)$$

they are said to be mutually ***orthogonal***.

Wave functions that are both orthogonal and normalised are called ***orthonormal.***

19.18 OPERATORS

An operator is a mathematical instruction or procedure to be carried out on a function so as to get another function.

The result of an 'operator' on a function gives another function.

(Operator) · (Function) = (Another function)

The function on which the operation is carried out is called an ***operand***. The above equation does not mean that the function is multiplied with the operator. An operator written alone has no significance.

A few examples are given below:

1. $\frac{d}{dx}(x^4) = 4x^3$. Hence, $\frac{d}{dx}$ which stands for differentiation w.r.t. x is the operator, x^4 is the operand and $4x^3$ is the result of operation.

2. $\int x^3 dx = x^4/4 + C$. Here, $\int dx$ which stands for integration w.r.t. x is the operator, x^3 is the operand and $x^4/4 + C$ is the result of operation.

Similarly, taking the ***square root, cube root or multiplication by a constant k,*** etc., are different operations which can be carried on any function.

In case the symbol used for operation is not self-explanatory, a suitable letter or some symbol for the operator is used with the symbol (^) over it, i.e. a carat is put over the symbol.

Algebra of Operators

The operators follow certain rules similar to those of algebra, as given below:

1. Addition and Subtraction of Operators If $\hat{A}$ and $\hat{B}$ are two different operators, and F is the operand then

$$(\hat{A} + \hat{B})f = \hat{A}f + \hat{B}f \qquad \ldots(19.48a)$$

$$(\hat{A} - \hat{B})f = \hat{A}f - \hat{B}f \qquad \ldots(19.48b)$$

2. Multiplication of Operators If $\hat{A}$ and $\hat{B}$ are two different operators and f is the operand, the expression $\hat{A}\hat{B}f$ implies that f is operated first by the operator $\hat{B}$ to get the result, say f', and then f' is operated by the operator $\hat{A}$ to get the final result, say f'', i.e., $\hat{A}\hat{B}f$ implies that $\hat{B}f = f$ and then $\hat{A}f = f''$ so that we have

$$\hat{A}\hat{B}f = f'' \qquad \ldots(19.49)$$

Thus, the order of using the operators is from right to left as written in the given expression.

If the same operation is to be done a number of times in continuation, it is shown by a power of the operator. For example, $\hat{A}\hat{A}f$ is written as $\hat{A}f$

or

$$\hat{A}\hat{A}f = \hat{A}^2 f \qquad \ldots(19.50)$$

It may be noted that usually

$$\hat{A}\hat{B}f \neq \hat{B}\hat{A}f \qquad \ldots(19.51)$$

Suppose $\hat{A} = x$, $\hat{B} = \dfrac{d}{dx}$ and $f(x) = x^2$,

Then $$\hat{A}\hat{B}f = x\frac{d}{dx}(x^2) = x(2x) = 2x^2$$

$$\hat{B}\hat{A}f = \frac{d}{dx}x(x^2) = \frac{d}{dx}x^3 = 3x^2$$

In case, $$\hat{A}\hat{B}f = \hat{B}\hat{A}f \qquad \ldots(19.52)$$

i.e., if the change of order of the operators gives the same result, the operators are said to be ***commute***.

The ***commutator*** of the operators $\hat{A}$ and B represented as $[\hat{A}, B]$ is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

As stated above, if $\hat{A}B = B\hat{A}$, the operators are said to commute and hence, $[\hat{A}, B] = 0$

3. Linear Operators An operator $\hat{A}$ is said to be linear if for the two functions f and g,

$$\hat{A}(f+g) = \hat{A}f + \hat{A}g \qquad \ldots(19.53)$$

i.e. the operator on the sum of the two functions gives the same result as the sum of two results obtained by carrying out the same operation on the two functions separately. For example, d/dx, d^2/dx^2, etc., are linear operators. Taking the square or taking the square root, etc., are nonlinear, because we may not get the same result with the operator on the sum of the two functions and the sum of the operations on two functions separately.

(a) Laplacian Operator This is a very common operator used in quantum mechanics. It is represented by ∇^2 (pronounced as 'del' squared) and is defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \ldots(19.54)$$

The Schrodinger wave equation, viz.

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m(E-V)}{h^2}\psi = 0$$

may be written in terms of Laplacian operator in the form,

$$\nabla^2\psi + \frac{8\pi^2 m(E-V)}{h^2}\psi = 0 \qquad \ldots(19.55)$$

(b) Hamiltonian Operator The Schrodinger wave equation may also be written in the form

$$\nabla^2\psi = \frac{-8\pi^2 m(E-V)}{h^2}\psi$$

or $$\nabla^2\psi = \frac{-8\pi^2 m}{h^2}(E\psi - V\psi)$$

or $$\frac{-h^2}{8\pi^2 m}\nabla^2\psi + V\psi = E\psi$$

or $$\left(\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right)\psi = E\psi \qquad \ldots(19.56)$$

This equation implies that the operation $\left(\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right)$ carried out on the function ψ is equal to the total energy multiplied with the function ψ. The operator $\left(\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right)$ is called Hamiltonian operator and is represented as $\hat{H}$.

Thus,

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V \qquad \ldots(19.57)$$

Equation (19.56) may, therefore, be written as

$$\hat{H}\psi = E\psi \qquad \ldots(19.58)$$

This is a brief form of writing the Schrodinger wave equation.

In this equation, ψ is called the eigen function and E is called the eigen value.

Such an equation is, therefore, called ***eigen value equation***. Thus, for Schrodinger wave equation, we can write

(Energy operator) (Wave function) = (Energy) × (Wave function)

This is a general result as it is equally applicable to all other ***observables,*** i.e. measureable properties of a system. Thus, in general, we can write (Operator corresponding to an observable) (Wave function) = (Value of observable) × (Wave function)

Example 1 *Find the commutator* $= \left[x, \frac{d}{dx}\right]$.

Solutionr By definition of commutator,

$$\left[x, \frac{d}{dx}\right] = \left[x\frac{d}{dx} - \frac{d}{dx}x\right]$$

Let us operate this on some arbitrary function $\psi(x)$.

$$\left[x\frac{d}{dx} - \frac{d}{dx}x\right]\psi = x\frac{d\psi}{dx} - \frac{d}{dx}(x\psi)$$

$$= x\frac{d\psi}{dx} - x\frac{d\psi}{dx} - \psi\frac{dx}{dx} = (-1)\psi$$

Thus, $$\left[x, \frac{d}{dx}\right] = -1$$

Example 2 Find the *commutator of the operators for momentum and position, the two conjugate properties of Heisenberg's uncertainty principle.*

Solutionr Operator for momentum $= \hat{p} = \frac{h}{2\pi i}\frac{\partial}{\partial x}$

Operator for position = $\hat{x}$ = Multiplication by x

Operator for position = $\hat{x}$ = Multiplication by x

$$[\hat{p}, \hat{x}]\psi = (\hat{p}\hat{x} - \hat{x}\hat{p})\psi = \hat{p}\hat{x}\psi - \hat{x}\hat{p}\psi \quad \ldots(i)$$

$$\hat{p}\hat{x}\psi - \frac{h}{2\pi i}\frac{\partial}{\partial x}(\hat{x}\psi) - \frac{h}{2\pi i}\frac{\partial}{\partial x}(x\psi)$$

$$= \frac{h}{2\pi i}\left(x\frac{\partial\psi}{\partial x} + \psi\right) = \frac{h}{2\pi i}x\frac{\partial\psi}{\partial x} + \frac{h}{2\pi i}\psi \quad \ldots(ii)$$

$$\hat{x}\hat{p}\psi = \hat{x}\frac{h}{2\pi i}\frac{\partial\psi}{\partial x} = x\frac{h}{2\pi i}\frac{\partial\psi}{\partial x} \quad \ldots(iii)$$

Substituting the values from Eqs. (ii) and (iii) in Eq. (i), we have

$$[\hat{p}, \hat{x}]\psi = \frac{h}{2\pi i}\psi \quad \text{or} \quad [\hat{p}, \hat{x}] = \frac{h}{2\pi i} \simeq h$$

Example 3 *Prove that* $[\hat{A}^2, \hat{B}] = \hat{A}[\hat{A},\hat{B}] + [\hat{A},\hat{B}]\hat{A}$

Solution:

$$\text{RHS} = \hat{A}(\hat{A}\hat{B} - \hat{B}\hat{A}) + (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{A}$$

$$= \hat{A}^2\hat{B} - \hat{A}\hat{B}\hat{A} + \hat{A}\hat{B}\hat{A} - \hat{B}\hat{A}^2$$

$$= \hat{A}^2\hat{B} - \hat{B}\hat{A}^2 = [\hat{A}^2, \hat{B}]$$

Expressions for Operators The expression for an operator can be obtained by the following procedure.

Step 1 The operator is allowed to operate on the operand.

Step 2 The results of calculation are arranged such that the operand appears on both sides in a way that it can be cancelled from both sides.

Example 4 *Derive an expression for the following operator:*

$$\left(\frac{d}{dx}x\right)^2\psi(x)$$

Solution: Taking the operand as $\psi(x)$, we have

$$\left(\frac{d}{dx}x\right)^2\psi(x) = \left(\frac{d}{dx}x\right)\left(\frac{d}{dx}x\right)\psi = \left(\frac{d}{dx}x\right)\left(\frac{d}{dx}x\psi\right)$$

$$= \frac{d}{dx}x\left(x\frac{d\psi}{dx} + \psi\frac{dx}{dx}\right) = \frac{d}{dx}x\left(x\frac{d\psi}{dx} + \psi\right)$$

$$= \frac{d}{dx}\left(x^2\frac{d\psi}{dx} + x\psi\right) = \left(x^2\frac{d^2\psi}{dx^2} + \frac{d\psi}{dx}(2x)\right) + \left(x\frac{d\psi}{dx} + \psi\frac{dx}{dx}\right)$$

$$= x^2\frac{d^2\psi}{dx^2} + 2x\frac{d\psi}{dx} + x\frac{d\psi}{dx} + \psi = x^2\frac{d^2\psi}{dx^2} + 3x\frac{d\psi}{dx} + \psi$$

$$= \left(x^2\frac{d^2}{dx^2} + 3x\frac{d}{dx} + 1\right)\psi$$

Removing ψ from both sides, we get

$$\left(\frac{d}{dx}x\right)^2 = x^2\frac{d^2}{dx^2} + 3x\frac{d}{dx} + 1$$

Example 5 *Derive an expression for the following operator* $\left(\frac{d}{dx} + x\right)^2$.

Solution: Taking the operand as $\psi(x)$, we have

$$\left(\frac{d}{dx} + x\right)^2\psi(x) = \left(\frac{d}{dx} + x\right)\left(\frac{d}{dx} + x\right)\psi = \left(\frac{d}{dx} + x\right)\left(\frac{d\psi}{dx} + x\psi\right)$$

$$= \frac{d}{dx}\left(\frac{d\psi}{dx} + x\psi\right) + x\left(\frac{d\psi}{dx} + x\psi\right)$$

$$= \frac{d^2\psi}{dx^2} + \left(x\frac{d\psi}{dx} + \psi\right) + x\frac{d\psi}{dx} + x^2\psi$$

$$= \frac{d^2\psi}{dx^2} + 2x\frac{d\psi}{dx} + x^2\psi + \psi$$

$$= \left(\frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1\right)\psi$$

Removing ψ from both sides, we get

$$\left(\frac{d}{dx} + x\right)^2 = \frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1$$

19.19 POSTULATES OF QUANTUM MECHANICS

The postulates of quantum mechanics which can lead to the derivation of Schrodinger equation are given as under:

1. For every time-independent state of a system, a function ψ of the coordinates can be written which is single valued, continuous and finite throughout the configuration space. This function describes the state of the system completely.
2. To each observable quantity in classical mechanics, like position, velocity, momentum, energy, etc., there corresponds a certain mathematical operator in quantum mechanics, the nature of which depends upon the classical expression for the observable quantity. For example,
   (a) The operator corresponds to a position coordinate multiplied by the value of that coordinate, i.e., the operator for a position coordinate x is the multiplier x.
   (b) The operation representing the momentum (p) in the direction of any coordinate q is the differential operator

$$\frac{h}{2\pi i}\frac{\partial}{\partial q} \quad \text{or} \quad -\frac{ih}{2\pi}\frac{\partial}{\partial q} \quad \left(\because i^2 = -1 \text{ or } i \times i = -1 \text{ or } \frac{1}{i} = -i\right)$$

(Sometimes, we use the symbol $\hbar$ (read as $\hbar$ cross) and $\hbar = \frac{h}{2\pi}$)

where h is Planck's constant and $i = \sqrt{-1}$

For example, the operator for linear momentum parallel to the x-axis is

$$\hat{p} = \frac{h}{2\pi i}\frac{\partial}{\partial x}$$

This means that to find the linear momentum of a particle parallel to the x-axis, we use the eigenvalue equation

$$\hat{p}\psi = p\psi$$

i.e. we differentiate the wave function ψ with respect to x and multiply the result with $h/2\pi i$ and then from the eigen-value equation, we can know the value of the momentum p.

For three-dimensional systems, the operators are obtained by summation of the corresponding operators. For example,

(a) For momentum, $\hat{p} = \frac{h}{2\pi i}\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right)$

(b) For kinetic energy, $\hat{T} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$

(c) For total energy, $\hat{H} = \frac{-h^2}{8\pi^2 m}\nabla^2 + V(x, y, z) \quad (\because E = T + V)$

3. If ψ is a well-behaved function for the given state of a system and $\hat{A}$ is a suitable operator for the observable quantity or property then the operator on ψ by the operator $\hat{A}$ gives ψ multiplied by a constant value (say, a) of the observable property, i.e.

$$\hat{A}\psi = a\psi \qquad \ldots(19.59)$$

The given state is called the eigen state of the system, ψ is called the eigen function and a is called the eigen value. The above equation is a general expression for ***eigen value equation***.

4. ***The only possible measured values of an observable are the eigen values obtained from the eigen value equation given in postulate (3) above. Thus if the wave function ψ of the system is***

an eigen function of the operator for the observable then measurement of that observable gives the eigen value. If the wave function ψ of the system is not an eigen function then the value of the observable obtained on measurement has a probability that can be calculated from the wave function.

5. If a number of measurements are made over the configuration space then the average value of the quantity (represented by $\bar{a}$) is given by,

$$\bar{a} = \frac{\oint \psi^* \hat{A} \psi d\tau}{\oint \psi^* \psi d\tau} \qquad \ldots(19.60)$$

where $\oint$ represents integration over the whole of the configuration space This postulate can be understood from Eq. (19.59)

$$a = \frac{\hat{A}\psi}{\psi}$$

But this expression does not give a constant value of a because it involves the function of the variable coordinates. By multiplying the numerator and the denominator by the complex conjugate ψ^* and integrating over the whole of the configuration space, the result obtained is no longer a function of coordinates and gives an average value of the constant a.

How to Test Whether the Given Function is an Eigen Function of the Given Operator?
Operate on the function with the operator and check whether the result is a constant factor times the original function. If so, the given function is an eigen function of the given operator.

Example 6 *Find out whether the function cos ax is an eigen function of (a) d/dx, and (b) d^2/dx^2. What is the corresponding eigen value if any?*

Solution:

(a) Here, $\psi = \cos ax$

$$\frac{d\psi}{dx} = \frac{d}{dx}(\cos ax) = -a \sin ax$$

Hence, cos ax is not an eigen function of d/dx

(b) $$\frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2}(\cos ax) = \frac{d}{dx}\left(\frac{d}{dx}\cos ax\right)$$

$$= \frac{d}{dx}(-a \sin ax) = -a^2 \cos ax = -a^2 \psi$$

Hence, cos ax is an eigen function of $\frac{d^2}{dx^2}$, Eigen value = $-a^2$

Example 7 *Determine whether e^{ax} is an eigen function of the operator d/dx and find the corresponding eigen value if any. Show that e^{ax^2} is not an eigen function of d/dx.*

Solution: In the first case, $\psi = e^{ax}$

$$\frac{d\psi}{dx} = \frac{d}{dx}(e^{ax}) = ae^{ax} = a\psi$$

Hence, e^{ax} is an eigen function of d/dx and its eigen value = a

In the second case,

$$\psi = e^{ax^2}$$

$$\frac{d\psi}{dx} = \frac{d}{dx}(e^{ax^2}) = 2axe^{ax^2} = 2ax\psi$$

Thus, the result obtained is not a constant factor multiplied with ψ but a variable factor, $2ax$ multiplied with ψ. Hence, e^{ax^2} is not an eiegn function of d/dx.

Example 8 *If all the eigen functions of two operators $\hat{A}$ and $\hat{B}$ are the same functions, prove that $\hat{A}$ and $\hat{B}$ commute with each other.*

Solution: Let us suppose the eigen functions of the operators $\hat{A}$ and $\hat{B}$ are ψ_i and the corresponding eigen values are a_i and b_i respectively. Then eigen-value equations will be $\hat{A}\psi_i = a_i\,\psi_i$ and $\hat{B}\psi_i = b_i\psi_i$

The eigen functions of the operator $\hat{A}\,\hat{B}$ are obtained as follows:

$$\hat{A}\hat{B}\,\psi_i = \hat{A}(\hat{B}\psi_i) = \hat{A}(b_i\,\psi_i) = b_i\hat{A}\psi_i = b_i a_i\,\psi_i$$

The eigen functions of the operator $\hat{B}\,\hat{A}$ are obtained as follows:

$$\hat{B}\hat{A}\psi_i = \hat{B}(\hat{A}\psi_i) = \hat{B}(a_i\,\psi_i) = a_i\hat{B}\psi_i = a_i b_i\,\psi_i$$

As $b_i\,a_i = a_i\,b_i$, this means $\hat{A}\hat{B}\psi_i = \hat{B}\hat{A}\,\psi_i$ *or* $\hat{A}\hat{B} = \hat{B}\hat{A}$

Hence, they commute with each other.

Example 9 *Show that the function ψ = cos ax cos by cos cz is an eigen function of the Laplacian operator. What is the corresponding eigen value?*

Solution: Laplacian operator $\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$

$$\text{Hence, } \nabla^2\psi = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(\cos ax \cos by \cos cz)$$

$$= \cos by \cos cz \frac{\partial^2}{\partial x^2}(\cos ax) + \cos ax \cos cz \frac{\partial^2}{\partial y^2}(\cos by) + \cos ax \cos by \frac{\partial^2}{\partial z^2}(\cos cz)$$

$$= \cos by \cos cz(-a^2 \cos ax) + \cos ax \cos cz(-b^2 \cos by) + \cos ax \cos by(-c^2 \cos cz)$$

$$\left[\because \frac{\partial^2}{\partial x^2}(\cos ax) = \frac{\partial}{\partial x}(-a \sin ax) = -a^2 \cos ax \text{ and so on}\right]$$

$$= -(a^2 + b^2 + c^2)\cos ax \cos by \cos cz$$

$$= -(a^2 + b^2 + c^2)\,\psi$$

As $(a^2 + b^2 + c^2)$ is constant, hence the given function is an eigen function of the Laplacian operator. Eigen value = $-(a^2 + b^2 + c^2)$.

Example 10 *If ψ_1 and ψ_2 are the proper functions of an atom, show that any linear combination of these wave functions will also be a proper wave function of the Schrodinger equation.*

Solution: Consideration for proper or eigen wave functions for a system of constant energy (E) is given by

$$H\psi = E\psi$$

where, H is the Hamitonian operator.

Thus, $\hat{H}\psi_1 = E\psi_1, \ \hat{H}\psi_2 = E\psi_2$

Linear combination of ψ_1 and ψ_2 may be represented by ψ as

$$\psi = c_1\psi_1 + c_2\psi_2$$

where c_1 and c_2 are constants.

$\therefore$
$$\begin{aligned}\hat{H}\psi &= \hat{H}[c_1\psi_1 + c_2\psi_2] \\ &= c_1\hat{H}\psi_1 + c_2\hat{H}\psi_2 \\ &= c_1E\psi_1 + c_2E\psi_2 \\ &= E(c_1\psi_1 + c_2\psi_2) \\ &= E\psi\end{aligned}$$

Hence, ψ is also a proper function of the Schrodinger equation.

Example 11 *which of the following wave functions are acceptable in quantum mechanics, over the range when x goes from 0 to 2?*

(a) sin x

(b) tan x

(c) cos x + sin x

Solution:

(a) sin x is continuous, single valued and finite in the given range of x. It is acceptable (sin x varies between –1 and 1 in the given range).

(b) tan x is infinite for $x = \frac{\pi}{2}$. It is not acceptable.

(c) cos x + sin x is continuous, single valued and finite in the given range. It is acceptable (cos x + sin x), and varies between –1 to +1 in the given range.

Example 12 *If two operators $\hat{A}$ and $\hat{B}$ commute then they have the same set of eigen functions. Justify it.*

Solution: Suppose the operator $\hat{A}$ has eigen function ψ.

Then $\hat{A}\psi = a\psi$

where "a" is the eigen value

since $\hat{A}$ and $\hat{B}$ commute, $\hat{A}\hat{B}\psi = \hat{B}\hat{A}\psi = \hat{B}a\psi = a\hat{B}\psi$

This shows that $\hat{B}\psi$ is an eigen function of the operator $\hat{A}$ with eigen value a.

This is possible only if $(\hat{B}\psi)$ is a multiple of ψ, i.e.

$$\hat{B}\psi = b\psi$$

where b is constant.

In other words, "ψ" is also an eigen function of $\hat{B}$.

19.20 | DERIVATION OF SCHRODINGER WAVE EQUATION BASED ON THE POSTULATES OF QUANTUM MECHANICS

Using the postulates of quantum mechanics, The schrodinger wave equation can be derived in a simple manner as follows:

Consider a single particle, e.g. an electron of mass m moving with a velocity v. Its total energy E is

the sum of its kinetic energy (T) and potential energy (V), i.e.

$$E = T + V \qquad \ldots(19.61)$$

Put

$$T = \frac{1}{2} mv^2 = \frac{P^2}{2m} \qquad \ldots(19.62)$$

where p represents the total momentum of the particle.

Further, we know that,

$$p^2 = p_x^2 + p_y^2 + p_z^2$$

where p_x, p_y and p_z are the momenta of the electron along the three mutually perpendicular directions along the three axes.

$$T = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \qquad \ldots(19.63)$$

Substituting this value in Eq. (19.61), we get

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V \qquad \ldots(19.64)$$

According to the second postulate of quantum mechanics, the operators for the momenta p_x, p_y and P_z are

$$p_x = \frac{h}{2\pi i}\frac{\partial}{\partial x} \quad p_y = \frac{h}{2\pi i}\frac{\partial}{\partial y} \quad p_z = \frac{h}{2\pi i}\frac{\partial}{\partial z}$$

V is the function of position coordinates and hence, the operator for V is V itself.

The operator for the energy E is the Hamitonian operator, H.

Hence, Eq. (19.64) takes the form (taking into consideration the algebraic rules of the operator)

$$\hat{H} = \frac{1}{2m}\left[\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right)^2\right] + V$$

$$= -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V$$

$$= -\frac{h^2}{8\pi^2 m}\nabla^2 + V \qquad \ldots(19.65)$$

where, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ represents the Laplacian operator.

According to the third postulate, we have

$$\hat{H}\psi = E\psi$$

$$\hat{H}\psi - E\psi = 0 \qquad \ldots(19.66)$$

where, E is the eigen value of the energy for the given state of system.

Substituting the value of H from Eq. (19.65) into Eq. (19.66), we get

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right) - E\psi = 0 \qquad \ldots(19.67)$$

which can be rearranged and written in the form

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \ldots(19.68)$$

which is the required Schrodinger wave equation in one of the common forms.

19.21 PARTICLE IN A ONE-DIMENSIONAL BOX

A particle in a box provides us the application of Schrodinger wave equation to the translational motion of a particle like an electron, atom, etc. It also explains as to why the energies associated are quantised.

The motion of the particle in a one-dimensional box is like the flow of an electron in a wire but still it is called ''particle in a box" and a general case can be considered in which we may assume that a single particle, e.g. a gas molecule of mass m, is restricted to move in a region of space from $x = 0$ to $x = a$ and that its potential energy within a box is constant and taken as equal to zero for the sake of convenience (Fig. 19.26). In order that the particle may remain within the box, it is essential to assume that the potential energy on or outside the wall is very high (= ∞) so that as soon as the particle reaches the walls, it is reflected back into the box.

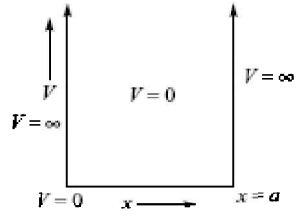


Fig. 19.26 *A particle in a one-dimensional box with PE = 0 inside the box and PE = ∞ on the walls of the box and outside the box.*

Schrodinger wave equation for one dimension is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \ldots(19.69)$$

where ψ has been taken as the function of x coordinate only. Outside the box, $V = \infty$, therefore for outside the box, Eq. (19.69) becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - \infty)\psi = 0 \qquad \ldots(19.70)$$

Neglecting E in comparison to ∞, Eq. (19.70) reduces to

$$\frac{d^2\psi}{dx^2} - \infty\psi = 0 \left(\frac{8\pi^2 m}{h^2} \times \text{Infinity} = \text{Infinity} \right)$$

$$\frac{d^2\psi}{dx^2} = \infty\psi$$

$$\psi = \frac{1}{\infty}\frac{d^2\psi}{dx^2} = \text{Zero} \qquad \ldots(19.71)$$

This proves that outside the box, $\psi = 0$ which implies that the particle cannot go outside the box.

For the particle within the box, $V = 0$, therefore the Schrodinger wave Eq. (19.69) takes the form,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \qquad \ldots(19.72)$$

For the given state of the system, the energy E is constant which is one of the postulates of the quantum mechanics. Therefore, we put

$$\frac{8\pi^2 m}{h^2} E = k^2 \qquad \ldots(19.73)$$

where k^2 is constant, independent of x.

Equation (19.72), then becomes,

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \ldots(19.74)$$

A general solution of this differential equation is given by

$$\psi = A \sin kx + B \cos kx \qquad \ldots(19.75)$$

where A and B are constants.

Depending upon the value of A, B and k, ψ can have many values. But all the values are not acceptable. Only those values of ψ are acceptable which satisfy the boundary conditions, viz.

$$\psi = 0 \text{ at } x = 0 \text{ and } x = a$$

Putting $\psi = 0$ when $x = 0$, Eq. (19.75) becomes

$$0 = B \sin 0 + B \cos 0$$

$$= 0 + B \qquad (\because \sin 0 = 0 \text{ and } \cos 0 = 1)$$

i.e. $B = 0$

Thus, when $x = 0$, Eq. (19.75) becomes (by putting $B = 0$),

$$\psi = A \sin kx \qquad \ldots(19.76)$$

Now putting $\psi = 0$ when $x = a$, Eq. (19.76) becomes

$$0 = A \sin ka$$

i.e., $$\sin ka = 0 \qquad \ldots(19.77)$$

This equation holds good only when the values of ka are integral multiplies of π, i.e.

$$ka = n\pi \qquad \ldots(19.78)$$

where n is an integer, i.e. $n = 0, 1, 2, 3, \ldots$ However, the value $n = 0$ may be excluded because it makes $k = 0$ and hence $\psi = 0$ for any value of a between 0 and a, i.e., within the box. This is not true because the particle is always assumed to be present within the box.

From Eq. (19.78),

$$k = \frac{n\pi}{a} \qquad \ldots(19.79)$$

Substituting this value in Eq. (19.76), we get

$$\psi = A \sin\left(\frac{n\pi}{a} \cdot x\right) \qquad \ldots(19.80)$$

This gives the expression for the eigen function ψ. The expression for eigen value of the energy may be obtained as follows:

From Eq. (19.73),

$$E = \frac{k^2 h^2}{8\pi^2 m} \qquad \ldots(19.81)$$

Substituting the value of k from Eq. (19.79), we get

$$E = \frac{(n\pi/a)^2 h^2}{8\pi^2 m}$$

$$E = \frac{n^2 h^2}{8ma^2} \qquad \ldots(19.82)$$

Equations (19.80) and (19.82) are the solutions of the Schrodinger wave equation for a particle in a one-dimensional box.

The value of A in Eq. (19.80) can be obtained by normalisation of wave function.

The process of ***normalisation of the wave function*** can be carried out as follows:

$$\int_0^a \psi\psi^* d\tau = 1$$

Substituting the value of $\psi(= \psi^*)$ from Eq. (19.80), we get

$$A^2 \int_0^a \sin^2 \frac{n\pi}{a} x\,dx = 1$$

or $$A^2 \cdot \frac{a}{2} = 1 \qquad \left[\text{as} \int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx = \frac{a}{2}\right]$$

$$A = \sqrt{\frac{2}{a}}$$

Trigonometric relation $2\sin^2 x = 1 - \cos 2x$

$$\sin^2 x = \frac{1 - \cos 2x}{2}$$

Hence, the normalised wave function (which will also be a solution of the Schrodinger equation) is

$$\psi = \boxed{\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)}$$

If there are any two eigen functions ψ_m, and ψ_n corresponding to two different value of n then ψ_m and $\psi_n$will be orthogonal to each other. This can be derived as under:

$$\int_0^a \psi_m \psi_n dx = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{n\pi x}{a}\right)dx$$

$$= \frac{2}{a}\int_0^a \frac{1}{2}\left[\cos(m-n)\frac{\pi x}{a} - \cos(m+n)\frac{\pi x}{a}\right]dx = \frac{1}{a}\left[\frac{\sin(m-n)\frac{\pi x}{a}}{(m-n)\frac{\pi}{a}} - \frac{\sin(m+n)\frac{\pi x}{a}}{(m+n)\frac{\pi}{a}}\right]_0^a$$

$[\because \quad 2\sin A \sin B = \cos(A - B) - \cos(A + B)]$

$$= \frac{1}{\pi}\left[\frac{\sin(m-n)\frac{\pi x}{a}}{(m-n)} - \frac{\sin(m+n)\frac{\pi x}{a}}{(m+n)}\right]_0^a = \frac{1}{\pi}\left[\frac{\sin(m-n)\pi}{(m-n)} - \frac{\sin(m+n)\pi}{(m+n)}\right] = 0$$

[$\because$ m and n are integers and $m \neq n$; therefore, $(m - n)$ and $(m + n)$ are also integers and $\sin N\pi = 0$, where N is an integer.]

Results from the Study of a Particle in a Box Expression for energy for a particle in a one-dimensional box is

$$E = \frac{n^2 h^2}{8ma^2} \qquad \ldots(19.83)$$

where m is the mass of the particle and a is the length of the box ($x = 0$ to $x = a$).

(a) Quantization of Energy Since n can have only integral values equal to 1, 2, 3, etc., therefore, from Eq. (19.83), it follows that the energy E associated with the motion of a particle in a box can have only discrete values, i.e. the energy is quantised.

The integer n is called the ***quantum number*** of the particle.

Further, putting $n = 1, 2, 3, \ldots$ etc., the discrete energy levels obtained for the particle of mass m confined in the box of length a are shown in Fig. 19.27. It is important to note that as the quantum number n increases, the separation between them increases. It may also be noted that energy levels also depends upon the box length a. As a increases, i.e., the space available to the particle increases, energy quanta becomes smaller and energy levels more closer together. If the box length becomes very large, quantisation disappears "and there is a smooth transition from quantum behaviour to classical behaviour (continuous change)."

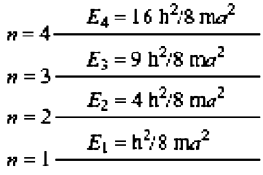


Fig. 19.27 *Discrete energy levels of a particle of mass m confined in a box of length a*

(b) Existence of Zero Point Energy Minimum value of $n = 1$ ($n = 0$ is ruled out, as discussed earlier).

Substituting this value in Eq. (19.83), we get

$$E = \frac{h^2}{8ma^2}$$

This implies that the minimum energy possessed by the particle is not zero but has a definite value. This is called ***zero point energy***.

(c) Non-quantisation of Energy for the Particle If the walls of the box are removed, so that the particle is free to move in a field whose potential energy values do not follow any restriction. Then the boundary conditions are no longer applicable and so the constants A, B and k can have any value. The energy of the particle is then given by the equation

$$E = \frac{k^2 h^2}{8\pi^2 m}$$

As the constant k can have any value, the energy of the free particle is not quantised.

19.22 | CALCULATION OF EXPECTATION VALUES USING WAVE FUNCTION

Physical property of a particle moving in one dimension which does not depend upon time can be calculated from the time-independent wave function $\psi(x)$ of the system. In these calculations, the probability of finding the particle in any region of the one-dimensional space is calculated using Born's postulates according to which the probability $P(x)\,dx = \psi(x)\,\psi^*(x)\,dx$.

Thus, the wave function helps us calculate observables like position, momentum, etc. However, if we carry out an experiment to measure the position x of the particle, $\psi(x)$ may not give the result of

that particular experiment. But if we repeat the experiment a number of times, the value of the position x calculated from $\psi(x)$ is the same as the mean value of the different experiments. **This mean (or average) value, denoted by $\langle x \rangle$, is called the expectation value of the observable x.**

1. Expectation Value of Position x According to one of the postulates of quantum mechanics, as operator for the position coordinate x is the multiplier x, therefore, the expectation value $\langle x \rangle$ will be given by,

$$\langle x \rangle = \int \psi^* x \psi dx = \int x \psi^* \psi dx = \int x P(x) dx \qquad \ldots(19.84)$$

where $P(x)\,dx$ is the probability calculated by Born's postulate.

2. Expectation Value for Any Observable Quantity, G To calculate the expectation value of any other physical quantity (or observable) G, remember that the operator for G is represented by $\hat{G}$ and apply the basic postulates of quantum mechanics. The expectation value $\langle G \rangle$ is given by

$$\langle G \rangle = \int_{-\infty}^{\infty} \psi^* \hat{G} \psi \, dx \qquad \ldots(19.85)$$

which would be same as the mean value of the results of the repeated experiments for the measurement of G in the state $\psi(x)$.

It may be noted that G is not a simple factor like e. It is an operator for the quantity G.

Hence, $\int \psi^* \hat{G} \psi dx$ cannot be rearranged to give $\int \hat{G} \psi^* \psi dx$. Thus, G must be allowed to operate on ψ. For example, according to one of the postulates of quantum mechanics, for the momentum px, the operator px is $-\frac{ih}{2\pi}\frac{d}{dx}$ i.e. take a derivative with respect to x and multiply the result by $-ih/2\pi$.

19.22.1 Expectation Values of x, x^2, p_x and p^2_x for a Particle in a One-Dimensional Box of Length a

For a particle in a one-dimensional box, we have the relation

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

ψ_n is a normalised wave function.

Therefore

1. $$\langle x \rangle = \int_0^a \psi x \psi dx = \int_0^a x \psi^2 dx = \int_0^a x \cdot \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$\frac{2}{a}\int_0^a x \cdot \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a}\int_0^a x \cdot \left[\frac{1 - \cos\left(\frac{2n\pi x}{a}\right)}{2}\right] dx$$

[Trigonometric relation $2\sin^2 A = 1 - \cos 2A$]

Integrate the definite integral by parts using the formula

$$\int (uv) dx = u \int v dx - \int \left[\frac{du}{dx} \int v dx\right] dx$$

The value of the integral comes out to be zero.

$$= \frac{2}{a}\left(\frac{a^2}{4}\right) = \frac{a}{2} \qquad \ldots(19.86)$$

2. $$\langle x^2 \rangle = \int_0^a \psi x^2 dx = \int_0^a x^2 \psi^2 dx = \frac{2}{a}\int_0^a x^2 \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{2}{a}\int_0^a x^2 \left[\frac{1-\cos\left(\frac{2n\pi x}{a}\right)}{2}\right] dx$$

$$\frac{2}{a}\left[\frac{a^3}{6} - \frac{a^3}{4n^2\pi^2}\right] \quad \frac{1}{a}\left[\frac{a^3}{3} - \frac{a^3}{2n^2\pi^2}\right]$$

$$\left(\frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}\right) \qquad \ldots(19.87)$$

3. $$\langle p_x \rangle_n \int_0^a \psi\left(\frac{-ih}{2\pi}\frac{d}{dx}\right)\psi dx \quad \int_0^a \left[\left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}\right]\left(\frac{-ih}{2\pi}\frac{d}{dx}\right)\left[\left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}\right] dx$$

$$\frac{-ih}{2\pi}\left(\frac{2}{a}\right)\int_0^a \sin\left(\frac{n\pi x}{a}\right)\left(\frac{n\pi}{a}\right)\cos\left(\frac{n\pi x}{a}\right) dx$$

$$\therefore \frac{-ih}{2\pi}\left(\frac{2}{a}\right)\frac{n\pi}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\cos\left(\frac{n\pi x}{a}\right) dx$$

$$= 0 \text{ (on integration by parts)} \qquad \ldots(19.88)$$

This result is justified, because the average momentum has to be zero as the particle in a box cannot continue to travel in one direction only. Also, note that the limits used are 0 and a in place of $-\infty$ to $+\infty$ because the wave function is known to be zero outside the box.

4. $$\langle p_x^2 \rangle_n = \int_0^a \left[\left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}\right]\left(\frac{-ih}{2\pi}\frac{d}{dx}\right)^2\left[\left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}\right] dx^* \quad \text{(The operator for } p_x^2 \text{ is } \hat{p}_x \hat{p}_x\text{)}$$

$$= \frac{-h^2}{4\pi^2}\left(\frac{2}{a}\right)\int_0^a \sin\left(\frac{n\pi x}{a}\right)\frac{d^2}{dx^2}\left(\sin\frac{n\pi x}{a}\right) dx$$

$$= \frac{-h^2}{4\pi^2}\left(\frac{2}{a}\right)\int_0^a \sin\left(\frac{n\pi x}{a}\right)\left[(-)\left(\frac{n\pi}{a}\right)^2 \sin\left(\frac{n\pi x}{a}\right)\right]dx^*$$

$\frac{d}{dx}(\sin x) = \cos x, \frac{d}{dx}(\cos x)$

$= -\sin x$. That is why $(-)$ sign appears.

$$= \left(\frac{h^2}{4\pi^2}\right)\left(\frac{2}{a}\right)\left(\frac{n\pi}{a}\right)^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{n^2h^2}{2a^3}\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx$$

$$= \frac{n^2h^2}{2a^3}\int_0^a \frac{1-\cos\frac{(2n\pi x)}{a}}{2}dx = \frac{n^2h^2}{4a^3}\left[\frac{x-\sin\frac{(2n\pi x)}{a}}{\frac{(2n\pi x)}{a}}\right]_0^a \qquad [\because 2\sin^2 A = 1-\cos^2 A]$$

$$= \frac{n^2h^2}{4a^3}\cdot a = \frac{n^2h^2}{4a^2} = 2mE \quad \left[\because E = \frac{n^2h^2}{8ma^2}\right]$$

---

* $\widehat{p_x^2} = (\hat{p}x)(\hat{p}x) = \left(\frac{-ih}{2\pi}\frac{d}{dx}\right)\left(-\frac{ih}{2\pi}\frac{d}{dx}\right) = -\frac{h^2}{4\pi^2}\frac{d^2}{dx^2}$

19.22.2 Calculation of Standard Derivation in x and p_x, i.e. Δx and Δp_x and Derivation of Heisenberg Uncertainty Principle.

The standard derivation in the position x for the particle in an eigen state of a one-dimensional box is given by

$$\Delta x = (\langle x^2\rangle - \langle x\rangle^2)^{1/2} \text{ (Note the difference between } \langle x^2\rangle \text{ and } \langle x\rangle^2) \qquad \ldots(19.89)$$

Substituting the values derived in Section 19.22.1,

$$\Delta x = \left[\left(\frac{a^3}{3} - \frac{a^2}{2n^2\pi^2}\right) - \left(\frac{a}{2}\right)^2\right]^{1/2} = \left[\left(\frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}\right)\right]^{1/2}$$

$$= a\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right) \qquad \ldots(19.90)$$

The standard derivation in the momentum, p_X for the particle is given by

$$\Delta p_x = (\langle p^2\rangle - \langle p\rangle^2)^{1/2} \qquad \ldots(19.91)$$

Substituting the values derived in Section 19.22.1,

$$\Delta p_x = (\langle p^2 \rangle)^{1/2} = \left(\frac{n^2h^2}{4a^2}\right)^{1/2} = \frac{nh}{2a} \qquad \ldots(19.92)$$

$$\therefore \quad \Delta x \cdot \Delta p = a\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2} \cdot \frac{nh}{2a} = \frac{nh}{2}\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{1/2}$$

$$= \frac{nh}{2} \times \frac{1}{2n\pi}\left(\frac{4n^2\pi^2}{12} - \frac{4n^2\pi^2}{2n^2\pi^2}\right)^{1/2}$$

$$= \frac{h}{4\pi}\left(\frac{n^2\pi^2}{3} - 2\right)^{1/2} \qquad \ldots(19.93)$$

The quantity on the right-hand side is $> \frac{h}{4\pi}$ because $(n^2\pi^2/3) > 2$ always.

Hence, $$\Delta x \cdot \Delta p > \frac{h}{4\pi} \qquad \ldots(19.94)$$

which is Heisenberg's uncertainty principle.

Example 13 *Calculate the probability offinding theparticle between 0.49a and 0.51a for the states ψ_1 and ψ_2.*

Solution:

$$\text{Probability} = \int_{0.49a}^{0.51a} \psi^2 dx = \int_{0.49a}^{0.51a} \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{2}{a}\int_{0.49a}^{0.51a} \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a}\int_{0.49a}^{0.51a} \frac{1 - \cos\left(\frac{2n\pi x}{a}\right)}{a} dx$$

$$= \frac{1}{a}\int_{0.49a}^{0.51a} \left[1 - \cos\left(\frac{2n\pi x}{a}\right)\right] dx = \frac{1}{a}\left[x - \frac{\sin\left(\frac{2n\pi x}{a}\right)}{\frac{2n\pi}{a}}\right]_{0.49a}^{0.51a}$$

$$= \frac{1}{n\pi}\left[\frac{n\pi x}{a} - \frac{1}{2}\sin\frac{2n\pi x}{a}\right]_{0.49a}^{0.51a}$$

Putting $n = 1$ and reading the value of sines of the angles from the tables, probability = 0.0399. Similarly, for $n = 2$, probability = 0.0001

Example 14 *What is the groundstate energy for an electron which is confined to a potential well (one dimensional box) having a width of 0.2 nm?*

Solution: The energy for a particle in a one-dimensional box is given by

$$E = \frac{n^2h^2}{8ma^2}$$

For the ground state, $n = 1$

For the electron $m = 9.11 \times 10^{-31}$ kg

We are given $a = 0.2$ nm $= 0.2 \times 10^{-9}$ m

Also, we know that $h = 6.626 \times 10^{34}$ Js

$$E = \frac{(1)^2(6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31} \times (0.2 \times 10^{-9})^2} = 1.506 \times 10^{-18} \text{ J}$$

$\therefore$ for 1 mole of electrons, the energy will be

$$E = \frac{(1.506 \times 10^{-18}) \times (6.022 \times 10^{23})}{10^3} \text{ kJ mol}^{-1}$$

$$= 907 \text{ kJ mol}^{-1}$$

19.23 PARTICLE IN A THREE-DIMENSIONAL BOX

Consider a single particle, e.g. a gas molecule of mass m restricted to move within a rectangular box of dimensions a, b and c along the X-axis, Y-axis and Z-axis respectively (Fig. 19.28). As assumed earlier that the potential energy of the particle within the box is constant (taken as equal to zero) and on the walls or outside, it suddenly rises to a very large value (= ∞).

Now, the Schrodinger wave equation for three dimensions is

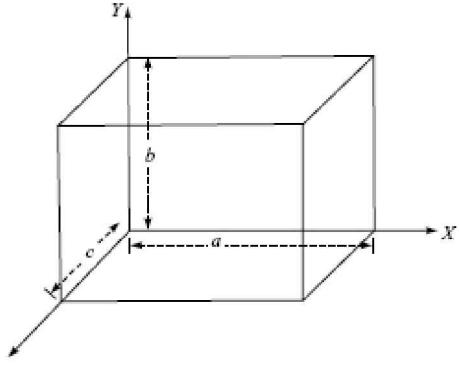


Fig. 19.28 *Particle in a three dimensional box.*

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \quad \ldots(19.95)$$

where E represents the total energy of the particle, V is the potential energy and ψ is the function of three coordinates x, y and z. For the particle within the box, $V = 0$. Hence Eq. (19.95) takes the form

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \quad \ldots(19.96)$$

To solve this differential equation, it is convenient to separate the variables. For this purpose, ψ, which is a function of x, y and z is taken as equal to the product of three functions $X(x)$, $Y(y)$ and $Z(z)$, each in one variable, i.e.,

$$\phi = X(x) \cdot Y(y) \cdot Z(z) \quad \ldots(19.97)$$

or for the sake of simplicity, we may write it as

$$\phi = XYZ \qquad \ldots(19.98)$$

Substituting this value of ϕ in Eq. (19.96), we get

$$\frac{\partial^2(XYZ)}{\partial x^2} + \frac{\partial^2(XYZ)}{\partial y^2} + \frac{\partial^2(XYZ)}{\partial z^2} + \frac{8\pi^2 m}{h^2} EXYZ = 0$$

or

$$YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m}{h^2} EXYZ = 0$$

Dividing throughout by XYZ, we get

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E = 0$$

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -\frac{8\pi^2 m}{h^2} E \qquad \ldots(19.99)$$

Total energy E of the particle is constant. Therefore, RHS of Eq. (19.99) is constant and we may put

$$\frac{8\pi^2 mE}{h^2} = k^2.$$

So we may write Eq. (19.99) as

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -k^2 \qquad \ldots(19.100)$$

Thus, the sum of the three terms is constant. Suppose we change the value of x, keeping ψ and z constant, the sum of the three terms should be again equal to the same constant, viz. k^2. This indicates that the first term on LHS of Eq. (19.100) is not only independent of y and z but is also independent of x. Likewise, the second and the third terms must also be independent of x and z. In other words, each term on the LHS of Eq. (19.100) must be constant and the sum of the three constants should be equal to k^2. Hence, we may write

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -k_x^2 \qquad \ldots(19.101a)$$

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -k_y^2 \qquad \ldots(19.101b)$$

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -k_z^2 \qquad \ldots(19.102)$$

where k^2_x and k^2_y and k^2_z are constants such that

$$k_x^2 + k_y^2 + k_z^2 = k^2 \qquad \ldots(19.103)$$

and the values of these constants are as follows:

$$k^2x = \frac{8\pi^2 m E_x}{h^2} \qquad \ldots(19.104a)$$

$$k^2y = \frac{8\pi^2 m E_y}{h^2} \qquad \ldots(19.104b)$$

$$k_z^2 = \frac{8\pi^2 m E_z}{h^2} \qquad \ldots(19.104c)$$

where E_x, E_y, and E_z represent the components of the energy in the directions parallel to the X-axis, Y-axis and Z-axis respectively such that

$$E = E_x + E_y + E_z \qquad \ldots(19.105)$$

Equations (19.101) to (19.102) may be rewritten as

$$\frac{\partial^2 x}{\partial x^2} + k^2 X = 0, \quad \frac{\partial^2 Y}{\partial y^2} + k_y^2 Y = 0 \quad \text{and} \quad \frac{\partial^2 Z}{\partial z^2} = k_z^2 Z = 0$$

Each of these equations is of the same form as for a particle in a one-dimensional box.

The solutions of these equations are

$$X = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi}{a} x, \; Y = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi}{b} y$$

and

$$Z = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi}{c} z \qquad \ldots(19.106a)$$

and

$$E_x = \frac{n_x^2 h^2}{8ma^2}, \quad E_y = \frac{n_y^2 h^2}{8mb^2}, \quad E_z = \frac{n_z^2 h^2}{8mc^2} \qquad \ldots(19.106b)$$

where n_x, n_y and n_z having integral values represent three quantum numbers in directions parallel to the three axes.

The normalised wave function for a particle in a three-dimensional box is

$$\begin{aligned} \psi &= XYZ \\ &= \left(\sqrt{\frac{2}{a}} \sin \frac{n_x \pi}{a} x\right)\left(\sqrt{\frac{2}{b}} \sin \frac{n_y \pi}{b} y\right)\left(\sqrt{\frac{2}{c}} \sin \frac{n_z \pi}{c} z\right) \\ &= \left(\sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{b} y\right) \sin\left(\frac{n_z \pi}{c} z\right)\right) \end{aligned} \qquad \ldots(19.107)$$

The total energy *(E)* will be given by

$$\begin{aligned} E &= E_x + E_y + E_z \\ &= \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2} \end{aligned}$$

or

$$\boxed{E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \qquad \ldots(19.108)$$

Thus, three quantum numbers follow from the solution of the Schrodinger wave equation in three dimensions.

When the sides of the three-dimensional box are equal,

$$a = b = c$$

The equation for the energy of a particle in a three-dimensional box

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \text{ reduces to}$$

$$E = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \qquad \ldots(19.109)$$

The different combinations of the values of quantum number n_x, n_y and n_z may give the same value of the energy E. For example, the following six combinations of the values 1, 2 and 3 give the same value of E.

n_x	1	1	2	2	3	3
n_y	2	3	1	3	1	2
n_z	3	2	3	1	2	1

Such an energy level having different states of the system (different wave functions) but having the same energy is said to be ***degenerate*** and the number of independent wave functions associated with the given energy level is called its ***degeneracy***.

The degeneracies of a few energy levels with the different quantum numbers are given below:

n_x, n_y, n_z	111	211	221	311	222	321	322
Degeneracy	1	3	3	3	1	6	3

As an example, the three states corresponding to the quantum numbers 211 will have the quantum numbers 211, 121 and 112. All these states will have energy $= \frac{h^2}{8ma^2}(4 + 1 + 1) \frac{3h^2}{4ma^2}$ [obtained by putting the values of n_x, n_y and n_z in Eq. (19.109)]

This is illustrated in Fig. 19.29.

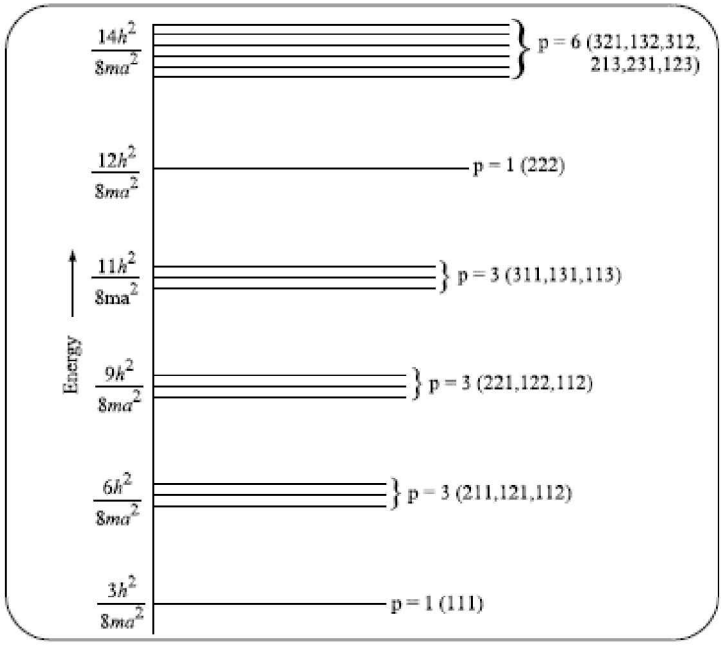


Fig. 19.29 *Representation of degeneracy level, for a particle in cubical box.*

It may be mentioned here that degeneracies arise in quantum mechanics when there is some element of symmetry. If the symmetry is broken, e.g. by taking a box whose sides have different lengths, the degeneracy disappears.

Example 15 *Calculate the expected ground-state energy of a hydrogen atom electron assumed to be present in a three-dimensional cubical box of 0.1 nm length if the ground-state energy of the electron in a one-dimensional box of 0.3 nm length is 4 eV.*

Solution: For a one-dimensional box, for ground state $n = 1$ so that

$$E_1 = \frac{n^2h^2}{8ma^2} = \frac{(1)^2\,(h)^2}{8m\,(0.3\times10^{-9})^2} = 4\text{ eV}$$

$$\frac{h^2}{8m} = 4\times(0.3\times10^{-9})^2 \qquad \ldots(i)$$

For a three-dimensional box for ground state,

$$n_x = n_y = n_z = 1 \text{ so that } E_{1,1,1} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

or
$$E_{1,1,1} = \frac{h^2}{8m(0.1\times10^{-9})^2}(1^2 + 1^2 + 1^2) \qquad \ldots(ii)$$

Substitute the value of $h^2/8m$ from Eq. (i) into Eq. (ii).

$$E_{1,1,1} = \frac{4 \times (0.3 \times 10^{-9})^2}{(0.1 \times 10^{-9})^2}(1^2 + 1^2 + 1^2) = 4 \times 3^2 \times 3 \text{ eV}$$

$$= 108 \text{ eV}$$

Example 16 *Calculate the energy required for a transition from $n_x = n_y = n_z = 1$ to $n_x = n_y = n_z = 2$ for an electron in a cubic hole of a crystal having edge length = 1 Å.*

Solution: The energy of a particle in a cubic hold (a three-dimensional box) is given by

$$E = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$$

Hence, $l = 1 \text{ Å} = 10^{-10}\text{m}$ $m = 9.11 \times 10^{-31}$ kg

$\therefore$ for $n_x = n_y = n_z = 1$

$$E_{1,1,1} = \frac{(6.626 \times 10^{-34})^2}{8(9.11 \times 10^{-31})(10^{-10})^2}(1^2 + 1^2 + 1^2) = 1.8072 \times 10^{-17} \text{ J}$$

For $n_x = n_y = 1, n_z = 2$

$$E_{1,1,2} = \frac{(6.626 \times 10^{-34})^2}{8(9.11 \times 10^{-31})(10^{-10})^2}(1^2 + 1^2 + 2^2) = 3.6144 \times 10^{-17} \text{ J}$$

Hence, $\Delta E = (3.6144 \times 10^{-17} - 1.8072 \times 10^{-17})\text{ J} = 1.8072 \times 10^{-17} \text{ J}$

Example 17 *An electron is confined to an infinite one-dimensional box of 4 Å width. Calculate its energy (in eV) in the fourth energy level.*

Solution: For a one-dimensional box,

$$E = \frac{n^2 h^2}{8mL^2}$$

Example 18 *An electron is confined to a molecule of 1 nm length. What is its minimum energy? What is the probability offinding it in the region of the molecule lying between x = 0 and x = 0.2 nm?*

Solution: The system of an electron confined to length of 1 nm is just like a particle in a one dimensional box, so energy is

For minimum energy $n = 1$, we get

The probability of finding the electron in the given region is

Example 19 *What will happen if the walls of the one-dimensional box are suddenly removed?*

Solution: When the walls of a one-dimensional box are suddenly removed, the particle in it becomes free to move without any restriction on the value of potential energy.

Accordingly, it can possess any value of energy, i.e. the energy of the particle is no longer quantised, rather it becomes continuous.

19.25 SCHRODINGER WAVE EQUATION IN TERMS OF POLAR (SPHERICAL) COORDINATES

The Schrodinger equation in three dimensions is

In order to apply it to hydrogen and hydrogen-like particles, if is convenient to express the above equation in terms of polar coordinates (r, θ, ϕ) (Fig. 19.30) for which the transformations are

Fig. 19.30 *Cartesian and spherical co-ordinates (PQ is perpendicular on the plane XOY)*

Substituting these values for x, y and z in Eq. (19.110) and simplifying, the Schrodinger equation is obtained in spherical coordinates as follows:

Schrodinger Wave Equation for Hydrogen-like Particles

The Schrodinger wave equation for the motion of a single particle is given by

where m is the mass of the particle, E is its total energy, V is its potential energy and x, y, z, are the coordinates of the particle.

For hydrogen-like particles, the mass m is replaced by the reduced mass (μ) of the system given by the equation

where m_e and m_n represent the mass of the electron and the nucleus respectively (as $m_e < m_n$, in fact $\mu \approx m_e$).

A hydrogen-like atom can have two types of motions, the revolution of the electron round the nucleus and the translational motion of the centre of mass. Taking only the revolution of the electron around the nucleus (assuming that the nucleus does not move), E will represent the electronic energy.

Thus, Eq. (19.112) for a hydrogen-like atom becomes,

Here, x, y, z, represent the coordinates of the centre of mass of the system.

This is the same equation as that of a single particle of mass μ (which is nearly equal to that of the electron) moving in a field of potential V.

For hydrogen-like particles, the electron is moving under the central force field of the nucleus. Hence, if $-e$ is the charge on the electron and $+Ze$ is the charge on the nucleus (Z being the atomic number of the element) and r is the distance between the electron and the nucleus, the value of V will be given by

Substituting this value of V in Eq. (19.114), the Schrodinger wave equation for hydrogen-like particles in terms of spherical coordinates, can be written using Eq. (19.113)

Force acting between the particles is given by

19.26 SEPARATION OF VARIABLES

ψ is a function of three variables r, θ and ϕ [Eq. (19.116b)]. To separate the variables, as before we suppose that $\psi(r, \theta, \phi)$ is a product of three functions $R(r)$, $\Theta(\theta)$ $\Phi(\phi)$, each being a function of one variable only, as indicated, i.e.

or for the sake of simplicity, we may write

Differentiating this equation to get different derivatives required in Eq. (19.116b) above and substituting these values in that equation,

Multiplying throughout by r^2 and dividing by $R\,\Theta\,\Phi$, we get

Writing the terms of the radial variables r on LHS and those of the angular variables θ and ϕ on RHS Eq. (19.118) takes the form

As r, θ and ϕ are independent variables, Eq. (19.119) holds good if each side is equal to the same constant, say equal to β. Thus,

(called the ***radical equation***)

(called the ***angular equation***)

To further separate the terms of θ and ϕ, multiply Eq. (19.121) throughout by $\sin^2\theta$. Thus,

Again this equation holds good if each side is equal to a constant. Using the constant as m^2, we get

Thus, the Schrodinger wave equation for the hydrogen-like atoms has been separated into three equations, viz. (19.122), (19.123) and (19.124) in r, θ and ϕ respectively.

For a hydrogen-like atom, it is found that $\beta = l\,(l + 1)$ where l is zero or an integer (i.e. $l = 0, 1, 2, 3, \ldots$)

19.27 EXPRESSIONS FOR ANGULAR SPHERICAL WAVE FUNCTIONS

The solutions of equations in θ and ϕ give the expressions for the angular wave function Θ and Φ Equation in the variable Φ (Eq. 19.124) is

Its solution to provide the normalised eigen function is

where $m = 0, \pm 1, \pm 2, \ldots \pm l$. The positive and negative values represent different possible solutions. Equation in the variable θ (Eq. (19.123)),

Its solution putting $\beta = l\,(l + 1)$ is

where $P_l^{|m|}$ represents associated Legendre polynomial of degree l and order m defined by the expression

in which $P_l(x)$ is defined by the expression

The solutions for the angular equation (19.121) given by $\Theta\ \phi$, are called ***spherical harmonics***. Their values depend upon the quantum numbers l and m. The first few spherical harmonics (angular wave functions) are given in Table 19.2.

Table 19.2 *First few spherical harmonics (angular wave functions for hydrogen-like atoms)*

19.28 EXPRESSION FOR THE RADIAL WAVE FUNCTION

The expression for the radial wave function (R) is obtained by solving Eq. (19.120) in the variable r. The complete solution of the equation being complicated, the expression for R is directly given as under:

where N is the normalisation constant, given by

ρ is the new variable in place of r, defined by

in which n is a new parameter defined by,

and a_0 is a constant defined by

and is called ***associated legendre polynomial*** in ρ of degree $(n + l) - (2l + 1)$ and order $(2l + 1)$. It is defined by the expression

in which $L_{n+l} = e$ is called Legendre polynomial of degree $n + l$ and is defined by

The above equations being quite complex for the level the book is meant for, the values for the normalised radical wave functions R for the first three values of n and the corresponding possible values of l are directly given in Table 19.3.

Table 19.3 *A few normalised radical wave functions for hydrogen-like atoms*

Expression for The Energy for Hydrogen-Like Particles

Rearranging Eq. (19.132), Sec. 19.27, we get

This expression gives the values of the energy corresponding to different values of n. Replacing μ by n_e (mass of the electron), we get an equation which was put forward by Bohr in which n corresponds to ***principal quantum number*** and can have integral values, i.e.,

$$n = 1, 2, 3, \ldots$$

From Eq. (19.136), it may be noted that the energy of the electron depends only on the value of the principal quantum number n and is independent of the values of l and n. Now as the quantum number n lies only in the radial wave function $R(r)$, it may be concluded that the energy of the electron depends only on its distance from the nucleus and not upon angular value.

Substituting the values of the various constants in Eq. (19.136), we get the value of E for hydrogenlike particles

For H-atom, $Z = 1$ and for ground state, $n = 1$. Hence, energy of the electron in the first Bohr orbit $(E_1) = -13.6$ eV. The energies of the electron in different excited states can be found by substituting the appropriate value of n. Similarly, the energies of electrons in ground state and different excited states for H-like particles can be calculated by substituting the corresponding values of Z and n.

19.29 QUANTUM NUMBERS FROM SCHRODINGER WAVE EQUATION

To solve the Schrodinger wave equation, it is first separated into three equations, each in one variable, i.e., r, θ, and ϕ. Each of these equations is then solved to obtain the expression for the functions $R(r)$, $\Theta(\theta)$ and $\Phi(\phi)$. The expression for these functions involve n, l and m. For example, the expression for R involves n and l that for θ involves l and m, and that for ϕ involves m only. Hence, we may write for the eigen function

It is found that the solutions of the Schrodinger wave equation obtained in terms of expressions for R, Θ and Φ are acceptable solutions only if they follow the following restrictions about n, l and m:

i.e. $-l$ to $+l$ including zero.

The values of n, l and m are the same as those for principal quantum number, azimuthal quantum number and magnetic quantum number respectively. Thus, these three quantum numbers can be obtained from the solutions of the Schrodinger wave equation.

19.30 CONCEPT OF ORBITAL

Heisenberg's uncertainty principle does not approve the Bohr's concept of definite orbitals. The quantum mechanical approach helps us calculate the value of ψ for an electron of known values of n, l and m. ψ^2 gives the probability of finding the electron at a point.

We can visualise three-dimensional space around the nucleus within which the probability of finding the electron under consideration is maximum. Such a three-dimensional space is called an ***orbital.*** This term is the quantum mechanical analogue of the term ***orbit.*** Depending upon the values of l, these orbitals or electrons are given the following symbols.

Value of l	Symbols for the orbital
0	s
1	p
2	d
3	f

Further, depending upon the value of l for a given value of n, the different orbitals or electrons are given different names as follows:

Values of n	Value of l	Designation of orbital
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d

19.31 SHAPES OF ORBITALS

The shape of an orbital can be found from the probabilities at different points around the nucleus. These can be obtained by finding the values of the wave function $\psi(r, \theta, \phi)$ (because ψ^2 gives the probability) which in turn is the product of the radial wave function $R(r)$ and the angular wave function $\Theta(\theta)\ \Phi(\phi)$. Representing their dependence on the quantum numbers n, l and m (i.e. the quantum numbers which they give on their solutions), we can write,

The radial wave function* R *gives the energy and size of the orbitals whereas the angular wave function Θ, Φ, gives the shape and orientation of the orbitals.

Before we take up the shapes of different orbitals, we shall observe the types of curves that are obtained when we plot ψ^2 versus distance (r) from the nucleus. Such plots are known as ***probability distribution curves***. However, since only $R(r)$ varies with r and the product $\Theta \cdot \Phi$ does not depend upon r, therefore plots ψ^2 versus r will be similar to those for $R(r)$. The values of the radial wave function R, for the electron in first two orbitals (Table 19.3) are as follows:

The plot of R^2 vs r obtained for the above two orbitals are as shown in Fig. 19.31.

Fig. 19.31 *Plots of $R^2_{1,0}$ versus r for electrons of 1s and 2s orbitals*

These plots, however, lead to unbelievable results. From these plots, we observe that $R^2_{n,l}$ should be maximum at $r = 0$. If $R^2_{n,l}$ represents the probability, this means that the probability of finding the electron should be maximum at the nucleus. But this cannot be true. This anomaly is solved by dividing the space around the nucleus into different concentric shells of small thickness dr and finding the probability in these shells. This probability is called ***radial probability***.

It is equal to the product of $R^2_{n,l}$ and volume of the shell of thickness dr is given by (Fig. 19.32)

Fig. 19.32 *Shell of thickness for around the nucleus*

As dr is very small, dr^2, dr^3, etc, can be neglected.

The radial probability distribution can be obtained by plotting $4\pi r^3 R^2_{n,l}$ versus r. Such plots are called ***radial probability distribution curves***. For 1 s and 2 s electrons, these plots are shown in Fig. 19.33.

Radial probability is the product of two terms, viz. $4\pi r^2$ and $R^2_{n,l}$. At the nucleus, though R^2 is large, $r = 0$. Hence, radial probability at the nucleus is zero. As r increases, $4\pi r^2$ increases but $R^2_{n,l}$ decreases. Hence, the plots of the type shown in Fig. 19.33 are obtained.

The radial probability distribution curves for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals are given in Fig. 19.34 for comparison.

The number of nodes, i.e. the regions at which the radial probability is zero = $n - l - 1$. The distance of the highest peak gives the ***radius of maximum probability***. In case of the hydrogen atom, it is 0.529 Å (Fig. 19.33) which is same as Bohr's radius. While Bohr's model postulates that the electron in a hydrogen atom revolves in a fixed orbit at a distance of 0.529 Å from the nucleus, the quantum mechanical model says that probability of finding the electron is maximum at a radius of 0.529 Å but the electron also keeps on moving closer or farther than this distance from the nucleus.

Fig. 19.33 *Radial probability distribution curves for 1s and 2s electrons*

Fig. 19.34 *Radial probability distribution curves for 1 s, 2s, 2p; 3s,3p and 3d orbitals*

Another important feature may be observed by comparing the radial probability distribution curves of 3*s*, 3*p* and 3*d* electrons. Their radii of maximum probability are in the order $3s > 3p > 3d$. In other words, 3*s* is more penetrating than 3*p* or 3*d* electrons. Thus, their probability of occurrence closer to the nucleus is in the order $3s > 3p > 3d$.

1. Shapes of s-orbitals For an *s*-orbital, $l = 0$. Hence, $m = 0$.

The angular wave function is given by,

Thus, the angular wave function for the s-orbital is independent of the angles of θ and ϕ. This means that it will have symmetrical geometry in all directions. Hence, an *s*-orbital has a ***spherical*** shape. However, 1*s* has no radial node, 2*s* has one and 3*s* has two radial nodes. They will have the shapes as shown in Fig. 19.35.

Fig. 19.35 *Shapes of 1s, 2s and 3s orbitals.*

2. Shapes of p-orbitals For any *p*-orbital, $l = 1$. Hence, $m = +1, -1, 0$. Their angular wave functions as given in Table 19.2 are represented as under

To convert these angular wave functions into shapes of *p*-orbitals, we change them into cartesian coordinates, using the relations

Substituting these values, equations (19.138a, b, c) take the form

Thus, it may be seen that these wave functions are functions of x, y and z respectively. Hence, they are called p_x, p_y, and p_z wave functions. Any of these wave functions when plotted in the three-dimensional space gives a ***dumb-bell*** shape as shown in Fig. 19.36. Plots show that when x, y, z are

positive, these functions are also positive and when x, y, z, are negative, these functions are negative.

Fig. 19.36 *Shapes of p_x p_y and p_z orbitals.*

3. Shapes of d-orbitals For a d-orbital, $l = 2$. Hence, $m = -2, -1, +1, +2$, and 0. Thus, there are five d-orbitals. Their corresponding angular wave function, (Table 19.2) and their values after changing into cartesian coordinates (as done in case of p-orbitals) are given below:

Thus, it may be seen that these wave functions vary with xy, yz, xz, $x^2 - y^2$, $x^2 - y^2$ and z^2 respectively. Hence, they are represented by d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2} respectively. When we plot the wave functions in the three-dimensional space, we get the shapes as shown in Fig. 19.37.

The first three shapes are double dumb-bell shapes lying ***between*** the ***axes***. The fourth is also a double dumb-bell shape but ***lying along the axes***. The fifth (d_{z^2}) is a dumb-bell shape ***symmetrical about z-axis but*** with a *dough-nut* shape in the centre in the xy plane. The signs of the wave functions may be explained by taking the example of the wave function (1). If x and y both are positive or both are negative then as xy will be positive, the wave function will be positive. If either x or y is negative then as xy will be negative, the wave function will also be negative. The signs of the wave functions (2) and (3) can be explained in a similar manner. In the wave function (4), x may be positive or negative, x^2 will always be positive whereas y may be positive or negative, $-y^2$ will always be negative. Hence, lobes along the x-axis are always positive while those along the y-axis are always negative. In the wave function (5), as z^2 is always positive, lobes along the z-axis are always positive but the dough-nut (in the xy plane) has a negative sign.

Fig. 19.37 *Shapes of d-orbitals*

Further, the shapes of 4d orbitals will be similar to those of 3d-orbitals. They will differ in two aspects, size of 4 d orbitals will have one node whereas 3 d orbitals will have no node. Number of radial nodes in any orbital = $n - l - 1$.

The following two results may be kept in mind while solving problems on quantum mechanics.

1. Just as in cartesian coordinates, volume element $d\tau = dx\, dy\, dz$, in polar coordinates, $d\tau = r^2\, dr \sin\theta\, d\theta\, d\phi$.
2.

Example 20 *Show that 1 s and 2 s wave functions of the hydrogen atom given by*

are orthogonal to each other.

Solution: ψ_{1s} and ψ_{2s} will be orthogonal to each other if they satisfy the following condition

For polar coordinates, putting $d\tau = r^2 dr \sin\theta\, d\theta\, d\phi$, we have

The first two integrals may be solved by applying the formula

Solution of the other two integrals is given below:

Thus, the condition of orthogonality is satisfied. We can say that 1s and 2s the wave functions of the hydrogen atom are othogonal to each other.

Example 21 *Prove that the 1s wave function of the hydrogen atom given by*

is a normalised wave function where a_0 represents Bohr radius.

Solution: The wave function ψ_{1s} will be a normalised wave function if it satisfies the following condition:

In polar coordinates, volume element $d\tau = r^2 dr \sin\theta\, d\theta\, d\phi$
Substituting this value of $d\tau$ and given value of ψ_{1s},

Each of the integrals may be solved separately as follows:
Evaluate the first integral using the formula

Thus, the condition of the normalised wave function is satisfied. Hence, it is a normalised wave function.

Example 22 *Calculate the average distance of the electron from the nucleus in the ground state of the hydrogen atom. Given that the normalised wave function for 1 s electron of hydrogen atom is*

Solution: The average value of the distance, i.e. the variable r is equal to the expectation value which is calculated by using the following formula

In the present case,

Example 23 *How do spectral distribution curves of black-body radiation prove (a) Stefan-Boltzmann's law, and (b) Wien displacement law?*

Solution:

(i) The area under the curve at any temperature gives the total energy emitted by a black body per second. The area is found to be proportional to fourth power of temperature. Hence, $E_B \propto T^4$. This is Stephen-Boltzmann's law.

(b) Product of the wavelength (λ_m) corresponding to maximum emittance and temperature is constant, that is

This is Wien displacement law.

Example 24 *Name the basic principles on which (a) classical mechanics is based, and (b) quantum mechanics is based. Name the phenomena which the classical mechanics fails to explain but quantum mechanics can explain.*

Solution: Classical mechanics is based on Newton's laws of motion and electromagnetic wave theory. Quantum mechanics is based on Heisenberg's uncertainty principle, de Broglie concept of dual nature of matter, Schrodinger wave equation and Planck's quantum theory. Classical mechanics fails to explain black-body radiation, photoelectric effect, heat capacities of solids, and atomic and molecular spectra, while a satisfactory explanation of these phenomena is provided by quantum mechanics.

Example 25 *What is the difference in heat capacities of solids when classical mechanics is applied*

and when quantum mechanics is applied.

Solution: When classical mechanics is applied, the heat capacity of all mono-atomic solids comes out to be constant and equal to $3R$ (Dulong and Petit's law). Experimentally, it is found to be true only at a high temperature. At low temperature, the value is found to be less than $3R$ and decreases with decrease of temperature. Quantum mechanics is able to explain the anomalies.

Example 26 *What is Compton effect? Write expression for Compton shift. Prove that Compton shift is doubled if the angle between the incident and the scattered rays is doubled from 90° to 180°.*

Solution: *Compton effect* states, "If monochromatic X-rays are allowed to hit a material of low atomic weight, e.g. graphite, the scattered radiations contain not only wavelengths of that of the incident X-rays but also contain radiations of higher wavelengths.''

Expression for Compton shift is given by the relation

where θ is the angle between the incident and the scattered X-rays.

Example 27 *What are the conditions which an eigen function (ψ) must satisfy?*

Solution:

(a) ψ must be single valued and finite.

(b) ψ must be continuous.

(c) ψ must become zero at infinity.

Example 28 *What is the commutator of two operators $\hat{A}$ and $\hat{B}$? When are the operators said to commute?*

Solution: Commutator of two operators $\hat{A}$ and $\hat{B}$, represented as $[\hat{A}, \hat{B}]$, is given by

If $\hat{A}\hat{B} = \hat{B}\hat{A}$ so that $[\hat{A}, \hat{B}] = 0$, the operators are said to commute.

Example 29 *What is a sinusoidal wave equation?*

Solution: The upward displacement (y) of a wave at any time (t) travelling in the x-direction with velocity v, wavelength λ, frequency ν and amplitude A is represented as

This is called sinusoidal wave equation

Example 30 *Write expressions for the following:*

(a) Probability of finding electron in a small volume element in terms of

(i) Cartesian coordinates

(ii) Polar coordinates

(b) Condition for a normalised wave function

(c) Condition for orthogonality of two wave functions.

Solution:

(a) (i) Probability = $\psi\psi^* d\tau = \psi\psi^* \, dx \, dy \, dz$ (in Cartesian coordinates)

(ii) Probability = $\psi\psi^* r^2 dr \sin\theta \, d\theta \, d\phi$ (in polar coordinates)

(b) For a wave function ψ to be a normalised wave function, the following condition is to be

satisfied.

(c) For two wave functions ψ_m and ψ_n to be orthogonal to each other, the following condition is to be satisfied.

Example 31 *The angular wave function ($\Theta\Phi$) for the one of the d-orbitals is given by*

Prove that opposite lobes of the d-orbitals have the same sign.

Solution:

If *x* and *y* are both positive or both negative, *xy* will be positive. Hence, the wave function will be positive as seen in the lobes with positive sign. If either *x* or *y* is negative then *xy* will be negative and hence, wave function will be negative as seen in the lobes with negative sign.

Example 32 *What happens to the energy of the particle in a one-dimensional box if the length of the box is made larger?*

Solution: Energy of the particle in a one-dimensional box is given by

If '*a*' is made larger, values of *E* becomes smaller. Consequently, energy levels move close together. If the box length becomes very large, quantisation disappears and there is a smooth transition from quantum behaviour to classical behaviour. This is called Bohr's *correspondence principle.*

Example 33 *Normalise the wave function by finding the value of the constant A when the particle is restricted to move in a one-dimensional box of width 'a'.*

Solution: For a normalised wave function

Example 34 *Knowing the wave function of a system, how is energy of the system calculated?*

Solution: According to the Schrodinger wave equation,

Multiplying both sides of the equation with ψ^* and integrating over the space ($-\infty$ to $+\infty$),

As *E* is constant, this equation can be written as

If ψ is a real function, the above equation can be written as

where Hamiltonian operator

SUMMARY

1. The branch of science based on Newton's laws of motion and Maxwell's electromagnetic wave

theory to explain motion and energy is called *classical mechanics*.

2. Classical mechanics does not provide satisfactory explanation for *black body radiation, photoelectric effect, atomic and molecular spectra and heat capacities of solids*.
3. A body that completely absorbs radiant energy falling on it is called a perfectly *black body*.
4. *Kirchhofs law:* At any temperature, the ratio of emissive power (or emittance) of a body to the absorptive power is constant, independent of the nature of the surface and is equal to the emissive power of a perfectly black body.
5. *Wien's displacement law:* The wavelength λ_m for which the emittance of a black body is maximum is inversely proportional to its absolute temperature.
6. According to Planck's radiation law, energy is emitted or absorbed not continuously but discontinuously in the form of packets of energy called *quanta*.
7. When a beam of light with frequency equal to or greater than a particular value (called threshold value) is allowed to strike the surface of a metal, electrons are ejected instantaneously from the surface of the metal. This is called *photoelectric effect*.
8. The branch of science which takes into consideration de Broglie concept of dual nature of matter and Planck's quantum theory and is able to explain the phenomenon related to small particles is known as *quantum mechanics*.
9. de Broglie advanced the idea that all material particles such as electrons, protons, atoms, molecules, etc., possessed *dual character of matter and wave*.
10. According to *Heisenberg uncertainty principle*, the position and velocity of a particle cannot be measured simultaneously with certainty.
11. Three dimensional space around the nucleus within which probability of finding the electron under consideration is maximum is called orbital.
12. The radial wave function gives the energy and size of the orbital whereas the angular wave functions give the shape and orientation of the orbitals

KEY RELATIONS

1. Kirchhoff's law:
2. Stephan's fourth power law: $E = \sigma T^4$
3. Boltzmann's law: $\lambda_m T$ = constant
4. Planck s radiation law:
5. Heisenberg uncertainty principle:
6. Compton effect:
7. Schrodinger wave equation:
8. Normalised wave function: $\oint \psi_i \psi^*_i \, d\tau = 1$

   Orthogonal wave function: $\oint \psi_i \psi^*_j \, d\tau = 0$
9. Particle in a one-dimensional box:
10. Particle in a three-dimensional box

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. Classical mechanics does not provide satisfactory explanation for the following:
   (a) Black-body radiation
   (b) Photoelectric effect
   (c) Heat capacities of solids
   (d) All the above
2. A quantitative relationship between the energy absorbed and energy emitted by a body was forward by
   (a) Einstein
   (b) Kirchhoff
   (c) Hess
   (d) Fermi
3. Total amount of energy emitted by a perfectly black body per unit area per unit time is directly proportional to
   (a) T
   (b) T^2
   (c) T^4
   (d) T^3
4. The Schrodinger wave equation in three dimensions is given by
   (a)
   (b)
   (c)
   (d)
5. Expression for energy for a particle in a one-dimensional box is
   (a)
   (b)
   (c)
   (d)
6. Compton shift in the scattered radiations $\Delta\lambda$ is given by
   (a)
   (b)
   (c)
   (d)

Answers

1. (d)
2. (b)
3. (c)
4. (a)
5. (a)
6. (c)

SHORT-ANSWER QUESTIONS

1. State and explain Kirchhoff's law about black body radiation.
2. List the main points of difference between classical mechanics and quantum mechanics. What is the relation between the two?
3. What do you understand by a 'normalised eigen function'? How do we normalise a wave function?
4. How can you explain that the energy of a free particle is not quantised?
5. How does the study of particle in three-dimensional box in quantum mechanics lead to the concept of degeneracy?
6. What are probability distribution curves? What is their shortcoming? How is it overcome by radical probability distribution curves?
7. With the help of the phenomenon of black body radiation, explain how classical mechanics failed and it led to the origin of quantum mechanics.
8. What is a sine wave? Give examples of sine waves. Write an expression for it. What type of plots do we get keeping time or position constant? What is a sinusoidal wave equation?
9. Write the expression for energy for the particle in a one-dimensional box. How can you justify

   (a) quantisation of energy?

   (b) existence of zero point energy?
10. What do you understand by expectation value of an observable in quantum mechanics?

    Write expressions for the expectation values of (a) position x, and (b) any other observable G (e.g. momentum).
11. How do the three quantum numbers follow from the solutions of Schrodinger wave equation?
12. Show that the normalised wave functions of a particle in a one-dimensional box are orthogonal for any pair of different values of n.
13. What do you understand by eigen value and eigen function? What are the conditions which eigen functions must satisfy?
14. Write an expression for the energy of hydrogen-like atoms as obtained by quantum mechanics. How is it identical with the expression obtained by Bohr?
15. How does classical mechanics fail to explain the spectral distribution of black-body radiation? What is Planck's radiation law? How do Wien's law and Rayleigh Jean's law follow from it?
16. How do we proceed to find out the probability if ψ does not come out to be real?
17. When are the two eigen functions said to be (a) mutually orthogonal, and (b) orthonormal?
18. Why does quantum mechanics lead to the concept of orbital?
19. Write the expression for the angular and the radial wave function. What do different symbols signify?

GENERAL QUESTIONS

1. What is 'classical mechanics'? "What are its limitations? Name the two mechanics that have been put forward to overcome the limitations of classical mechanics. Name the scientists responsible for each of them. What is the basic difference between the two mechanics?
2. Briefly describe the spectral distribution of black-body radiation. How do the following laws follow from it?

   (a) Stefan-Boltzmann's law

   (b) Wien's displacement law

3. What is Compton effect? What is Compton shift? Write the expression for Compton shift and explain the results obtained for scattering angles of 0°, 90° and 180°. How does it explain the results of Heisenberg's uncertainty principle?
4. What is the concept of particle in a one-dimensional box? What is the Schrodinger wave equation for such a case? How can this equation be solved for ψ and E?
5. Write the Schrodinger wave equation for hydrogen-like atom in spherical polar coordinates. How can you separate the variables in this equation to get expressions each containing one variable only?
6. Derive expressions for standard derivations in x and p_x and hence deduce Heisenberg's uncertainty principle.
7. State and explain Heisenberg's uncertainty principle.
8. What is an operator? When are operators said to commute? Explain with an example that the operators usually do not commute. What is the commutator of the two operators $\hat{A}$ and $\hat{B}$? What is its value when the operators commute?
9. Derive expression for the eigen function for a particle in a one-dimensional box. How can this function be normalised? Write an expression for normalised wave function.
10. Briefly explain Born's interpretation of wave function or explain the significance of wave function (ψ).
11. Using the concept of quantum mechanics, describe the shapes of s, p and d-orbitals.
12. What do you understand by radial probability? Draw and discuss radial probability distribution curves for 1s, 2s, 3s, 3p and 3d orbitals.
13. Derive Planck's radiation law. How can it be verified experimentally?
14. Briefly explain how classical mechanics fails when applied to the following:
    (a) Photoelectric effect
    (b) Heat capacity of solids.
15. Briefly explain de Broglie hypothesis related to dual nature of matter. Derive the de Broglie relation. How has the dual nature of electrons been verified experimentally?
16. Applying de Broglie relationship, derive Schrodinger wave equation.
17. Derive expressions for the expectation values of x, x^2, p_x and p^2_x.
18. Apply Schrodinger wave equation to a particle in one-dimensional box and obtain the expression for the eigen function and eigen value of the energy.
19. What are the main postulates of Bohr model of atom? What are its defects?
20. What is the basic equation on which quantum mechanics is based? Derive the equation in the usual form.
21. What are the postulates of quantum mechanics? Based on the postulates of quantum mechanics, derive the Schrodinger wave equation.
22. Describe expression for the normalised eigen function for a particle in a three-dimensional box.
23. Derive expression for the total energy for a particle in a three-dimensional box.
24. On the basis of angular wave functions, justify the different designations given to three p-orbitals and five d-orbitals
25. Evaluate the commutator

[Ans. 0]



Quantum Mechanics and Chemical Bonding

20

LEARNING OBJECTIVES

- Correlate chemical bonding and quantum mechanics.
- Understand valence bond theory and apply it to study H_2 molecule
- Learn molecular orbital theory
- Understand linear combination of atomic orbitals (LCAO)
- Visualise the physical picture of bonding and antibonding wave functions
- Learn the main points about bonding and antibonding molecular orbitals
- Study the variation of electron probability density along internuclear axis in bonding and antibonding molecular orbitals
- Understand the formation of molecular orbitals from atomic orbitals
- Learn the concept of σ, σ^*, π and π^* orbitals and their characteristics
- Understand the concept of hybridization and quantum mechanical principles of hybridization
- Calculate the coefficients of atomic orbitals in different hybrid orbitals
- Compare valence bond and molecular-orbital models.

20.1 QUANTUM MECHANICS AND CHEMICAL BONDING

There are two theories to explain the nature of chemical bonding and to predict the properties of molecules such as bond distance, bond dissociation energy, dipole moment, etc. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). According to VBT, atoms are considered to retain their ***identity*** and a bond is formed as a result of interaction of only the **valence electrons** of the atoms, (i.e. half-filled orbitals overlap to form a covalent bond). Fully filled orbitals do not participate in bonding. Molecular orbital theory considers the molecule as a collection of nuclei and all the electrons of the molecule are distributed in different energy levels of a group of nuclei. Energy levels of an atom are called atomic orbitals, while the energy levels of the molecule are called molecular orbitals. According to MOT, all the atomic orbitals of an atom overlap with atomic orbitals of comparable energy of the other atoms. These theories are being discussed separately.

20.2 VALENCE BOND THEORY

It was put forward by Heitler and London in 1927 and was further extended by Slater and Pauling. Some basic quantum mechanical principles involved in the theory are given below:

1. The total wave function (ψ) of two independent systems with wave functions ψ_A and ψ_B is equal

to their product, i.e. it is given by

$$\psi = \psi_A \psi_B \qquad \ldots(20.1)$$

2. The total energy (E) of the two independent systems with energies E_A and E_B is equal to their sum.

$$E = E_A + E_B \qquad \ldots(20.2)$$

3. The total Hamiltonian is also equal to the sum of their values for independent systems.

$$\hat{H} = \hat{H}_A + \hat{H}_B \qquad \ldots(20.3)$$

4. For many-electron systems, the total wave function is a linear combination of the different wave functions involved, i.e.

$$\psi = c_1\psi_1 + c_2\psi_2 + \ldots \qquad \ldots (20.4)$$

where coefficients c_1, c_2, etc., are found by variation method so that ψ is closest to the true wave function corresponding to which the energy of the system is minimum.



Fig. 20.1 *Walter Heitler (1904-1981) was a German physicist who made contributions to the quantum field theory. He brought chemistry under quantum mechanics through his theory of valence bonding.*



Fig. 20.2 *Fritz London was a German-American theoretical physicist. His fundamental contributions to the theories of chemical bonding and of intermolecular forces are today considered classic and are discussed in standard textbooks of physical chemistry.*

5. The square of the coefficient of any function gives the contribution of that wave function towards total wave function and is usually called the ***weight*** of that wave function. For the function ψ to be normalised, the following condition must be satisfied.

$$c_1^2 + c_2^2 + c_3^2 + \ldots = 1 \qquad \ldots (20.5)$$

20.2.1 Application of Valence Bond Theory to the Study of H_2 Molecule

We start with two hydrogen atoms separated by a large distance so that there are no forces of interaction between them and the energy of the system is taken as zero. Let the two H atoms be represented by H_A and H_B and the associated electrons by e_1 and e_2 respectively. Thus, the two H-atoms may be represented as $H_A(e_1)$ and $H_B(e_2)$. Also, suppose the wave functions associated with these electrons are represented by $\psi_A(1)$ and $\psi_B(2)$ respectively. The total wave function for the two separated hydrogen atoms will be given by

$$\psi = \psi_A(1)\, \psi_B(2) \qquad \ldots (20.6)$$

If we plot the value of E as a function of intermolecular distance, a curve I is obtained as shown in Fig. 20.3. It may be seen that energy of the system decreases with distance till a minimum is reached. This represents the formation of the H_2 molecule. The decrease in energy corresponding to this minimum represents the bond energy and the distance represents the bond length. This curve has been obtained by using the wave function as represented by Eq. (20.6). The bond energy is found to be only 24 kJ mol^{-1} while the actual (experimental) value is 458 kJ mol^{-1}. Similarly, bond distance is fond to be 90 pm which is much different from the actual bond length of the H_2 molecule, viz. 74 pm. This shows that the wave function used in the above calculations, viz. $\psi_A(1)$ $\psi_B(2)$ is not accurate. Hence, some other interactions between the two hydrogen atoms are taking place and need to be taken into consideration to arrive at a better wave function. The different possible interactions are discussed as under:

1. Exchange of Electrons In writing the above wave function, it was assumed that the electron e_1 belongs to H_A and e_2 belongs to H_B. However, as the electrons are actually indistinguishable after the overlap of the two atomic orbitals, electron e_1 may be under the influence of the, nucleus of H_B and also the electron e_2 may be under the influence of the nucleus of H_A. Thus the system may exist in two different states as follows:

$$\text{(i) } H_A(e_1)\, H_B(e_2) \qquad \text{(ii) } H_A(e_2)\, H_B(e_1) \qquad \ldots (20.7)$$

The wave functions corresponding to these two states may be written as

$$\psi_{\text{I}} = \psi_A(1)\, \psi_B(2), \quad \psi_{\text{II}} = \psi_A(2)\, \psi_B(1) \qquad \ldots (20.8)$$

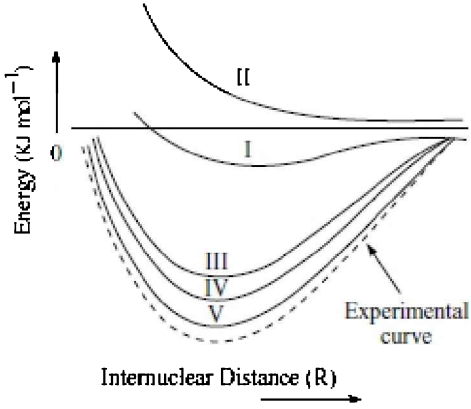


Fig. 20.3 *Variation of energy with internuclear distance for H_2 molecule*

The total wave functions of the system will then be a linear combination of the above two wave functions, i.e.

$$\psi_{VB} = c_1\psi_{\text{I}} \pm c_2\ \psi_{\text{II}}$$

$$= c_1\psi_A(1)\ \psi_B(2) \pm c_2\psi_A(2)\ \psi_B(1) \qquad \ldots(20.9)$$

For H_2 molecules, as both atoms are same, put $c_1 = c_2 = 1$. Hence

$$\psi_{VB} = \psi_A(1)\ \psi_B(2) \pm \psi_A(2)\ \psi_B(1) \qquad \ldots(20.10)$$

Thus, there are two possible linear combinations of the wave functions corresponding to wave functions represented by ψ_+ and ψ_-, i.e.

$$\psi_+ = \psi_A(1)\ \psi_B(2) + \psi_A(2)\ \psi_B(1) \qquad \ldots(20.11)$$

$$\psi_- = \psi_A(1)\ \psi_B(2) - \psi_A(2)\ \psi_B(1) \qquad \ldots(20.12)$$

If the energies are calculated as a function of intermolecular distance by employing the wave function ψ_-, the curve II is obtained which shows that energy increases when the atoms are brought close together. This represents a ***nonbonding state.*** On the other hand, if energies are calculated as a function of intermolecular distance by using the wave function ψ_+, the curve III is obtained. It represents decrease of energy with minimum at particular distance and hence represents a ***bonding state***.

Using this wave function, the minimum in the curve is found to be at 303 kJ mol^{-1} at an internuclear distance of 80 pm. Thus, both the values have come closer to the experimental values. ***The extra lowering of energy is due to the exchange of electrons between the two hydrogen atoms and is called exchange energy.*** Thus, exchange energy for H_2 molecule = 303 − 24 = 279 kJ mol^{-1}.

2. Screening Effect of Electrons When the atoms come close together, the electron of one atom shields the electron of the other atom from the nucleus. Thus, the electron does not feel full attraction by the nucleus. Thus, its effective nuclear charge is smaller than the actual nuclear charge. Taking this fact into consideration, the wave function was further improved. Using this wave function, energy versus internuclear distance curve IV is obtained as shown in Fig. 20.3. The minimum in this curve lies at 365 kJ mol^{-1} which shows a further improvement in the value.

3. Ionic Structure for H_2 Molecule Since the calculated value of 365 kJ mol^{-1} is still much lower than the experimental value of 458 kJ mol^{-1}, it requires further improvement in the wave function. It was suggested that when the atoms come closer together, both the electrons may lie close to the nucleus H_A or close to the nucleus H_B, giving rise to two possible ionic structures as

represented below

$$\text{III}\quad \overset{(e_1)}{\underset{(e_2)}{H_A H_B}} \qquad \text{IV}\quad \overset{(e_1)}{\underset{(e_2)}{H_A H_B}} \qquad \ldots(20.13)$$

$$(H_A^- H_B^+) \qquad (H_A^+ H_B^-)$$

Though the possibility of existence of these states is very little because repulsions between the electrons will be much larger than the attractions between H_A^- and H_B^+ or H_A^+ and H_B^-, yet by taking these structures into consideration, the wave function could be further improved. The wave functions corresponding to states III and IV may be written as

$$\psi_{III} = \psi_A(1)\ \psi_A(2)$$
$$\psi_{IV} = \psi_B(1)\ \psi_B(2) \qquad \ldots(20.14)$$

The total wave function due to these ionic structures (represented by ψ_{ionic}) may be obtained by a linear combination of ψ_{III} and ψ_{IV}. Thus,

$$\psi_{ionic} = \psi_{III} + \psi_{IV} = \psi_A(1)\ \psi_A(2) + \psi_B(1)\ \psi_B(2) \qquad \ldots(20.15)$$

Now combining the covalent and ionic wave functions, the complete wave function for the system may be written as

$$\psi = \psi_{covalent} + \lambda\psi_{ionic}$$
$$= [\psi_A(1)\ \psi_B(2) + \psi_A(2)\ \psi_B(1)] + \lambda[\psi_A(1)\ \psi_A(2) + \psi_B(1)\ \psi_B(2)] \qquad \ldots(20.16)$$

where λ gives the extent of contribution of the ionic structures towards bonding and is usually called ***mixing coefficient***. Its value for H_2 is found to be 0.17.

Using the above wave function, the minimum in the curve (shown at V) is obtained at 388 kJ mol^{-1}, thus bringing the value still closer to the experimental value of the bond energy of 458 kJ mol^{-1}. The bond distance is found to be 75 pm which agrees fairly well with the experimental value of 74 pm.

Further improvement in the wave function have been done but these will not be discussed here.

It may be mentioned that valence bond theory leads to the concept that a molecule or ion may exist in different structures, none of which represents the actual structure and the actual structure is in between the different structures. This phenomenon is called ***resonance*** and the different structures are called ***resonating structures.*** Thus, the concept of resonance follows from VBT.

20.3 MOLECULAR ORBITAL THEORY

This theory developed by Hund, Mulliken, Huckel and others differs from valence bond theory mainly in the fact that the electron in a molecule is not considered to be under the influence of a particular nucleus but is under the influence of all the nuclei present. The total wave function is the product of the wave functions for various electrons involved in bonding. The main points of the theory are listed below:

1. A molecule is considered as a group of nuclei and all the electrons are distributed around this group in different energy levels like in an atom, the electrons are distributed in different energy levels around a single nucleus. The energy levels of a molecule are called molecular orbitals. While the atomic orbitals are ***monocentric,*** the molecular orbitals are ***polycentric***.
2. Each electron or each molecular orbital in the molecule is described by a wave function, (called molecular orbital wave function), the correct value of which can be found by a method called Linear Combination of Atomic Orbitals (LCAO method).
3. Each molecular orbital is associated with a definite amount of energy, the correct value of which can be calculated by applying the Schrodinger wave equation.

4. The significance of the molecular orbital wave function is same as that of the atomic orbital wave function. Thus, just as in an atom, $\psi^2 \, d\tau$ gives the probability of finding the electron in a volume element $d\tau$, in a molecule, $\psi^2 d\tau$ gives the ***probability density*** or ***electron charge density*** in the volume element $d\tau$.
5. The size, shape and energy of molecular orbitals depend upon the size, shape and energy of combining atomic orbitals. The atomic orbitals combining together lose their identity to form molecular orbitals.
6. Only those atomic orbitals combine to form molecular orbitals which have comparable energies and same symmetry with respect to the molecular axis such that sufficient overlapping is possible.
7. The filling of electrons into molecular orbitals takes place according to the same rules as followed by atomic orbitals, viz. Aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity.

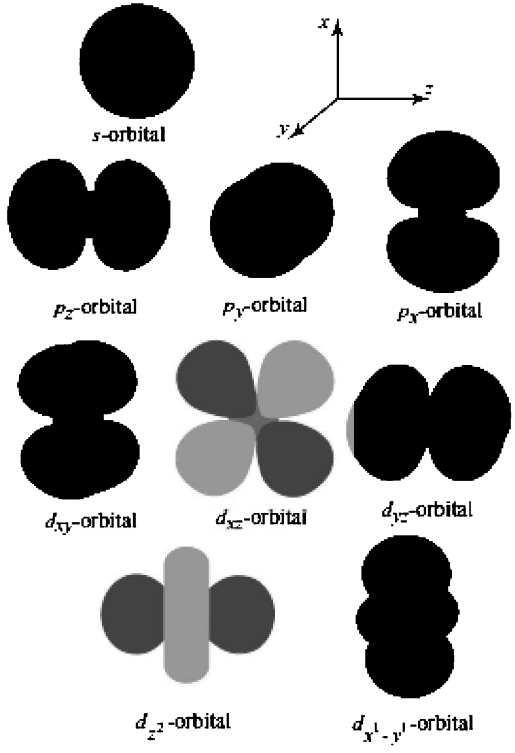


Fig. 20.4 *Three-dimensional shapes of atomic orbitals*

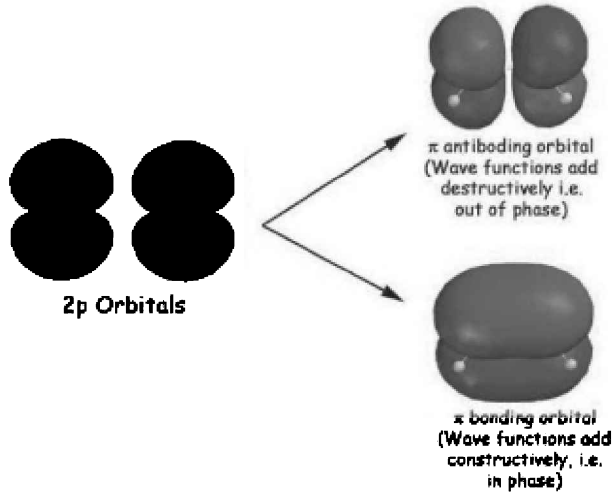


Fig. 20.5 *Formation of π-bonding and π-antibonding molecular orbitals*

Linear Combination of Atomic Orbitals (LCAO) H_2^+ Ion

We can construct a molecular orbital wave function by an approximation of Linear Combination of Atomic Orbitals, in short called ***LCAO approximation.*** To understand this method, let us consider the simplest case of hydrogen molecular ion (H_2^+).

The H_2^+ ion consists of two protons H_A and H_B separated by a distance R and only one electron. The electron is considered moving in a molecular orbital under the influence of both the nuclei. When at some point of time, the electron is in the neighborhood of A (State I, shown in Fig. 2), it will behave as if it were moving in the atomic orbital of H_A and the effect of the nucleus of H_B will be negligible. Similarly, at some other point of time, the electron may be in the neighborhood of H_B so that the influence of the nucleus of H_A on the electron is negligible and the electron will behave as if it were moving in the atomic orbital of H_B (State II).

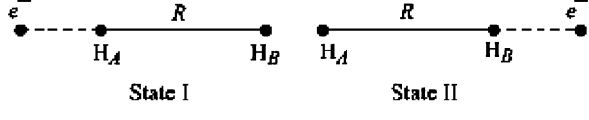


Fig. 20.2 *Two extremes in H_2^+ ion*

In the first case, the wave function of the electron will be ψ_A (i.e. like that of the electron in the atom H_A) and in the second case, the wave function of the electron will be ψ_B (i.e. like that of the electron in atom H_B). In between these two extremes, the electron may be under the influence of both the nuclei and hence may have characteristics of both the wave functions ψ_A and ψ_B. The wave function of the system, called ***molecular orbital wave function*** (ψ_{MO}) is then obtained as a linear combination of ψ_A and ψ_B according to the expression.

$$\psi_{MO} = c_1\psi_A + c_2\psi_B \qquad \ldots(20.17)$$

where c_1 and c_2 are coefficients of the wave functions ψ_A and ψ_B such that their squares, i.e. c^2_1

and c^2_2 give their contribution (weightage) towards the molecular orbital wave functions.

The coefficients c_1 and c_2 are found by variation method which gives minimum value of the energy E. The condition for getting minimum energy with respect to coefficients c_1 and c_2 is that we put $\partial E/\partial c_1 = 0$ and $\partial E/\partial c_2 = 0$. Combining results of different equations, we get a quadratic equation giving two values of E. These are represented by E_+ and E_-. The symbol E_+ represents molecular orbital with energy higher than of the combining atomic orbitals. These values are then substituted separately in the quadratic equation in the energy obtained above and we get two equations in terms of c_1 and c_2. Applying the normalisation condition for the molecular orbital wave function, we can calculate the values of c_1 and c_2 for the two molecular orbitals (one with energy E_+ and the other with E_-) as explained below:

As one of the basic principles of quantum mechanics, the function ψ is the acceptable solution of the Schrodinger wave equation only if it is normalised, i.e. it must satisfy the condition

$$\int \psi^2_{MO}\, d\tau = 1 \qquad \ldots(20.18)$$

i.e. $$\int (c_1\psi_A + c_2\psi_2)^2\, d\tau = 1 \qquad \ldots(20.19)$$

or $$\int c_1^2\, \psi_A^2\, d\tau + \int c_2^2\, \psi_B^2\, d\tau + \int 2c_1c_2\psi_A\psi_B\, d\tau = 1$$

or $$c_1^2 \int \psi_A^2\, d\tau + c_2^2 \int \psi_B^2\, d\tau + 2c_1c_2 \int \psi_A\psi_B\, d\tau = 1 \qquad \ldots(20.20)$$

As the atomic orbital wave functions ψ_A and ψ_B combining to form molecular orbital wave function are also normalised, we have

$$\int \psi_A^2\, d\tau = 1 \quad \text{and} \quad \int \psi_B^2\, d\tau = 1 \qquad \ldots(20.21)$$

Substituting these values in Eq. (20.20) and representing the integral $\int \psi_A\psi_B d\tau$ by S (called ***overlap integral*** between the orbitals ψ_A and ψ_B), we have

$$c_1^2 + c_2^2 + 2c_1c_2S = 1 \qquad \ldots(20.22)$$

For zero-overlap approximation, we put $S = 0$. Hence, the normalisation condition becomes,

$$c_1^2 + c_2^2 = 1 \qquad \ldots(20.23)$$

In case of H_2^+, as both the atoms are same, there will be equal contribution by the atomic wave functions ψ_A and ψ_B towards the molecular orbital wave function. Hence, we will have

$$c_1^2 = c_2^2 \qquad \ldots(20.24)$$

From Eqs (20.23) and (20.24),

$$c_1^2 = c_2^2 = \frac{1}{2}$$

or $$c_1 = \pm\, c_2 = \pm\, \frac{1}{\sqrt{2}} \qquad \ldots(20.25)$$

Thus, two sets of values are possible for c_1 and c_2, i.e. $+\frac{1}{\sqrt{2}}, +\frac{1}{\sqrt{2}}$ and $+\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}$

Substituting these values in Eq. (20.17), two linear combinations are possible—one by using the first set of values of c_1 and c_2 is represented by $\psi_{+(MO)}$ and the other by using second set of values represented by $\psi_{-(MO)}$:

$$\psi_{+(MO)} = +\frac{1}{\sqrt{2}}\psi_A + \frac{1}{\sqrt{2}}\psi_B = \frac{1}{\sqrt{2}}(\psi_A + \psi_B) \quad \ldots(20.26)$$

$$\psi_{-(MO)} = \frac{1}{\sqrt{2}}\psi_A - \frac{1}{\sqrt{2}}\psi_B = \frac{1}{\sqrt{2}}(\psi_A - \psi_B) \quad \ldots(20.27)$$

The wave function $\psi_{+(MO)}$ corresponds to the energy E_+ whereas $\psi_{-(MO)}$ corresponds to the energy E_-.

Equations (20.26) and (20.27) give the values of the wave functions according to LCAO-MO treatment of H_2^+ ion. Using these wave functions, energies (E_+ and E_-) are calculated for different internuclear distances R. A graph is then plotted between energy versus intemuclear distance.

The potential energy curves thus obtained for the H_2^+ ion are shown in Fig. 20.6. The potential energy curve of $\psi_{+(MO)}$ shows a minimum at 171 kJ mol^{-1} and internuclear distance of 132 pm. The actual (observed) values are 268 kJ mol^{-1} and 106 pm. There is no satisfactory agreement between the two. Hence, a number of further improvements have been suggested, discussion of which is beyond the scope of this level.

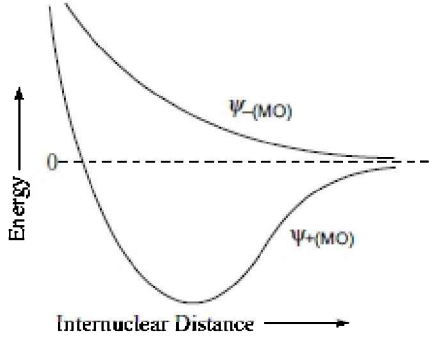


Fig. 20.6 *Plots showing variation of energy (calculated from $\psi_{+(MO)}$ and $\psi_{-(MO)}$) versus internuclear distance*

20.4 PHYSICAL PICTURE OF BONDING AND ANTIBONDING WAVE FUNCTIONS

We have seen from the LCAO-MO treatment of the H_2^+ ion that on calculation, two values of energy are obtained for this system, represented by E_+ and E_-. Their corresponding wave functions, represented by $\psi_{+(MO)}$ and $\psi_{-(MO)}$ are given by equations (20.26) and (20.27).

The value of E_+ is found to be lower than the energies of the combining atomic orbitals, i.e. E_A and E_B of the isolated atoms H_A and H_B. Thus, it leads to a greater stability and hence, is responsible for the bonding between H_A and H_B. The molecular orbital formed is, therefore, called ***Bonding Molecular Orbital (BMO)***. On the other hand, the value of E_- is higher than that of the combining atomic orbitals. The molecular orbital thus formed has lower stability and hence, is called ***Antibonding Molecular Orbitals (ABMO)***. Further, it is found that the extent of lowering of energy (for bonding orbital) is almost equal to the extent of increase is energy for antibonding orbital. Hence, a physical picture of the bonding and antibonding molecular orbitals formed from atomic orbitals may be represented as shown in Fig. 20.7.

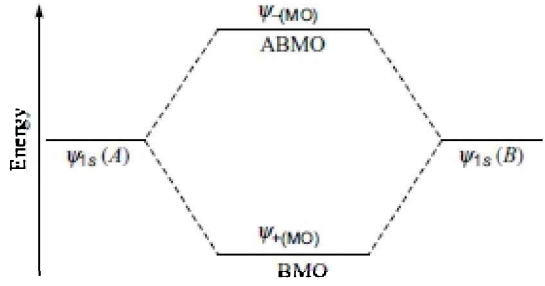


Fig. 20.7 *Representing the energy of bonding and antibonding molecular orbitals with respect to those of combining atomic orbitals*

Rewriting expressions (20.26) and (20.27), for the wave functions ψ_+ and ψ_-, we have

$$\psi_{+(MO)} = \frac{1}{\sqrt{2}}(\psi_A + \psi_B) \qquad \ldots(20.28)$$

$$\psi_{-(MO)} = \frac{1}{\sqrt{2}}(\psi_A - \psi_B) \qquad \ldots(20.29)$$

Squaring both sides of these equations, we have

$$\psi_+^2 = \frac{1}{2}(\psi_A^2 + \psi_B^2 + 2\,\psi_A\,\psi_B) \qquad \ldots(20.30)$$

$$\psi_-^2 = \frac{1}{2}(\psi_A^2 + \psi_B^2 - 2\psi_A\psi_B) \qquad \ldots(20.31)$$

ψ^2 gives the probability of finding the electron and $\psi_+^2 > \frac{1}{2}(\psi_A^2 + \psi_B^2)$ because there is an extra positive term in Eq. (20.30) and $\psi_-^2 < \frac{1}{2}(\psi_A^2 + \psi_B^2)$ [because there is a negative term in Eq. (20.31)].

It may be noted that the electron charge density in the region between the nuclei of the uncombined atomic orbitals, ψ_A and ψ_B, is $\frac{1}{2}\psi_A^2 + \frac{1}{2}\psi_B^2$ and not $\psi_A{}^2 + \psi_B{}^2$.

This shows that probability of finding the electron in the region between the nuclei increases in case of bonding molecular orbitals and it decreases in case of antibonding molecular orbitals compared to their probabilities in the separated atoms. The presence of greater electron density between the nuclei results in greater attraction of both the nuclei and hence decreases in energy and thus result in bonding.

As seen in Fig. 20.7, the antibonding molecular orbital has been raised by the same energy by which the bonding molecular orbital has been lowered.

Strictly speaking, if more precise calculations are carried out, the ABMO is raised slightly more in energy than the energy by which BMO is lowered, although the general pattern of the diagram remains the same. For example, if overlap integral (s) were not neglected, the wave functions ψ_+ and ψ_- would be given by

$$\psi_+ = \frac{1}{\sqrt{2+2S}}(\psi_A + \psi_B)$$

and

$$\psi_- = \frac{1}{\sqrt{2-2S}}(\psi_A - \psi_B)$$

instead of equations (20.28) and (20.29).

Main Points about Bonding and Antibonding Molecular Orbitals

1. Whenever two atomic orbitals ψ_A and ψ_B combine together, their linear combination gives rise to two new molecular orbitals ψ_+ and ψ_-.
2. The energy E_+ corresponding to molecular orbitals ψ_+ is lower than that of the combining atomic orbitals. Hence it is more stable than the combining atomic orbitals and is, therefore, called ***Bonding Molecular Orbital (BMO)***.
3. The energy E_- corresponding to molecular orbital ψ_- is higher than that of the combining atomic orbitals. Hence, it is less stable than the combining atomic orbitals and is, therefore, called ***Antibonding Molecular Orbital (ABMO)***.
4. The amount of lowering in energy of the BMO is almost equal to the increase in energy of the ABMO compared to the combining atomic orbitals.
5. The electrons belonging to atomic orbitals leave the atomic orbitals and enter the bonding and antibonding molecular orbitals in order of their increasing energies, the molecular orbitals with lower energy being filled first (according to Aufbau principle).
6. On the basis of LCAO calculations, is found that greater the extent of overlap between the combining atomic orbitals, greater is the lowering in energy of the bonding molecular orbitals. The main points of difference between BMO and ABMO are given in Table 20.1 below:

Table 20.1 *Comparison of bonding and antibonding molecular orbitals.*

Bonding Molecular Orbitals (BMO)	Antibonding Molecular Orbitals (ABMO)
1. They are formed by the ***additive effect*** of the atomic orbitals.	1. They are formed by the ***subtractive effect*** of the atomic orbitals.
2. Their energy is lower than that of combining atomic orbitals.	2. Their energy is higher than that of the combining atomic orbitals.
3. The electron charge density in the internuclear region is very high. As a result, the repulsion between the nuclei decreases and hence stability increases, i.e. it favours the formation of bonding.	3. The electron charge density in the internuclear region decreases. Hence, there is repulsion between the nuclei resulting in increase in energy and decrease in stability.
4. They are represented by σ, π, δ, etc.	4. They are represented by $\sigma^*, \pi^*, \delta^*$ etc.

20.5 VARIATION OF ELECTRON PROBABILITY DENSITY ALONG INTERNUCLEAR AXIS IN BONDING AND ANTIBONDING

20.5.1 Graphical Representation

1. Bonding Molecular Orbitals The wave functions of bonding molecular orbitals wave function of the two atomic orbitals wave functions (ψ_A and ψ_B) is given by

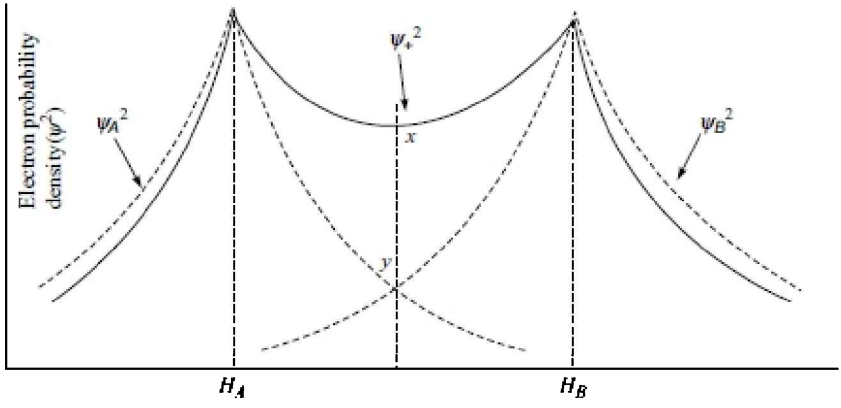


Fig. 20.8 *Representation of variation of electron probability density for BMO and ψ_A^2 and ψ_A^2 for separate atoms A and B along the internuclear axis*

$\psi_+ = \frac{1}{\sqrt{2}}(\psi_A + \psi_B)$ [Eq. (20.28) sec 20.4]. Hence, the electron probability density in the bonding molecular orbitals will be given by

$$\psi_+^2 = \frac{1}{2}(\psi_A + \psi_B)^2 = \frac{1}{2}\psi_A^2 + \frac{1}{2}\psi_B^2 + \psi_A\psi_B.$$

The sum $\frac{1}{2}\psi_A^2 + \frac{1}{2}\psi_B^2$ gives the electron probability density between the nuclei of the two atoms in the ***uncombined state*** (note that it is not equal to $\psi_A^2 + \psi_B^2$). However, ψ_A^2 and ψ_B^2 give the electron probability densities of the electrons in separate atoms *A* and *B* respectively. Plotting the values of ψ_A^2 (solid line) along internulear axis and also plotting the values of ψ_A^2 and ψ_B^2 (dotted lines) for the individual atoms *A* and *B*, the curves obtained are shown in Fig. 20.8 for ψ_+^2.

It may be seen from the plot that there is a greater ***electron probability density between the nuclei in BMO than in the uncombined atomic orbitals*** (look at the points *x* and *y*).

2. Antibonding Molecular Orbitals For the antibonding molecular orbitals, the wave function is $\psi_- = \frac{1}{\sqrt{2}}(\psi_A - \psi_B)$..

Hence, electron probability density will be given by

$$\psi_-^2 = \frac{1}{2}\psi_A^2 + \frac{1}{2}\psi_B^2 - \psi_A\psi_B.$$

Plotting the values as before, the curves obtained are shown in Fig. 20.9.

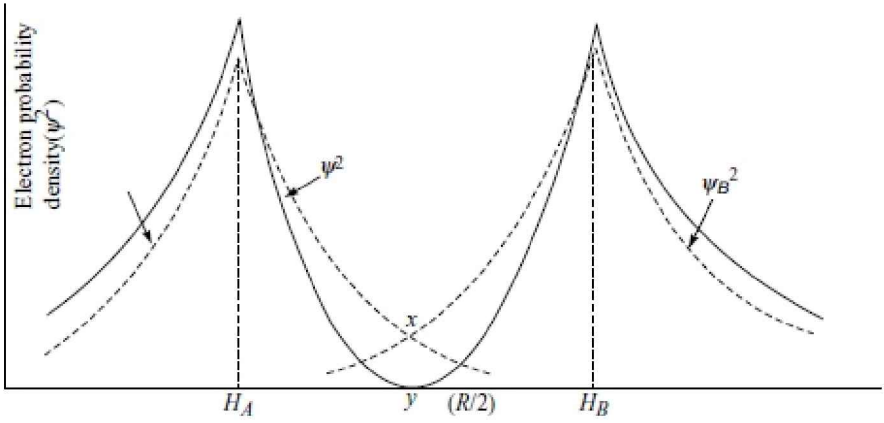


Fig. 20.9 *Representation of variation of electron probability density along internuclear axis for ABMO and ψ_A^2 and ψ_B^2 for separate atoms A and B*

Again, the curve for $\psi_^2$ has been shown by a solid line and those for ψ_A^2 and ψ_B^2 have been shown by dotted lines.

From the plot, it may be seen that ***electron probability density in the middle of the nuclei (corresponding to distance R/2) in the ABMO is almost zero***. This means that the electrons tend to stay away from this region. Consequently, there is a greater repulsion between the nuclei. There is a plane passing through the point exactly in the centre between the two nuclei and perpendicular to the internuclear axis on which the electron probability density in ABMO is zero. This plane is called the ***nodal plane***.

20.5.2 Three-dimensional Contour Diagrams

Electron probability densities are calculated at different points around both the nuclei. Regions showing the equal probability density are joined together. The resulting surface that we obtain is called a ***contour***.

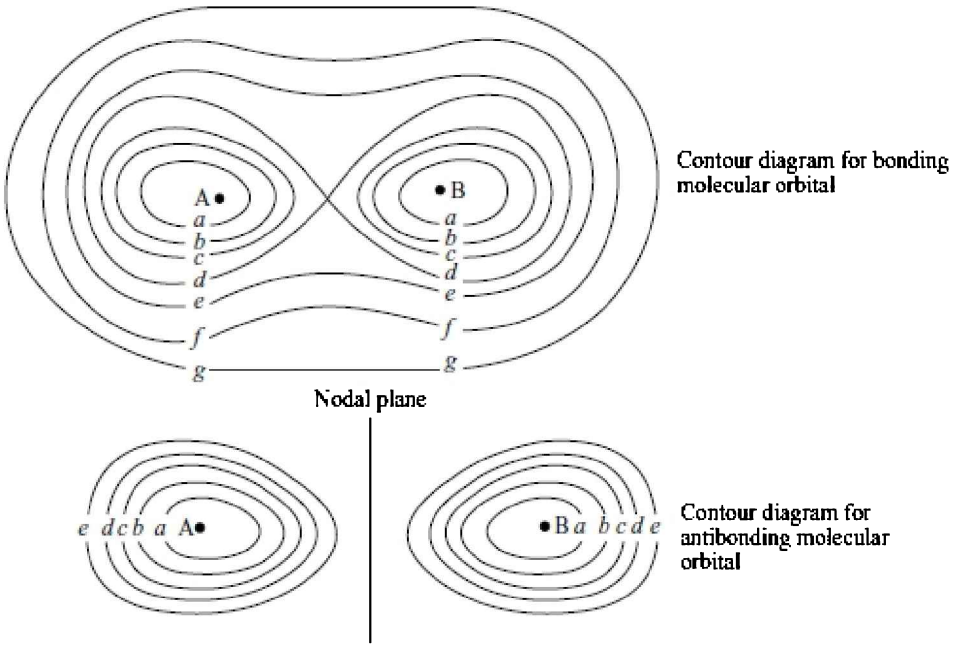


Fig. 20.10 *Electron probability density contour diagrams for bonding and antibonding molecular orbitals*

A number of contours are obtained around both the nuclei for bonding and antibonding molecular orbitals, as shown in Fig. 20.10.

We observe that in a BMO, the electron probability density tends to concentrate towards the internuclear region whereas in the ABMO, it tends to shift away from the internuclear region.

20.6 FORMATION OF MOLECULAR ORBITALS FROM ATOMIC ORBITALS

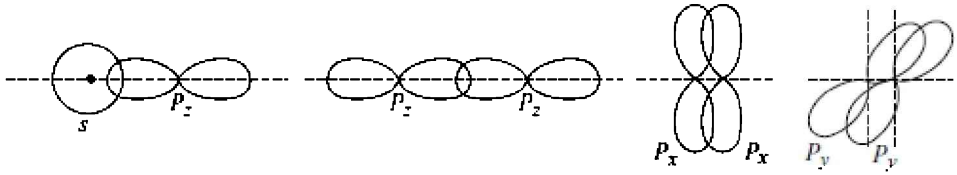
Just any two atomic orbitals cannot combine to form molecular orbitals. They combine to form molecular orbitals only if the following conditions are satisfied:

1. Combining Atomic Orbitals must Possess Comparable Energies Thus, in the formation of a homonuclear diatomic molecules A_2 (like H_2, O_2, etc.), 1*s* orbitals of one atom can combine with 1*s* of the other, 2*s* of one atom with 2*s* of the other, and so on. 1*s* orbitals of one atom cannot combine with 2*s* of the other because of a big difference of energy. However, such combinations may be displayed by heteronuclear diatomic molecules (A–B).

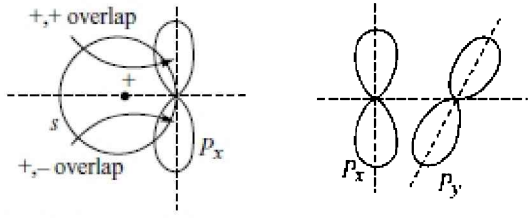
We can explain it by saying that if the combining atomic orbitals (ψ_A and ψ_B) have comparable energies, their coefficients c_A and c_B have comparable values. As a matter of fact, if two combining atoms are identical, they will have same coefficients, i.e. $c_A = c_B$.

2. Combining Atomic Orbitals must Overlap to a Considerable Extent Greater the extent of overlap, greater is the electrons density in the internuclear region and hence greater is the attraction on the electron density by both nuclei and smaller is the repulsion between the nuclei.

3. Combining Atomic Orbitals must be Symmetrical with Respect to Their Molecular Axis For example, taking the *Z*-axis as the internuclear axis, an *s*-orbital can overlap with p_z, orbitals or a p_z orbital can overlap with p_z-orbitals but s-orbital cannot overlap with p_x or p_y orbital. Similarly, p_x can overlap with p_x or p_y can overlap with p_y, but p_x cannot overlap with p_y as illustrated in Fig. 20.11.



(a) Combinations allowed due to same symmetry about molecular axis



(b) Combinations not allowed due to lack of symmetry about molecular axis

Fig. 20.11 *(a) Combinations allowed (b) Combinations not allowed*

This may also be explained in terms of the signs of the wave functions. In *s*-p_x overlap, the area of +, + overlap is equal to the area of +, – overlap. Thus, the two areas are equal but opposite in sign. Hence, +, + overlap is cancelled by the +, – overlap and there is no net overlap.

20.7 CONCEPT OF σ, σ*, π, π* ORBITALS AND THEIR CHARACTERISTICS

For *homonuclear diatomic molecules* (H_2, O_2, etc.) only similar atomic orbitals have comparable energies, hence only similar atomic orbitals of the two atoms can combine to form molecular orbitals (i.e. 1s of one atom with 1s of the other, 2*s* with 2*s* and 2*p* with 2*p*, and so on and. Representing the combining atomic orbitals and the molecular orbitals formed with proper signs of the wave function, the formation of molecular orbitals is represented in Fig. 20.12. It may be noted that when 1*s* combines with 1*s* or 2*s* with 2*s* or $2p_z$ with $2p_z$ (taking *Z*-axis as the internuclear axis), the atomic orbitals overlap along the internuclear axis resulting into formation of molecular orbitals whose electron charge density is symmetrical about the molecular axis. In each case, two molecular orbitals are formed, the bonding molecular orbital (formed by additive effect) is called σ-molecular orbitals which has high electron charge density in the internuclear region whereas the corresponding antibonding molecular orbitals (formed by subtractive effect) is called σ*-molecular orbital in which case the electron density in the internuclear region decreases and hence the repulsion between the nuclei increases.

Additive effect implies +ve wave function combining with +ve wave function. The result is (+) × (+) = +ve, i.e. electron density in the internuclear region increases. Subtractive effect means +ve wave function combining with +ve wave function. The result is (+) × (–) = –ve, i.e. there is no electron density in the internuclear region. To represent the particular atomic orbitals combining to

form molecular orbitals, symbols of the atomic orbitals are written along with the molecular orbitals.

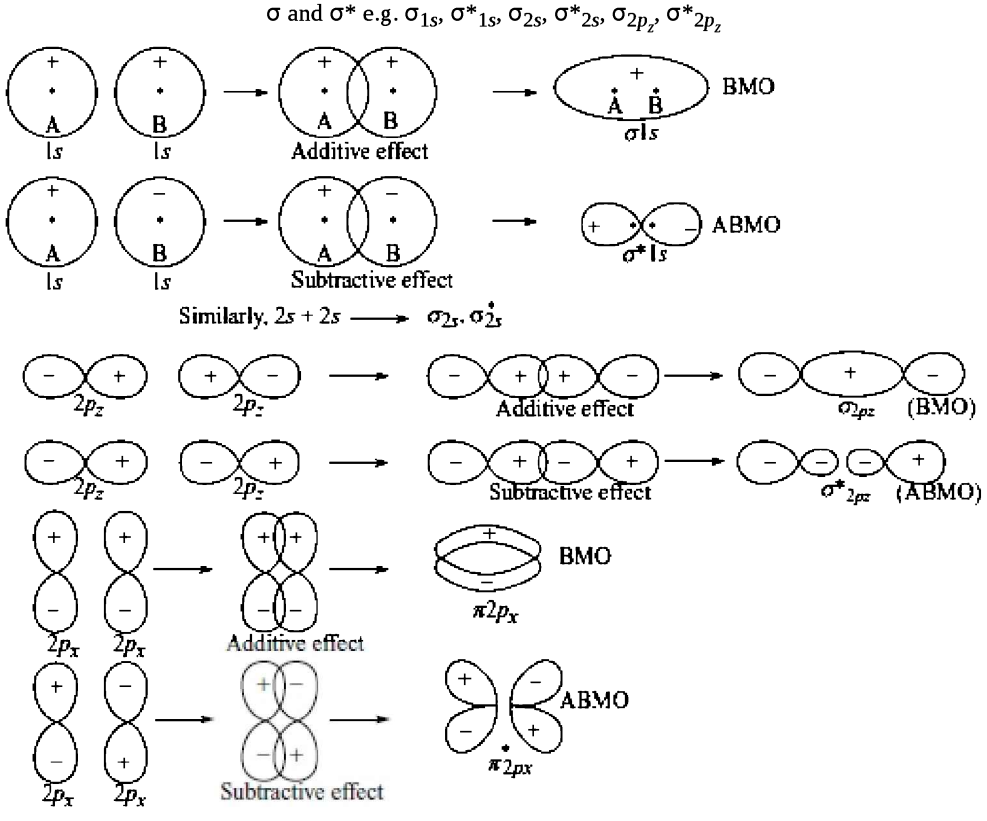


Fig. 20.12 *Formation of bonding and antibonding molecular orbitals from atomic orbitals*

If we take Z-axis as the internuclear axis, the p_x orbital of one atom combines with p_x orbital of the other atom to give sideways overlapping. The molecular orbitals formed in such a case do not have symmetrical electron density about the molecular axis. The bonding molecular orbital in this case is called π-molecular orbitals and the corresponding antibonding molecular orbital is called π^*-molecular orbital. And to indicate that $2p_x$ orbitals are involved in the formation of molecular orbitals, we represent then by π_{2p_x} and $\pi^*_{2p_x}$. Similarly, if $2p_y$ orbital of one atom combines with $2p_y$ orbital of other atom, molecular orbitals formed are unsymmetrical and are represented by π_{2p_y} $\pi^*_{2p_y}$.

In summary, molecular orbitals which are formed by the overlap of the atomic orbitals along the internuclear axis and which have symmetrical electron charge density about the internuclear axis are called σ-molecular orbitals, if they are bonding and are called σ*-molecular orbitals if they are anti-bonding. Similarly, molecular orbitals, which are formed by the sideways overlap of atomic orbitals in a direction perpendicular to the internuclear axis and have unsymmetrical electron charge density about the internuclear axis, are called π-molecular orbitals if they are bonding and are called π^* molecular orbitals if they are antibonding.

Gerade and Ungerade Molecular Orbitals If a molecular orbital is symmetrical with respect to its centre, it is called grade (g) and if it is unsymmetrical, it is called ungerade (u). For example,

σ_{1s}, σ_{2s}, σ_{2pz}, π^*_{2px} and π^*_{2py} are gerade molecular orbitals and hence represented as $\sigma_g 1s$, $\sigma_g 2s$, $\sigma_g 2pz$, $\pi_g 2px$, $\pi_g 2py$. On the other hand σ^*_{1s}, σ^*_{2s}, σ^*_{2pz}, π_{2px} and π_{2py} are ungerade and represented correspondingly using the subscript *u*.

For heteronuclear diatomic molecules, the contribution by the two wave functions ψ_A and ψ_B is not equal towards the molecular orbital wave function. In such cases, different atomic orbitals of the two atoms may combine to form molecular orbitals. For example, consider the formation of HCl molecule.

The electronic configuration of $_{17}$Cl is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$. In the formation of HCl, 1s orbitals of the H-atom combines with $3p_z$ orbitals of the Cl atom to form σ and σ* molecular orbitals, although, the two atomic orbitals involved possess much different energies.

20.8 FORMATION OF H_2 MOLECULE

In this case, since both the atomic orbitals are identical, their wave functions will contribute equally towards the molecular orbital wave function. Hence, applying LCAO approximation, the molecular orbital wave function can be taken as the sum of the atomic orbital wave functions (i.e. coefficients c_1 and c_2 can be ignored).

In H_2 molecules, there are two nuclei (protons), H_A and H_B. The two electrons may be written as 1 and 2. Let us consider the first electron 1. The situation will be like that of H_2^+ ion. As the electron is under the influence of both the nuclei (H_A and H_B), therefore, if atomic orbital wave functions of atoms H_A and H_B are ψ_A and ψ_B respectively then by LCAO approximation, the molecular orbital wave function for the electron 1 can be written as,

$$\psi_1 = \psi_A(1) + \psi_B(1) \qquad \ldots(20.32)$$

Similarly, as the electron 2 is also under the influence of both the nuclei, by LCAO approximation, the molecular orbital wave function of the electron 2 can be written as

$$\psi_2 = \psi_A(2) + \psi_B(2) \qquad \ldots(20.33)$$

Thus, the total molecular orbital wave function will be given by

$$\psi_{MO} = \psi_1\ \psi_2 = [(\psi_A(1) + \psi_B(1))]\ [(\psi_A(2) + \psi_B(2))] \qquad \ldots(20.34)$$

Using the molecular orbital wave function given by Eq. (20.34), the energy is calculated for different internuclear distances and a graph is plotted between energy versus internuclear distance as usual and the values corresponding to the minimum in the curve are found and compared with the experimental values. The calculated value of bond dissociation energy and the equilibrium internuclear distance are 258.6 kJ mol^{-1} and 85 pm respectively. The experimental values are found to be 458.1 kJ mol^{-1} and 74.1 pm. Thus, the result obtained is worse than that obtained by the valence bond method.

A number of modifications have been done both in the valence bond method as well as molecular orbital method to obtain a wave function which gives results in close agreement with the experimental values. However, these are beyond the scope of this book.

20.9 HYBRIDISATION

"Hybridisation is a process of mixing of different atomic orbitals of the same atom which may have slightly different energies and different shapes such that a redistribution of energy takes place between them to form new orbitals of exactly same shape and energy." The new orbitals formed are known as hybrid orbitals. The number of hybrid orbitals formed is equal to the number of atomic orbitals mixed together. For example, if one 2*s* and one 2*p* orbital mix, the hybridisation is called *sp*

hybridisation and the two orbitals formed are *sp* hybrid orbitals. If one 2*s* and two 2*p* orbitals mix, the hybridisation is called sp^2 and the three orbitals formed are called sp^2 hybrid orbitals. Similarly, if one 2*s* and three 2*p* orbitals mix, the hybridisation is called sp^3 and the four orbitals formed are called sp^3 hybrid orbitals. Hybrid orbitals have one lobe much bigger in size than the other on the opposite side. Due to bigger size of the lobe, they undergo better overlapping with the hybridised or unhybridised orbitals of the other atom and, hence, form a comparatively stronger bond. *sp*, sp^2, sp^3 hybridisation is illustrated in Fig. 20.13.

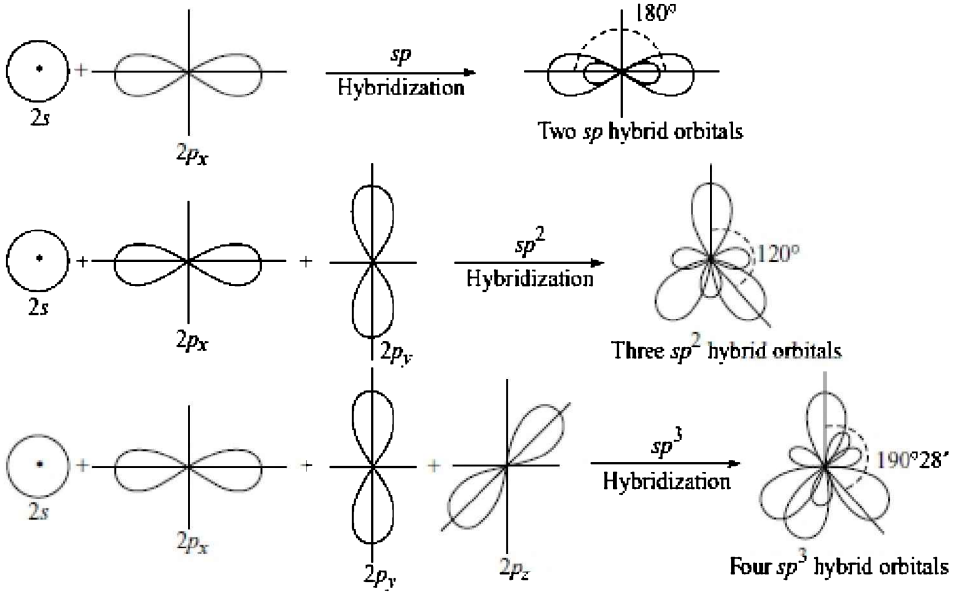


Fig. 20.13 *Formation of sp, sp^2 and sp^3 hybrid orbitals*

20.10 QUANTUM MECHANICAL PRINCIPLES OF HYBRIDISATION

The following quantum mechanical principles are involved in the formation of hybrid orbitals from atomic orbitals.

1. The hybrid orbitals are formed by linear combination of atomic orbitals belonging to the same atom. Thus,

$$\psi_1 = a_1\psi_s + b_1\psi_{px} + c_1\psi_{py} + d_1\psi_{pz}$$
$$\psi_2 = a_2\psi_s + b_2\psi_{px} + c_2\psi_{py} + d_2\psi_{pz} \text{ and so on}$$

2. As the *s*-orbital is spherically symmetrical, its charge density will be equally distributed among the *n* possible hybrid orbitals, i.e. square of the coefficient of *s*-orbitals will be equal in all the *n* hybrid orbitals which means that the *s*-orbital in each hybrid orbital will have square of coefficient = 1/*n*

3. Each wave function (hybrid or atomic) is normalised.

Thus,

$$\int \psi_1^2 \, d\tau = 1$$
$$\int \psi_2^2 \, d\tau = 1$$
$$\int \psi_s^2 \, d\tau = 1$$
$$\int \psi_p^2 \, d\tau = 1 \quad \text{and so on...}$$

4. The wave function of the hybrid orbitals as well atomic orbitals are orthogonal to each other. Thus, $\int \psi_1 \psi_2 d\tau = 0$ and $\int \psi_s \psi_p d\tau = 0$

5. In the formation of sp^2 hybrid orbitals, the first hybrid orbital may be considered to have maximum charge density along *X*-axis. Then p_y and p_z will not contribute towards this hybrid orbital.

6. In the formation of sp^3 hybrid orbitals, the second orbital may be considered to be in a plane, say *xz* plane, *py* will not contribute towards this hybrid orbital.

20.11 CALCULATION OF THE COEFFICIENTS OF ATOMIC ORBITALS IN DIFFERENT HYBRID ORBITALS

Calculations have been done separately for *sp*, sp^2 and sp^3 hybrid orbitals as described below.

1. Calculation of Coefficient of Atomic Orbitals in sp Hybrid Orbitals The wave functions for the two hybrid orbitals may be written as

$$\psi_1 = a_1 \psi_s + b_1 \psi_p \quad \ldots(20.35)$$
$$\psi_2 = a_2 \psi_s + b_2 \psi_p \quad \ldots(20.36)$$

(a) As the charge density is distributed equally among the two hybrid orbitals (two *sp* hybrid orbitals),

$$a_1^2 = a_2^2 = \frac{1}{2} \quad \ldots(20.37)$$

$\therefore$
$$a_1 = a_2 = \frac{1}{\sqrt{2}} \quad \ldots(20.38)$$

(b) As ψ_1 is a normalised wave function,

$$\int \psi_1^2 \, d\tau = 1 \text{ or } \int (a_1 \psi_s + b_1 \psi_p)^2 \, d\tau = 1 \quad \ldots(20.39)$$

or
$$a_1^2 \int \psi_s^2 \, d\tau + b_1^2 \int \psi_p^2 \, d\tau + 2 a_1 b_1 \int \psi_s \psi_p \, d\tau = 1 \quad \ldots(20.40)$$

As atomic wave functions ψ_s and ψ_p are normalised and they are also orthogonal to each other,

$$\int \psi_s^2 \, d\tau = 1, \int \psi_p^2 \, d\tau = 1, \int \psi_s \psi_p \, d\tau = 0 \quad \ldots(20.41)$$

From equations (20.40) and (20.41), we have

$$a_1^2 (1) + b_1^2 (1) + 2 a_1 b_1 (0) = 1$$

i.e.
$$a_1^2 + b_1^2 = 1 \quad \ldots(20.42)$$

But $a_1 = \frac{1}{\sqrt{2}}$ [see Eq. (20.37))

$$\frac{1}{2} + b_1^2 = 1 \quad \text{or} \quad b_1^2 = \frac{1}{2} \quad \text{or} \quad b_1 = \frac{1}{\sqrt{2}} \qquad \ldots(20.43)$$

(c) As ψ_1 and ψ_2 are orthogonal to each other, we have

$$\int \psi_1 \psi_2 \, d\tau = 0$$

This means

$$a_1 a_2 + b_1 b_2 = 0 \qquad \ldots(20.44)$$

Substituting the values of a_1, a_2 and b_1, we get

$$\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) + \left(\frac{1}{\sqrt{2}}\right) b_2 = 0$$

i.e.
$$\frac{1}{2} + \frac{1}{\sqrt{2}} b_2 = 0 \quad \text{or} \quad b_2 = -\frac{1}{2} \times \sqrt{2} = -\frac{1}{\sqrt{2}} \qquad \ldots(20.45)$$

Thus, the wave function for the two *sp* hybrid orbitals are

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_s + \psi_p) \qquad \ldots(20.46)$$

$$\psi_2 = \frac{1}{\sqrt{2}} (\psi_s - \psi_p) \qquad \ldots(20.47)$$

2. Calculation of Coefficients of Atomic Orbitals in sp^2 Hybrid Orbitals The wave functions for the three sp^2 hybrid orbitals may be written as

$$\psi_1 = a_1 \psi_s + b_1 \psi_{px} + c_1 \psi_{py} \qquad \ldots(20.48)$$

$$\psi_2 = a_2 \psi_s + b_2 \psi_{px} + c_2 \psi_{py} \qquad \ldots(20.49)$$

$$\psi_3 = a_3 \psi_s + b_3 \psi_{px} + c_3 \psi_{py} \qquad \ldots(20.50)$$

(a) As the charge density of *s*-orbital is equally distributed among the three hybrid orbitals

$$a_1^2 = a_2^2 = a_3^2 = \frac{1}{3}$$

or
$$a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$$

(b) Let us assume that ψ_1 has maximum charge density along the *X*-axis. It will have contribution only from *s* and p_x orbitals and the contribution from p_y orbital will be zero, i.e. $c_1 = 0$

(c) As ψ_1 is a normalised wave function, we have

$$a_1^2 + b_1^2 = 1 \text{ But } a_1 = \frac{1}{\sqrt{3}}$$

$$\therefore \frac{1}{3} + b_1^2 = 1 \quad \text{or} \quad b_1^2 = \frac{2}{3} \quad \text{or} \quad b_1 = \sqrt{\frac{2}{3}}$$

(d) ψ_1 and ψ_2 are orthogonal to each other and also ψ_1 and ψ_3 are orthogonal to each other. That means

$$\int \psi_1 \psi_2 \, d\tau = 0 \quad \text{and} \quad \int \psi_1 \psi_3 \, d\tau = 0$$

We can write the above results as

$$a_1 a_2 + b_1 b_2 = 0 \quad \text{and} \quad a_1 a_3 + b_1 b_3 = 0$$

or $$b_2 = -\frac{a_1 a_2}{b_1} = -\frac{(1/\sqrt{3})(1/\sqrt{3})}{\sqrt{2}/3} = -\frac{1}{\sqrt{6}}$$

and $$b_3 = -\frac{a_1 a_3}{b_1} = -\frac{(1/\sqrt{3})(1/\sqrt{3})}{\sqrt{2}/3} = -\frac{1}{\sqrt{6}}$$

(e) As ψ_2 is a normalised wave function, we have

$$\int \psi_2^2 \, d\tau = 1 \quad \text{or} \quad a_2^2 + b_2^2 + c_2^2 = 1$$

or $$c_2^2 = 1 - (a_2^2 + b_2^2) = 1 - \left(\frac{1}{3} - \frac{1}{6}\right) = \frac{1}{2}$$

or $$c_2 = \frac{1}{\sqrt{2}}$$

(f) As ψ_3 is a normalised wave function, we have

$$\int \psi_3^2 \, d\tau = 1 \quad \text{or} \quad a_3^2 + b_3^2 + c_3^2 = 1$$

or $$c_3^2 = 1 - (a_2^2 + b_2^2) = 1 - \left(\frac{1}{3} + \frac{1}{6}\right) = 1 - \frac{1}{2} = \frac{1}{2}$$

or $$c_3 = \pm \frac{1}{\sqrt{2}}$$

c_2 and c_3 cannot be identical. If we take +ve sign for c_2 [see under (e) above], we have to take −ve sign for c_3, i.e. we take $c_3 = -\frac{1}{\sqrt{2}}$. (only then the condition of orthogonality between ψ_2 and ψ_3 will be satisfied, i.e. $a_2 a_3 + b_2 b_3 + c_2 c_3 = 0$).

Thus, the wave functions for the three sp^2 hybrid orbitals are

$$\psi_1 = \frac{1}{\sqrt{3}} \psi_s + \sqrt{\frac{2}{3}} \psi_{px}$$

$$\psi_2 = \frac{1}{\sqrt{3}} \psi_s - \frac{1}{\sqrt{6}} \psi_{px} + \frac{1}{\sqrt{2}} \psi_{py}$$

$$\psi_3 = \frac{1}{\sqrt{3}} \psi_s - \frac{1}{\sqrt{6}} \psi_{px} - \frac{1}{\sqrt{2}} \psi_{py}$$

3. Calculation of Coefficients of Atomic Orbitals of sp^3 Hybrid Orbitals The wave functions for the four sp^3 hybrid orbitals can be written in terms of the following four equation;

$$\psi_1 = a_1 \psi_s + b_1 \psi_{px} + c_1 \psi_{py} + d_1 \psi_{pz}$$
$$\psi_2 = a_2 \psi_s + b_2 \psi_{px} + c_2 \psi_{py} + d_2 \psi_{pz}$$
$$\psi_3 = a_3 \psi_s + b_3 \psi_{px} + c_3 \psi_{py} + d_3 \psi_{pz}$$
$$\psi_4 = a_4 \psi_s + b_4 \psi_{px} + c_4 \psi_{py} + d_4 \psi_{pz}$$

(a) As the charge density of the *s*-orbital is distributed equally among the four sp^3 hybrid orbitals, we have

$$a_1^2 + a_2^2 + a_3^2 + a_4^2 = 1$$

or
$$a_1^2 = a_2^2 = a_3^2 = a_4^2 = \frac{1}{4}$$

$$a_1 = a_2 = a_3 = a_4 = \frac{1}{2}$$

(b) Assuming that ψ_1 is aligned along the *X*-axis, the contribution from ψ_{py} and ψ_{pz} will be taken as zero,

i.e. $c_1 = 0 \quad \text{and} \quad d_1 = 0$

(c) As ψ_1 is a normalised wave function, we have

$$\int \psi_1^2 \, d\tau = 1 \quad \text{or} \quad a_1^2 + b_1^2 + c_1^2 + d_1^2 = 1 \quad \text{or} \quad a_1^2 + b_1^2 = 1 \qquad (\because c_1 = d_1 = 0)$$

$\therefore$
$$b_1^2 = 1 - a_1^2 = 1 - \left(\frac{1}{2}\right)^2 = \frac{3}{4}$$

or
$$b_1 = \sqrt{\frac{3}{4}} = \frac{\sqrt{3}}{2}$$

(d) As ψ_1 is orthogonal with ψ_2, ψ_3 and ψ_4 separately, we have the following three relations:

$$\int \psi_1 \psi_2 \, d\tau = 0, \quad \int \psi_1 \psi_3 \, d\tau = 0, \quad \int \psi_1 \psi_4 \, d\tau = 0$$

$$a_1 a_2 + b_1 b_2 = 0, \quad a_1 a_3 + b_1 b_3 = 0 \quad a_1 a_4 + b_1 b_4 = 0$$

or
$$b_2 = -\frac{a_1 a_2}{b_1}, \quad b_3 = -\frac{a_1 a_3}{b_1}, \quad b_4 = -\frac{a_1 a_4}{b_1},$$

But
$$a_1 = a_2 = a_3 = a_4 = \frac{1}{2} \text{ (Derived above)}$$

$\therefore$
$$b_2 = b_3 = b_4 = \frac{-\frac{1}{2}\cdot\frac{1}{2}}{\sqrt{3}/2} = -\frac{1}{2\sqrt{3}}$$

(e) Let us assume that the second hybrid orbital ψ_2 lies in the *xz* plane. Then *py* will not contribute towards ψ_2, i.e. $c_2 = 0$

(f) As ψ_2 is normalised, $\int \psi_2^2 d\tau = 1$. This means

$$a_2^2 + b_2^2 + c_2^2 + d_2^2 = 1$$

$$a_2^2 + b_2^2 + d_2^2 = 1 \qquad (\because c_2 = 0)$$

or $$d_2^2 = 1 - (a_2^2 + b_2^2)$$

$$= 1 - \left(\frac{1}{4} + \frac{1}{12}\right) = 1 - \frac{1}{3} = \frac{2}{3}$$

or $$d_2 = \sqrt{\frac{2}{3}}$$

(g) As ψ_2 is orthogonal with ψ_3 and ψ_4 separately, we have the following two relations.

$$\int \psi_2 \psi_3 \, d\tau = 0, \quad \int \psi_2 \psi_4 \, d\tau = 0$$

i.e. $$a_2 a_3 + b_2 b_3 + d_2 d_3 = 0, \quad a_2 a_4 + b_2 b_4 + d_2 d_4 = 0$$

or $$d_3 = \frac{a_2 a_3 + b_2 b_3}{d_3} \quad \text{and} \quad d_4 = -\frac{a_2 a_4 + b_2 b_4}{d_2}$$

or $$d_3 = -\frac{1/4 + 1/12}{\sqrt{2/3}} = -\frac{1}{\sqrt{6}} \quad \text{and} \quad d_4 = -\frac{1/4 + 1/12}{\sqrt{21/3}} = \frac{-1}{\sqrt{6}}$$

Thus, $$d_3 = d_4 = -\frac{1}{\sqrt{6}}$$

(h) As ψ_3 is normalised, $\int \psi_3^2 \, d\tau = 1$. This means

$$a_3^2 + b_3^2 + c_3^2 + d_3^2 = 1$$

or $$c_3^2 = 1 - (a_3^2 + b_3^2 + d_3^2) = 1 - \left(\frac{1}{4} + \frac{1}{12} + \frac{1}{6}\right) = \frac{1}{2}$$

$\therefore$ $$c_3 = \pm \frac{1}{\sqrt{2}}$$

To satisfy the condition of orthogonality between ψ_3 and ψ_4 and the normalisation condition of ψ_4, we take $c_4 = -\frac{1}{\sqrt{2}}$

Thus, the wave functions for the four sp^3 hybrid orbitals are

$$\psi_1 = \frac{1}{2}\psi_s + \frac{\sqrt{3}}{2}\psi_{px}$$

$$\psi_2 = \frac{1}{2}\psi_s - \frac{1}{2\sqrt{3}}\psi_{px} + \sqrt{\frac{2}{3}}\psi_{pz}$$

$$\psi_3 = \frac{1}{2}\psi_s - \frac{1}{2\sqrt{3}}\psi_{px} + \frac{1}{\sqrt{2}}\psi_{py} - \frac{1}{\sqrt{6}}\psi_{pz}$$

$$\psi_4 = \frac{1}{2}\psi_s - \frac{1}{2\sqrt{3}}\psi_{px} - \frac{1}{\sqrt{2}}\psi_{py} - \frac{1}{\sqrt{6}}\psi_{pz}$$

20.12 COMPARISON OF VALENCE BOND (VB) MOLECULAR ORBITAL (MO) MODELS

Points of Similarities

1. Both the VB and MO models take use of atomic orbital wave functions ψ_A and ψ_B of the electrons involved.
2. The bond is formed due to greater electron charge density in the internuclear region according to both models.
3. Both the models postulate that the bond is formed between the atoms due to overlap of their atomic orbitals.
4. Both the models assume that the combining atomic orbitals must have comparable energies and same symmetry with respect to their internuclear axis.

Points of Differences

1. According to VB theory, only the valence electrons take part in the bonding and hence, atoms do not lose their identify even after the overlap. According to the MO theory, all the electrons are distributed around all the nuclei taken together and hence, atoms lose their identify. The energy levels in which the electrons of the molecule are distributed are called molecular orbitals.
2. According to VB theory, only the half-filled orbitals of the valence shell take part in the bonding but according to MO theory all the atomic orbitals, i.e. half-filled or fully filled combine together provided they have comparable energies and same symmetries.
3. According to the VB model, the total wave function (ψ_{VB}) obtained as a linear combination of the two wave functions

$\psi_I = \psi_A(1)\,\psi_B(2)$ and $\psi_{II} = \psi_A(2)\,\psi_B(1)$ is given by

$$\psi_{VB} = \psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1) \qquad \ldots(20.51)$$

According to the MO model, total molecular orbital wave function is given by

$$\psi_{MO} = [\psi_A(1) + \psi_B(1)]\,[\psi_A(2) + \psi_B(2)] \qquad \ldots(20.52)$$

On multiplying out, this equation becomes

$$\psi_{MO} = \psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1) + \psi_A(1)\,\psi_A(2) + \psi_B(1)\,\psi_B(2) \qquad \ldots(20.53)$$

In this equation, the first two terms are same as those of ψ_{VB} in Eq. (20.51), Hence, Eq. (20.53)

becomes

$$\psi_{MO} = \psi_{VB} + \psi_A(1)\,\psi_A(2) + \psi_B(1)\,\psi_B(2) \quad \ldots(20.54)$$

The last two terms represent the ionic structures, i.e. when both the electrons are on *A* or both the electrons are on *B*.

Thus, The MO model justifies the contribution of ionic structure whereas in VB model, these terms were included later but were not present in the original VBT.

4. The VB theory leads to the concept of resonance whereas MO theory has nothing to do with resonance.

Example 1 *Using LCAO approximation, write down the complete wave function for a hetero-nuclear diatomic molecule AB assuming that it has 85% covalent character and 15% ionic character.*

Solution If AB were purely covalent, its wave function will be,

$$\psi_{\text{covalent}} = \psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1)$$

If AB were purely ionic, both electrons will be on the more electronegative atom (say B). Hence, its wave function will be

$$\psi_{\text{ionic}} = \psi_B(1)\,\psi_B(2)$$

when AB has both covalent and ionic character, its wave function will be

$$\psi = c_1\,\psi_{\text{covalent}} + c_2\,\psi_{\text{ionic}}$$

Such that $c_1^2 + c_1^2 = 1$

Here, we are given that $c_1^2 = 85\% = 0.85$ and $c_2^2 = 15\% = 0.15$

$$\therefore \quad c_1 = \sqrt{0.85} = 0.92,\ c_2 = \sqrt{0.15} = 0.39$$

$$\text{Hence,} \quad \psi = 0.92\,[\psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1)] + 0.39\,[\psi_B(1)\,\psi_B(2)].$$

Example 2 *What will be the wave function for BMO of a heteronuclear diatomic molecule AB, given the electron spends 70% of its time on the nucleus of A and 30% of its time on the nucleus of B.*

Solution According to the LCAO-MO method,

$$\psi_{MO} = c_A\psi_A + c_B\psi_B$$

The significance of the coefficients c_A and c_B is that their squares, i.e. $|c_A|^2$ and $|c_B|^2$ represent the weightages of ψ_A and ψ_B towards the total wave function. This means

$$|c_A|^2 = 70\% = 0.70 \text{ and } |c_B|^2 = 30\% = 0.30$$

$$c_A = \pm\sqrt{0.70} = \pm 0.84$$

and

$$c_B = \pm\sqrt{0.30} = \pm 0.55$$

Hence,

$$\psi_{MO} = 0.84\,\psi_A + 0.55\,\psi_B$$

Applying Chemistry to Life

Different theories of chemical bond help us predict the shapes of molecules. These shapes of molecules are connected to the characteristics shown by substances. Many biochemical processes are specific to the shapes of molecules involved. Researchers have explained how our sense of smell works. The odour of a molecule depends largely on which olfactory receptors it stimulates. Olfactory receptors are proteins located on the back of the nose. When a receptor is

stimulated, it triggers an electrical signal that travels to the brain. The scent is identified there. The shape of the molecule decides which olfactory receptor it will stimulate. Benzaldehyde alone, because of its shape, stimulates camphorlike, floral and pepperminty receptors.



Fig. 20.14 *Olfactory receptors*



Fig. 20.15 *Fragrances and olfactory receptors*

SUMMARY

1. There are two theories to explain the nature of chemical bonding and to predict the properties of molecules. These are (i) *valence bond theory* and (ii) *molecular orbital* theory.
2. According to VB theory, total wave function of two independent systems with wave functions ψ_A and ψ_B is equal to $\psi_A\ \psi_B$. Total energy E of two independent systems with energies E_A and E_B is equal to $E_A + E_B$.
3. In applying valence bond theory to the study of H_2 molecule, we take into consideration, the *exchange of electrons, screening effect of electrons* and *ionic structure* for H_2 molecule.
4. According to the MO theory, the electron in a molecule is not under the influence of a

particular nucleus but is considered to be under the influence of *all the nuclei*.5. A molecular orbital wave function is constructed by an approximation of linear combination of atomic orbitals (LCAO).

6. Corresponding to two atomic orbitals of similar energy, there are two molecular orbitals. (i) bonding MO having *lower* energy, and (ii) antibonding MO having *higher* energy compared to the *energy of atomic orbitals.*
7. There is a *greater* electron probability density between the nuclei in bonding molecular orbital than in the uncombined atomic orbitals.
8. Electron probability density in the middle of the nuclei in antibonding MO is *almost zero.*
9. The following *conditions* must be satisfied for the formation of molecular orbitals from atomic orbitals:

   (i) The combining orbitals must possess comparable energies.

   (ii) The combining orbitals must overlap to a considerable extent.

   (iii) The combining orbitals must be symmetrical with respect to their molecular axis.
10. *Hybridisation* is a process of mixing of different atomic orbitals of the same atom which may have slightly different energies and different shapes such that a redistribution of energy takes place between then to form new orbitals of exactly same shape and energy.

KEY RELATIONS

Valence Bond Theory

LCAO

$$\psi = \psi_A \psi_B,\ E = E_A + E_B$$

$$\psi = c_1 \psi_1 + c_2 \psi_2 + \ldots$$

$$\psi_+ = \psi_A(1)\,\psi_B(2) + \psi_A(2)\,\psi_B(1)$$

$$\psi_- = \psi_A(1)\,\psi_B(2) - \psi_A(2)\,\psi_B(1)$$

$$\psi_{1\,(MO)} = \frac{1}{\sqrt{2}}(\psi_A + \psi_B)$$

$$\psi_{(MO)} = \frac{1}{\sqrt{2}}(\psi_A - \psi_B)$$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. Valence bond theory of chemical bonding was put forward initially by

   (a) Heisenberg

   (b) Einstein

   (c) Heitler and London

   (d) dc Broglie
2. The phenomenon of resonance is explained by

   (a) molecular orbital theory

   (b) valence bond theory

(c) neither of the two

(d) both the above

3. Choose the incorrect answer:

(a) Bonding MO are formed by the additive effect of the atomic orbitals.

(b) The electron density in the internuclear region in bonding MO is very low.

(c) Energy of the antibonding MO is higher than that of the combining atomic orbitals.

(d) Antibonding MO are represented by σ^*, π^*, δ^*, etc.

4. The condition to be satisfied for the atomic orbitals to form molecule orbitals is

(a) they must possess comparable energies

(b) they must overlap to a considerable extent

(c) they must be symmetrical with respect to the molecular axis

(d) all the above

5. The coefficients of atomic orbitals in sp^2 hybrid orbitals is

(a) 0.5

(b) $\frac{1}{\sqrt{2}}$

(c) $\frac{1}{\sqrt{3}}$

(d) 0.33

6. The wave functions corresponding to ionic structures of hydrogen molecule, according to valence bond theory are

(a) $\psi_A(1)\,\psi_B(1),\ \psi_A(2)\,\psi_B(2)$

(b) $\psi_A(1)\,\psi_A(1),\ \psi_B(2)\,\psi_B(2)$

(c) $\psi_A(2)\,\psi_B(2),\ \psi_A(1)\,\psi_B(1)$

(d) $\psi_A(1)\,\psi_A(2),\ \psi_B(1)\,\psi_B(2)$

Answers

1. (c)
2. (b)
3. (b)
4. (d)
5. (c)
6. (d)

SHORT-ANSWER QUESTIONS

1. Taking the example of the H_2 molecule, explain how the energy is calculated for this molecule from wave function.
2. Write expressions for ψ_{VB} and ψ_{MO} for the H_2 molecule. How do they differ? What conclusion do you draw from it? Can this conclusion be generalised?

3. What do you understand by gerade the ungerade molecular orbitals? What is the criterion to check whether molecular orbital is gerade or ungerade? Explain with suitable examples.
4. What is Born-Oppenheimer approximation in quantum mechanics? How is it applied in the study of potential energy curve of the H_2^+ ion?
5. How is the Ritz linear combination method employed to arrive at the correct wave function? What is the advantage of this method?
6. Write expressions for the wave functions of BMO and ABMO using these expressions. How can you explain the electron probability in the internuclear region in the two cases?
7. How is the total molecular orbital wave function obtained for the H_2 molecule according to molecular orbital theory?
8. Apply quantum mechanics to obtain the wave functions of the two *sp* hybrid orbitals.
9. How are three-dimensional contour diagrams used to represent the electron probability density for bonding and antibonding molecular orbitals?
10. Taking exchange of electrons into consideration and ionic structures of H_2 molecules, write expression for ψ_{covalent} and ψ_{ionic} and for the complete wave function ψ.
11. Write expression for ψ_{MO} for H_2^+ ion according to LCAO method. Starting from it, how do you arrive at the expressions for $\psi_{+(MO)}$ and $\psi_{-(MO)}$?
12. Derive the values of the coefficients of atomic orbitals in the three sp^2 hybrid orbitals.
13. Compare the important characteristics of σ and π molecular orbitals.
14. Outline the main points of variation method to arrive at the correct wave function.
15. Taking the example of H_2^+ ions, explain how the energy is calculated for this species from wave function.
16. Write expressions for bonding and antibonding molecular orbital wave functions in terms of the combining atomic orbital wave functions ψ_A and ψ_B. Discuss graphically the variation of electron probability density for BMO and ψ_A^2 and ψ_B^2 along the internuclear axis.
17. What is hybridisation? What is meant by *sp*, sp^2 and sp^3 hybridisation. Why is the bond formed by a hybrid orbital stronger than that formed by an unhybridised orbital?
18. What are the criteria or the conditions for the formation of molecular orbitals from atomic orbitals?
19. List the basic idea of molecular orbital theory.

GENERAL QUESTIONS

1. How does the LCAO-MO treatment of H_2^+ ion lead to the concept of bonding and antibonding molecular orbitals? Represent them diagrammatically.
2. What are the main points of similarities and differences between VBT and MOT?
3. How does the electron probability density vary with internuclear distance? Represent these graphically as well as by contour diagrams.
4. Using LCAO for wave function for H_2^+, obtain the normalised wave function for BMO and ABMO without neglecting the overlap integral.
5. Compare the main features of the valence bond model with those of the molecular orbital model.

6. Derive expressions for Hamiltonian operator for (i) H_2^+ ion, (ii) H_2 molecule. How is the correct (true) wave function calculated by (i) variation method, and (ii) Ritz linear combination method? How are bond energy and bond length of these species calculated from suitable plots?
7. Apply quantum mechanical principles to calculate the coefficients of atomic orbitals in *sp*, sp^2 and sp^3 hybrid orbitals.
8. Discuss the application of valence bond theory to the study the bond dissociation energy and equilibrium bond distance of H_2 molecule. Explain at least three improvements that are made in the wave function to get better agreement of calculated value with the experimental value.
9. What are gerade and ungerade molecular orbitals? Explain with suitable examples.
10. Using LCAO-MO method, derive expressions for molecular orbital wave functions. Compare the calculated value of energy with the experimental value on the energy versus internuclear distance diagram.
11. Applying quantum mechanical principles, derive expressions for the wave functions of the two *sp* hybrid orbitals, three sp^2 hybrid orbitals and four sp^3 hybrid orbitals.
12. What do you understand by Linear Combination of Atomic Orbitals (LCAO)? How can it be applied to H_2^+ ion to calculate its energy? Comment on the values of the energy obtained?
13. Represent diagrammatically the formation of bonding and antibonding molecular orbitals formed by combination of 2*s* with 2*s* and 2*p* with 2*p* orbitals. How are they designated?
14. Discuss the application of LCAO-MO method to study the H_2 molecule. Compare the results obtained with the experimental values.



Spectroscopy 21

LEARNING OBJECTIVES

- Learn about electromagnetic radiations and the terms like *wavelength, wave number* and *frequency*
- Know rotational, vibrational and electronic energy of molecules
- Learn to set up an absorption spectrometer
- Define resolving power of a spectrometer
- Compare molecular spectroscopy and atomic spectroscopy
- Differentiate between absorption and emission spectroscopy
- Learn Born-Oppenheimer approximation
- Understand selection rules for rotational and vibrational spectra
- Learn width and intensities of spectral lines
- Learn lifetime broadening
- Understand the meaning of *degrees offreedom*
- Learn pure rotational spectra of diatomic molecules
- Compute the frequency, wave number and intensities of lines in rotational spectra
- Describe qualitatively a nonrigid rotor
- Learn selection rules for vibrational transitions in a simple harmonic oscillator
- Arrive at vibrational energy levels of an anharmonic oscillator
- Learn selection rules for vibration transmition of an anharmonic oscillator
- Explain vibrational-rotational spectra for a diatomic molecule taking it as an anharmonic oscillator
- Describe *P, Q, R* branches of rotational-vibrational spectra
- Learn Roman spectra and explain Rayleigh's line, Stokes' line and anti-Stokes' lines in Raman spectra
- Understand pure rotational Raman spectrum and rotational-vibrational Raman spectra in diatomic molecules
- Learn electronic spectra and related Born-Oppenheimer approximation
- Learn potential energy curve and Frank-Condon principle
- Understand electronic transitions in σ, π and *n* molecular orbitals

21.1 INTRODUCTION

Spectro means radiations and ***scopy*** means measurements. Thus, spectroscopy means measurement of radiations.

However, ***spectroscopy is defined as the branch of science which is associated with the***

interaction of radiations of different wavelengths with matter.

Our knowledge about molecular structure is derived from spectroscopy which deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by selection rules derived from quantum mechanics.

21.1.1 Electromagnetic Radiations

An electromagnetic radiations is the radiant energy emitted from any source in the form of heat or light or sound. Some of the characteristics of radiations are listed below.

1. Electromagnetic radiations possess particle nature as well as wave nature. Thus, they have a dual nature. A light beam consists of a stream of particles (photons) moving in the form of waves.
2. Electromagnetic radiations travel with the velocity of visible light, i.e. 2.998×10^8 ms^{-1}.
3. The electromagnetic waves have electric and magnetic fields associated with them at right angles to one another as shown in Fig. 21.1. Thus, if the radiation is moving along the *X*-axis, the magnetic field is oriented along the *Y*-axis and electric field is oriented along the *Z*-axis.

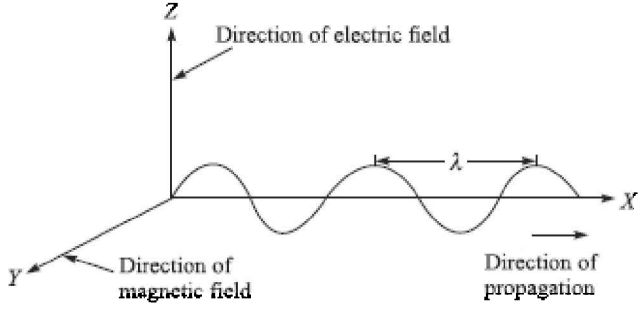


Fig. 21.1 *Electromagnetic radiation travelling in the form of waves and associated with electric and magnetic fields at right angles to each other.*

Visible light, *X*-rays, microwaves, radiowaves, etc., are all electromagnetic radiations. Collectively, they make up the electromagnetic spectrum (Fig. 21.2).

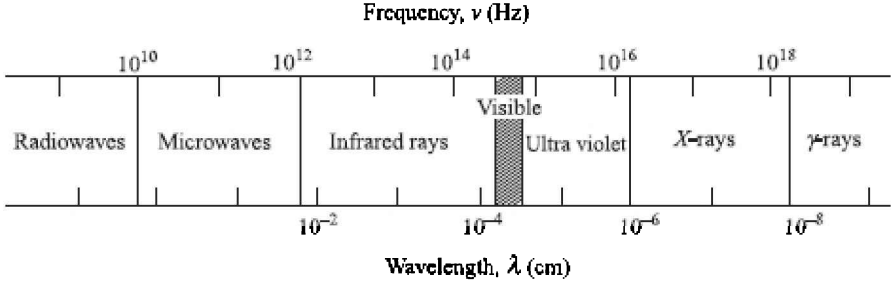


Fig. 21.2 *The electromagnetic Spectrum*

Electromagnetic radiations consist of electrical and magnetic waves oscillating at right angles to each other.

They travel away from the source with the velocity of light (*c*) in vacuum. Different terms used in the study of electromagnetic waves are discussed as under:

1. Frequency (ν) It is the number of successive crests (or troughs) which pass a stationary point

in one second. The unit is hertz; 1 Hz = 1 s^{-1}.

2. Wavelength (λ) It is the distance between successive crests (or troughs). λ is expressed in centimetres (cm), metres (m) or nanometres (1 nm = 10^{-9} m).

3. Wave Number ($\bar{\nu}$) It is the reciprocal of wavelength. Its unit is cm^{-1}.

$$\bar{\nu} = \frac{1}{\lambda}$$

Relation between Frequency, Wavelength and Wave Number Frequency and wavelength of an electromagnetic radiation are related by the equation

$$\nu\lambda = c \qquad \text{...(21.1a)}$$

or

$$\nu = \frac{c}{\lambda} \qquad \text{...(21.1b)}$$

where c is the velocity of light. It may be noted that wavelength and frequency are inversely proportional. That is, higher the wavelength, lower is the frequency; lower the wavelength higher is the frequency.

Further,

$$\bar{\nu} = \frac{1}{\lambda}\,cm^{-1} \qquad (21.1c)$$

From (21.1b) and (21.1c),

$$\nu = c\bar{\nu}$$

21.1.2 Energy of Electromagnetic Radiation

Electromagnetic radiation behaves as consisting of discrete wavelike particles called ***quanta*** or ***photons***. Photons possess the characteristics of wave and travel with the velocity of light in the direction of the beam. The amount of energy corresponding to 1 photon is expressed by ***Planck's equation***.

$$E = h\nu = hc/\lambda$$

where E is the energy of 1 photon (or quantum), h is Planck's constant (6.62×10^{-27} ergs-second), υ is the frequency in hertz; and λ is the wavelength in centimetres.

If N is the Avogadro number, the energy of 1 mole of photons can be expressed as

$$E = \frac{Nhc}{\lambda} = \frac{2.85 \times 10^{-3}}{\lambda}\ \text{kcal/mol}$$

21.2 ROTATIONAL, VIBRATIONALAND ELECTRONIC ENERGIES OF MOLECULES

1. Rotational Energy It involves the rotation of molecules or of parts of molecules about the centre of gravity (Fig. 21.3).

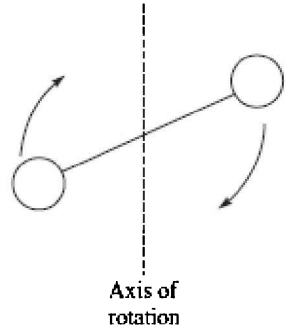


Fig. 21.3 *Molecular rotation in molecules*

2. Vibrational Energy It is associated with stretching, contracting or bending of covalent bonds in molecules. The bonds behave as spirals made of wire (Fig. 21.4).

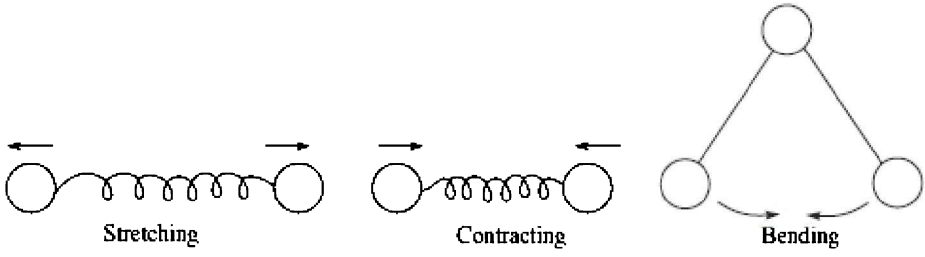


Fig. 21.4 *Vibrations within molecules*

3. Electronic Energy It involves changes in the distribution of electrons by splitting of bonds or the promotion of electrons into higher energy (Fig. 21.5).

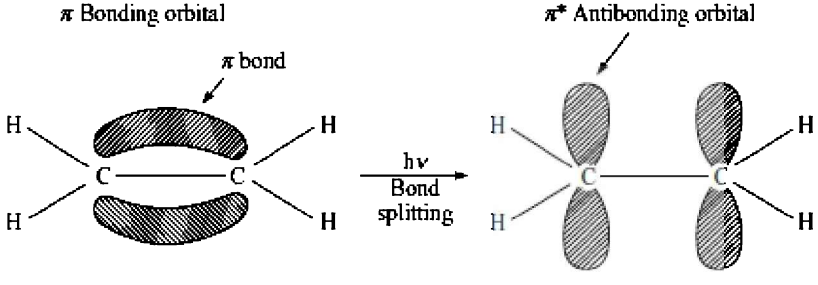


Fig. 21.5 *Splitting of π bond by absorption of energy.*

21.2.1 Experimental Set-up of Absorption Spectrophotometer

Absorption spectrum of a given sample is obtained experimentally with the help of an apparatus called ***absorption spectrophotometer*** (Fig. 21.6). Light of a range of wavelengths from the source is passed through the sample. The wavelengths corresponding to allowed molecular transitions are absorbed. The transmitted light is passed through a prism which resolves it into various wavelengths. It is then reflected from the mirror onto a detector. The prism is rotated so that light of

each given wavelength is focussed on the detector. The pen recorder records the intensity of radiation as a function of frequency and gives the absorption spectrum of the sample.

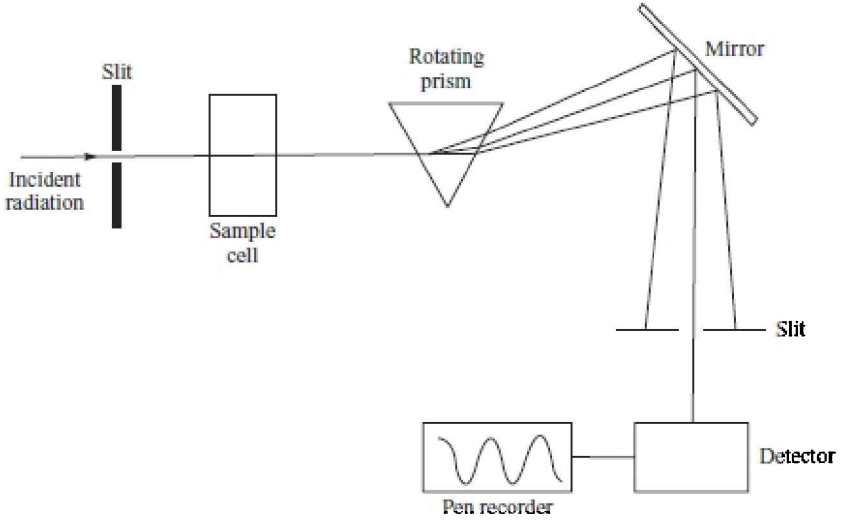


Fig. 21.6 *Working of absorption spectrophotometer*

Signal-to-Noise Ratio The signals produced in the analysis of a sample using a spectrophotometer consist of two parts:

(a) Signals produced due to the sample

(b) Signals produced due to other components (solvents, etc.) and the instrument used

The signals produced as in (b) are called ***noise***. The noise signals are unwanted and hinder sometimes the interpretation of signals. ***Noise may be defined as the random electronic signals that are usually visible as fluctuation of base line in the signal*** (Fig. 21.7). It is, therefore, always designed to root out the signals or at least to minimise them so that a correct interpretation of signals in the spectrum can be made.



Fig. 21.7 *The signle-to-noise ratio*

The amount of radiation absorbed by the sample depends upon the concentration. Therefore, the amount of noise obtained using an instrument determines the smallest concentration of the sample that can be measured accurately. With decreasing concentration of the sample, we observe greater difficulty in distinguishing noise from the signal. This leads to decreased precision in the measurements. The ability of an instrument to distinguish between noise and signal is expressed as

signal-to-noise ratio.

$$\frac{\text{Average signal amplitude}}{\text{Average noise amplitude}} = \frac{S}{N}$$

Obviously, a greater value of *S/N* indicates greater noise reduction or greater precision in measurement. It is important to understand that *S/N* ratio cannot be increased to simple amplification (increase of current), because the magnitude of both noise and signal increases. Thus, this does not solve the problem. Some techniques, for example, hardware techniques using filters and lock-in-amplifiers, and software techniques, using software algorithm of ensemble averaging and Fourier transformation, have been used with success to increase *S/N* ratio

21.2.2 Resolving Power

The resolving power of a spectrometer is its ability to distinguish between adjacent absorption bands or two very close spectral lines as separate entities.

Consider a prism whose base length is *b*. Suppose the light from a suitable source after crossing the lens L_1 is incident on the prism which disperses and resolves the radiation, and is focussed by the lens L_2 onto the detector (Fig. 21.8).

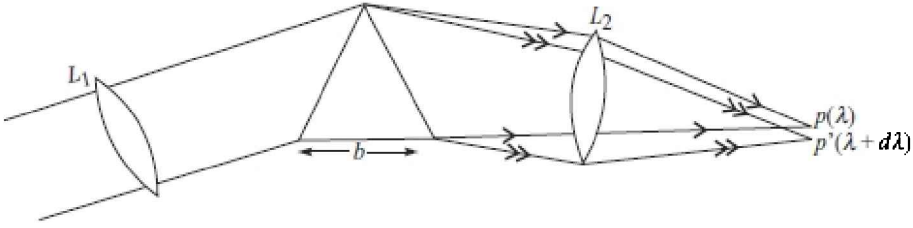


Fig. 21.8 *Dispersion by a prism*

Suppose, after dispersion, the two radiations separated out have wavelengths λ and λ + *d*λ; then the interval *d*λ gives the value of ***resolution***. Smaller the intervals, higher the resolution of the prism. The resolving power *R* of a dispersing element is given by

$$R = \frac{\lambda}{d\lambda}$$

If *n* is the refractive index and *b* is the base length of the prism then resolving power of the prism is given by

$$R = b\frac{dn}{d\lambda}$$

*dn/d*λ represents the change in refractive index of the material of the prism with change in wavelength of the incident radiation. Obviously, for high resolving power, *dn/d*λ should be large.

Another important factor on which the resolution depends is the width of the slit (aperture) of light used before lens L_1. It is expected that a narrower slit would give better resolution. However a narrow slit allows less total energy from the beam to reach the detector. As a result, we receive weak signals, which become indistinguishable from the noise. Thus, an optimum minimum width of the slit, which gives acceptable signal-to-noise ratio, has to be decided.

21.3 MOLECULAR SPECTROSCOPY VERSUS ATOMIC SPECTROSCOPY

In the case of atoms, electrons jump from a lower orbit to a higher orbit. When they start coming back to the lower orbit, emission of energy equal to the difference in the energies of the two orbitals takes place in the form of atomic spectrum.

However, in case of molecules, when the energy is absorbed, it may result into rotation, vibration or electronic transition depending upon the amount of energy absorbed. Just as electronic energy is quantised, i.e. there are only discrete electronic energy levels in an atom or a molecule, the rotational and vibrational energies are also quantised, i.e. there are only discrete rotational and vibrational energy levels in a molecule. The rotational, vibrational and electronic energy levels of a molecule are collectively called ***molecular energy levels***. The transition of energies can take place only between these levels. The result is a ***molecular spectra***. Just as the study of atomic spectra is helpful in the study of structure of atoms, the study of molecular spectra is one of the best experimental methods in studying the structure of molecules.

When the energy absorbed by a molecule is so large that an electron can jump from one electronic energy level to another (say $n = 1$ to $n = 2$) then as the energy required for transition from one vibrational energy level to another is much less and for one rotational level to another is still less, hence the electronic transition is also accompanied by the transition between the vibrational levels as well as the rotational level. The complete picture of electronic levels is shown in Fig. 21.9.

It is evident that each electronic level consists of a number of vibrational sublevels represented by $\upsilon = 0, 1, 2, 3$, etc., and further each vibrational level consists of a number of rotational sublevels represented by $J = 0.1, 2, 3$, etc. λ and J are called ***vibrational and rotational quantum numbers respectively***.

Due to a large number of energy levels involved in transition, the molecular spectra are much more complex than atomic spectra. However, just as atomic spectra help in the study of the structure of the atoms, the study of molecular spectra gives even more information about the structure and properties of molecules such as bond lengths, bond angles, bond strength, shapes, dipole moments, etc.

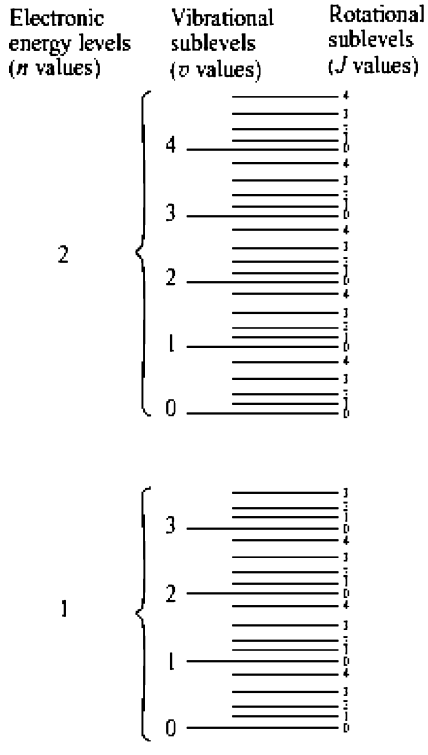


Fig. 21.9 *Molecular energy levels*

21.4 ABSORPTION AND EMISSION SPECTROSCOPY

An atom or a molecule has a number of energy levels which are quantised. The transitions take place only between these energy levels according to certain rules, called ***selection rules***. Transition between any two energy levels can take place in either of the following two ways:

1. The transition may take place from lower energy level to higher energy level by absorbing energy [Fig. 21.10 (a)]. It is then called ***absorption spectroscopy*** and the result obtained as a result of number of such transitions is called *"absorption spectrum"*. Absorption spectrum consists of ***dark*** lines.
2. The transition may take place from higher energy level to a lower energy level [Fig. 21.10 (b)], thereby emitting the excess energy as a photon. It is then called ***emission spectroscopy*** and the result obtained as a result of a number of such transitions is called ***"emission spectrum"***. Emission spectrum consists of ***bright*** lines.

In fact, a number of groups of closely spaced lines are observed. Each such group of closely spaced lines is called a ***band***. Thus, a number of ***bands*** are observed. We can, therefore, conclude that whereas atoms give line spectra, molecules give band spectra.

In either case, the energy of the photon $h\nu$ emitted or absorbed is given by Bohr's frequency formula,

$$E_2 - E_1 = h\nu$$

or in terms of wavelength number, = $\bar{\nu} = \frac{c}{\lambda}$

or in terms wave number, = $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$ (in cm^{-1} if λ in cm or velocity c in $cm\ s^{-1}$)

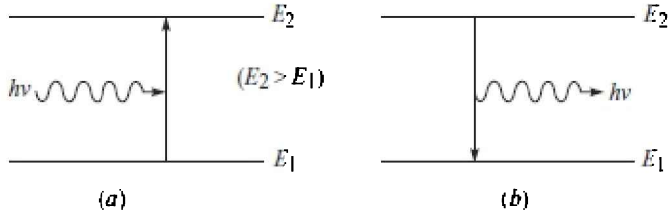


Fig. 21.10 *(a) Transition involving absorption of photon (b) Transition involving emission of photon*

It may be mentioned that emission and absorption spectroscopy gives the same information about the energy-level separations. However, the practical considerations decide as to which technique should be used. Generally, absorption spectra are easier to interpret than emission spectra.

21.5 TYPES OF MOLECULAR ENERGIES AND BORN-OPPENHEIMER APPROXIMATION

Four different types of energies possessed by a molecule are the following:

1. ***Translational Energy:*** This energy is due to translational linear motion of the molecule.
2. ***Rotational Energy:*** This is due to rotation of the molecule about an axis perpendicular to the internuclear axis (Fig. 21.3).
3. ***Vibrational Energy:*** This is due to the to-and-fro motion of the nucleus of the molecule without allowing any change in the centre of gravity of the molecule (Fig 21.4).
4. ***Electronic Energy:*** This is due to absorption of energy by the electron resulting in excitation to higher energy levels (Fig 21.5).

Born-Oppenheimer Approximation

According to the above postulate, ***the total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies,***

or $$E = E_t + E_r + E_v + E_e$$

It has been found that translation energy E_t is negligible compared to E_r, E_v and E_e. Therefore,

$$E = E_r + E_v + E_e$$

21.6 TYPES OF MOLECULAR SPECTRA

A molecule possesses quantised translational, rotational, vibrational and electronic energy levels. Within any two successive electronic energy levels, there are a number of different vibrational levels, and a number of different rotational levels. The energy difference between any two successive electronic levels is more than that between any two successive vibrational levels which in turn is more than that between any two successive rotational levels. It can be represented as

$$E_r << E_v << E_e$$

We are not taking into consideration translation energies E_t. The difference between two successive translational levels is so small that it cannot be determined experimentally. For practical purposes, translational energy is considered continuous and we do not observe any translational spectrum.

Different types of molecular spectra are described as under:

1. Pure Rotational (Microwave) Spectra If the energy absorbed by the molecules is such that it can cause transition only from one rotational level to another within the same vibrational level, the result obtained is called the rotational spectrum. These spectra are, therefore, observed in the ***far infrared region*** or in the ***microwave region*** whose energies are extremely small ($\bar{\nu}$ = 1 − 100 cm^{-1}). The spectra obtained is, therefore, also called *microwave* spectra.

2. Vibrational Rotational Spectra If the incident energy is sufficiently large so that it can cause a transition from one vibrational level to another within the same electronic level then as the energies required for the transitions between the rotational levels are still smaller, both types of transitions, viz. vibrational and rotational, will take place. The result is, therefore, a vibrational-rotational spectrum. Since such energies are available in the near infrared region, these spectra are observed in this region ($\bar{\nu}$ = 500 − 4000 cm^{-1}) and are called ***infrared spectra***.

3. Electronic Band Spectra If the incident energy is higher such that it can result in a transition from one electronic level to another then this will also be accompanied by vibrational level changes and each of these is further accompanied by rotational level changes. Such a group of closely spaced rotational lines is called a band. Thus, for a given electronic transition, a set of bands is observed. This set of bands is called a ***band group*** or ***band system***. Each electronic transition gives a band system. The complete set of band systems obtained due to different electronic transitions gives the electronic band spectrum of the gaseous molecule. If such high excitation energies are obtained from the visible and ultraviolet regions, these spectra are observed in the ***visible region*** (12,500–25,000 cm^{-1}) and ***ultraviolet*** region (25000–70000 cm^{-1}) respectively.

4. Raman Spectra This is also a type of vibrational-rotational spectrum but is based on scattering of radiation and not on the absorption of radiation by the sample. It is based upon the principle that when a sample is hit by monochromatic radiation of the visible region and scattering is observed at ***right angles to the direction of the incident beam,*** the scattered radiation has frequency equal to that of the incident beam (called ***Rayleigh scattering)*** as well as frequencies different (higher as well as lower) from that of the incident beam (called Raman scattering). The difference in frequencies of the incident beam and that of the scattered beam (called ***Raman frequencies)*** are similar to those observed for the vibrational and rotational transitions. However, by suitably adjusting the frequency of the incident radiation, Raman spectra are observed in the visible region (12500–25000 cm^{-1})

5. Nuclear Magnetic Resonance (NMR) Spectra This type of spectrum arises from the transitions between the ***nuclear spin energy levels*** of the molecule when an external magnetic field is applied on it. The energies involved in these transitions are very high which lie in the ***radio-frequency region*** (5–100 MHz). The method is based upon applying such frequencies on the sample so that it resonates with the applied frequency.

6. Electronic Spin Resonance (ESR) Spectra This type of spectrum arises from the transitions between the ***electron spin energy levels*** of the molecule when an external magnetic field is applied on it. They involve frequencies corresponding to microwave region (2000–9600 MHz). Frequencies of this range are applied on the sample to bring the sample in resonance condition.

ROTATIONAL SPECTRA

21.7 SELECTION RULES FOR ROTATIONAL AND VIBRATIONAL SPECTRA

Atomic spectrum, as well as molecular spectrum, are obtained due to transition taking place between energy levels. However, such transitions can take place only between definite energy levels and not between just any two energy levels. The ***restrictions thus applied on the transition are governed by certain rules called the selection rules***. If these rules are followed, the transition can take place and it is called an ***allowed transition***. If these are not followed, the transition cannot take place and it is called a ***forbidden transition***. The selection rules to be followed depend upon the type of transition.

The ***selection rules*** are generally expressed in terms of changes in quantum numbers for the allowed transitions. For example, for the pure rotational transition, the selection rule is $\Delta J = \pm 1$, where J represents rotational quantum number ($\Delta J = +1$ corresponds to ***absorption*** and $\Delta J = -1$ corresponds to ***emission)***. Similarly, for pure vibrational transition, the selection rules is $\Delta \upsilon = \pm 1$ where υ represents the vibrational quantum number.

The fundamental principle which forms the basis of selection rules is that for a molecule to absorb or emit a radiation frequency ν, it must possess a dipole at that frequency. Thus, a transition is allowed only if transition dipole moment, $\mu_{tr} \neq 0$. μ_{tr} will be zero for the molecule which has no dipoles. Hence, only the molecules like NO, CO, etc., which have permanent dipole give rotational spectra.

21.8 WIDTH AND INTENSITIES OF THE SPECTRAL LINES

21.8.1 Width of Spectra Lines

If the spectral line is sharp, it will appear in the spectrum as a vertical line with no width (Fig. 21.11a). On the contrary, if the line is not sharp, it will have a certain width as shown in Fig. 21.11(b).

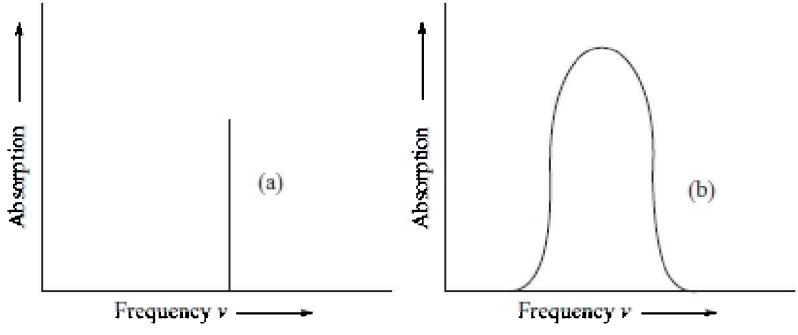


Fig. 21.11 *(a) A Sharp spectral line (b) A spectral line having width*

Factors Affecting Width of Spectral Lines The following two factors which contribute to the broadening of spectral lines.

(a) Doppler broadening

(b) Lifetime broadening

The two are described separately.

(a) Doppler Broadening This type of broadening occurs due to Doppler effect, which is applicable to gaseous samples.

Frequency of the radiation emitted or absorbed changes when the molecule is moving towards

or away from the observer.

If the molecule (source) emitting the frequency ν is moving away from the observer with a velocity v, the observer records the frequency of radiation as,

$$\nu' = \frac{\nu}{1 + \frac{v}{c}} \qquad \ldots(21.2)$$

If the molecule (source) is approaching the observer with a velocity v, the observer records the frequency of radiation as,

$$\nu' = \frac{\nu}{1 - \frac{v}{c}} \qquad \ldots(21.3)$$

It is found by calculation based on Maxwell distribution of velocities that if m is the mass of the gas molecule then at temperature T, the width of line at half the height is

$$\delta\nu = \frac{2\nu}{c}\left(\frac{2kT \ln 2}{m}\right)^{1/2} \qquad \ldots(21.4)$$

Doppler broadening increases with temperature because of increase in molecular velocities with temperature. It is, therefore, best to work at low temperatures to obtain spectra of maximum sharpness.

(b) Lifetime Broadening This broadening applies to samples in gases, liquids and solids including solutions. When the Schrodinger equation is solved for a system that is changing with time, it is not possible to specify energies of levels exactly. Suppose, on an average, a system remains in a state for the time τ (lifetime of the state); then energy level becomes uncertain to the extent δE given by the equation.

$$\delta E = \frac{h}{2\pi\tau} \qquad \ldots(21.5)$$

The quantity δE is called lifetime broadening. Equation (21.5) is analogous to the Heisenberg uncertainty principle and the quantity δE may also be called ***uncertainty broadening***.

We can see from Eq. (21.5) that δE and τ are inversely related. Thus, shorter the lifetime of the state involved in the transition, greater will be the broadening of the spectral line. No excited state lines lie in infinite lifetime. Therefore, all states are subject to some lifetime broadening.

Collision between the molecules or with the walls of the container is the main reason for finite lifetimes of the excited state.

If τ_{coll} is the mean time between collisions then the width of the resulting line as given by the relation

$$\delta E_{coll} - \frac{h}{2\pi\tau_{coll}} \qquad \ldots(21.6)$$

Broadening can be minimised by working at low pressures with a gaseous sample.

21.8.2 Intensity of Spectral Lines

Factors which determine the intensity of the spectral lines are

1. Population density of a state
2. Strength of the incident radiation
3. Probability of transition taking place between the energy levels

Greater the intensity of radiation, greater is the rate at which transitions take place resulting in

stronger absorption by the sample. Similarly, transition probability is decided by selection rules. If a transition is allowed, we expect a strong spectral line. If it is a forbidden transition, we obtain a weak spectral line (or no spectral line). Einstein explained how the population density of the states involved in the transition affects the intensity of the spectral lines. He suggested that the net rate of absorption in the presence of an electromagnetic field (i.e. incident radiation) is the outcome of the following processes:

1. Stimulated (by the incident radiation) absorption
2. Stimulated emission (emission of photon)
3. Spontaneous emission

The net absorption, as a result of the above three processes, is given by

$$R_{net} = (N - N') B\rho \qquad \ldots(21.7)$$

where, N = Number of molecules present in the lower state

N' = Number of molecules present in the upper state

B = Einstein coefficient of stimulated absorption

ρ = Energy density of the radiation at the frequency of transition

At any temperature T, the ratio of the population of the two states with energy E and E' can be obtained from Boltzmann distribution law,

$$\frac{N'}{N} = e^{-h\nu/kT} \qquad \ldots(21.8)$$

But $h\nu = E' - E = \Delta E$

If ΔE is large, from Eq. (21.8), N'/N will be small.

This means population in the upper state is small. Hence, the only absorption will be from the lower state. The stimulated emission from the upper state will also be small.

21.9 DEGREES OF FREEDOM

Consider a molecule made up of N atoms. We know that all the mass of the atom is concentrated in its nucleus and the nucleus is very small in size. Therefore, the atoms may be considered as mass points. To represent each mass point, we require three coordinates. Hence, to represent the instantaneous position of N mass points in space, we require $3N$ coordinates. This is how we introduce the term *degrees of freedom*.

Thus, a molecule made up of N atoms has $3N$ degrees of freedom.

When thermal energy is absorbed by a molecule, it is stored within the molecule in the form of

1. translational motion of the molecule
2. internal movement of the atoms within the molecule, i.e. rotational motion and vibrational motion

The translational motion of the molecule means the motion of the centre of mass of the molecule as a whole. The centre of mass of a molecule can be represented by three coordinates. Thus, there are ***three translational degrees of freedom***. The remaining $(3N - 3)$ coordinates represent the ***internal degrees of freedom***.

The internal degrees of freedom may be subdivided into

1. rotational degrees of freedom
2. vibrational degrees of freedom

For a rotational motion, there are two degrees of freedom for a linear molecule and three for a nonlinear molecule as shown in Fig. 21.12.

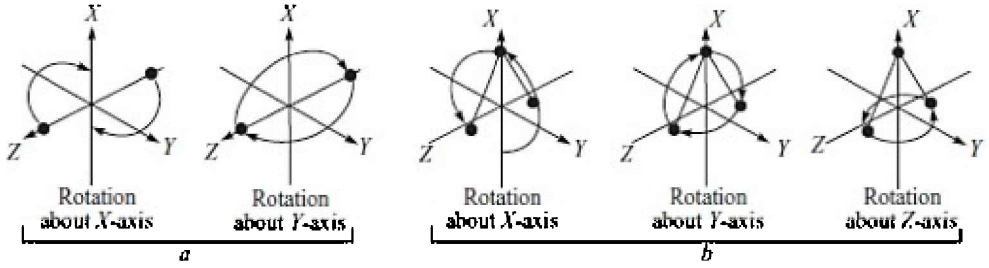


Fig. 21.12 *(a) Rotations of a linear molecule about two mutually perpendicular axes (b) Rotations of a nonlinear molecule about three mutually perpendicular axes.*

Remaining degrees of freedom for the ***linear*** molecules are equal to $(3N - 5)$ and for the ***nonlinear*** molecules, they are equal to $(3N - 6)$. These degrees of freedom represent the number of ***vibrational degrees*** of freedom.

Hence,

Vibrational degrees of freedom of a linear molecule containing N atoms = $3N - 5$

Vibrational degrees of freedom of nonlinear molecule containing N atoms = $3N - 6$

A few examples on the calculation of vibrational degrees of freedom are given below:

1. As a diatomic molecule ($N = 2$) is always linear, its vibrational degrees of freedom = $3N - 5 = 3 \times 2 - 5 = 1$
2. For the linear polyatomic molecule CO_2, $N = 3$. Hence, vibrational degrees of freedom $3N - 5 = 3 \times 3 - 5 = 4$. Similarly, for HC ≡ CH, $N = 4$. Hence, the vibrational degrees of freedom = $3N - 5 = 3 \times 4 - 5 = 7$.
3. For the nonlinear polyatomic molecule H_2O, $N = 3$. Hence, vibrational degrees of freedom = $3N - 6 = 3 \times 3 - 6 = 3$. Similarly, for HCHO, $N = 4$ and the vibrational degrees of freedom = $3N - 6 = 3 \times 4 - 6 = 6$.

The vibrational degrees of freedom represent the inter-atomic distances and angles needed to specify the geometry of the atomic framework within the molecule.

Also, the vibrational degrees of freedom represent the number of independent vibrational modes that can occur in the molecule, the vibrational energy being associated with each mode.

The three modes of vibration of a diatomic molecule like CO, four modes of vibration of linear tri-atomic CO_2 molecule and three modes of vibration of nonlinear triatomic H_2O molecule are illustrated in Fig. 21.13

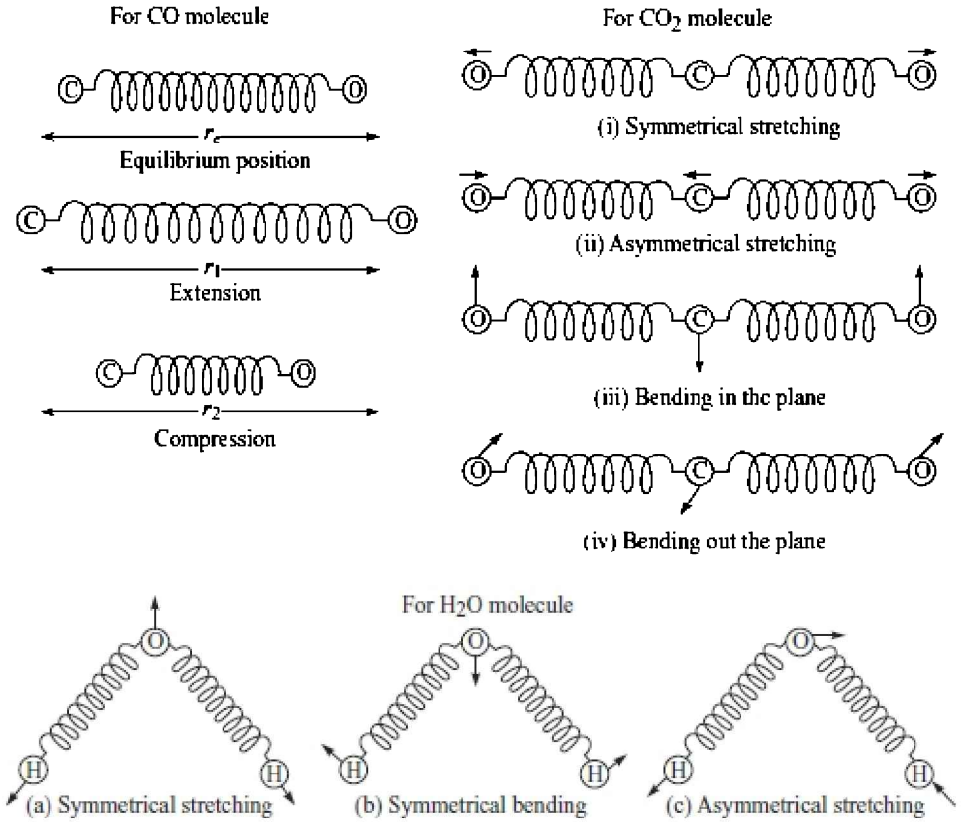


Fig. 21.13 *Normal modes of vibration of (a) diatomic molecule, CO, (b) linear triatomic molecule, CO_2 and (c) nonlinear triatomic molecule, H_2O*

21.10 PURE ROTATIONAL SPECTRA OF DIATOMIC MOLECULES

Energy Levels of a Rigid Rotator If a ***diatomic*** molecule is considered to a rigid rotator, i.e. a rigid dumb-bell joined along its lines of centres by a bond equal in length to the distance r_0 between the two nuclei (Fig. 21.14) then the allowed rotational energies of the molecule around the axis passing through the centre of gravity and perpendicular to the line joined the nuclei are given by

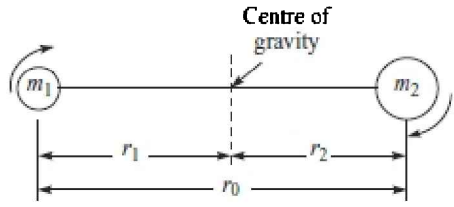


Fig. 21.14 *Rigid rotator.*

$$E_r = \frac{h}{8\pi^2 I} J(J+1)$$

where J is the rotational quantum number that can have value 0, 1, 2, 3… etc. I is the moment of inertia of the molecule about the axis of rotation, i.e.

$$I = \left[\frac{m_1 m_2}{m_1 + m_2}\right] r_0^2 = \mu r_0^2$$

where m_1 and m_2 are atomic masses of the two atoms of the diatomic molecule and

$$\frac{m_1 m_2}{m_1 + m_2} = \mu \text{ is called the } \textbf{\textit{reduced mass.}}$$

21.10.1 Derivation of the Expression for Rotational Energy

Centre of gravity of a diatomic molecule can be obtained on the basis of the following equation.

$$m_1 r_1 = m_2 r_2 \qquad \ldots(21.9a)$$

The moment of inertia of the diatomic molecule is given by.

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \ldots(21.9b)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_1 r_2 (m_1 + m_2) \qquad \ldots(21.9c)$$

But $r_1 + r_2 = r_0 \qquad \ldots(21.10)$

$\therefore$ from Eq. (21.9a), $m_1 r_1 = m_2 (r_0 - r_1)$

or $$r_1 = \frac{m_2 r_0}{m_1 + m_2} \qquad \ldots(21.11)$$

Similarly, $$r_2 = \frac{m_1 r_0}{m_1 + m_2} \qquad \ldots(21.12)$$

Substituting these values in Eq. (21.9b), we get

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r_0^2 + \frac{m_1^2 m_2}{(m_1 + m_2)^2} r_0^2$$

$$\frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} r_0^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$= \mu r_0^2 \quad \ldots(21.13)$$

$$\left(\text{where, } \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ is the reduced mass} \right)$$

By definition, angular momentum of a rotating molecule is given by

$L = I\omega$ where ω is the angular velocity (just as linear momentum is mass × velocity) Angular momentum is quantised whose values are given by,

$$L = \sqrt{J(J+1)}\,\frac{h}{2\pi} \quad \ldots(21.14)$$

where, $J = 0, 1, 2, 3, \ldots$, called the ***rotational quantum numbers***.

The energy of a rotating molecule is given by

$$E = \frac{1}{2} I\omega^2$$

$\therefore$ the quantised value of the rotational energy is given by

$$E_r = \frac{1}{2} I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \quad \ldots(21.15)$$

Substituting the value of L from Eq. (21.14), we get

$$E_r = J(J+1)\frac{h^2}{4\pi^2} \times \frac{1}{2I} \quad \text{or} \quad E_r = \frac{h^2}{8\pi^2 I} J(J+1) \quad \ldots(21.16)$$

Putting $J = 0, 1, 2, 3$, etc., in Eq. (21.16), pattern of the rotational energy levels obtained will be as shown in Fig. 21.15.

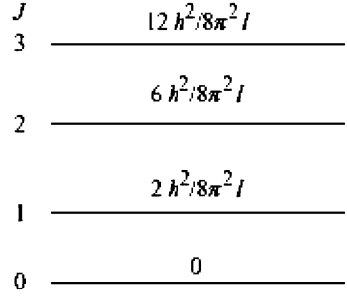


Fig. 21.15 *Rotational energy levels of a diatomic molecule treating it as a rigid rotator*

As can be seen above, the spacing between the energy levels increases as J increases, because of the factor $J(J + 1)$ in Eq. (21.16).

21.10.2 Frequency and Wave Number of Lines in the Rotational

Spectrum

Allowed rotational energies are given by the expression

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \ldots(21.17)$$

As $E = h\nu$, therefore, in terms of frequency, we can write Eq. (21.17) as

$$\nu = \frac{h}{8\pi^2 I} J(J+1) \qquad \ldots(21.18)$$

Also, $c = \nu\lambda = \nu/\bar{\nu}$ (because wave number $\bar{\nu} = 1/\lambda$). In terms of wave numbers, Eq. (21.18) can be written as

$$\bar{\nu} = \frac{h}{8\pi^2 Ic} J(J+1) \qquad \ldots(21.19)$$

Putting $\frac{h}{8\pi^2 Ic}$ equal to B, Eq. (21.19) reduces to

$$\bar{\nu} = BJ(J+1) \qquad \ldots(21.20)$$

where B is called ***rotational constant***.

Putting $J = 0, 1, 2, 3$, etc., in (21.20), ***the wave numbers*** of the different rotational levels will be

$$0, 2B, 6B, 12B, 20B, 30B, \ldots \text{ so on}$$

Suppose a transition takes place from a lower rotational level with rotational quantum number J to a higher rotational level with rotational quantum number J'.

The energy absorbed will be given by

$$\Delta E_r = E_r' - E_r \quad (\text{or } E_j' - E_j)$$

$$= \frac{h^2}{8\pi^2 I} J'(J'+1) - \frac{h^2}{8\pi^2 I} J(J+1)$$

$$= \frac{h^2}{8\pi^2 I} [J'(J'+1) - J(J+1)] \qquad \ldots(21.21)$$

According to the rotational selection rules, only those rotational transition are allowed for which $\Delta J = \pm 1$. Hence, in the present case, $J' = J + 1$

Substituting this value in Eq. (21.21), we get

$$\Delta E_r - \frac{h^2}{8\pi^2 I} [(J+1)(J+2) - J(J+1)]$$

$$= \frac{h^2}{8\pi^2 I} 2(J+1) \qquad \ldots(21.22)$$

To express in terms of wave numbers, we put

$$\Delta E_J = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$$

Hence, $$hc\bar{\nu} = \frac{h^2}{8\pi^2 I} \times 2(J+1)$$

or $$\bar{\nu} = \frac{h}{8\pi^2 Ic} \times 2(J+1)$$

$$\therefore \bar{\nu} = 2B(J+1) \qquad \ldots(21.23)$$

where $B = \dfrac{h}{8\pi^2 Ic}$ is rotational constant (as already explained).

$\bar{\nu}$ in Eq. (21.22) represents the wave numbers of the spectral lines which will be obtained as a result of the transitions between the rotational levels. Putting J' = 0, 1, 2, 3, etc. (i.e. for the transitions J = 0 to J' = 1; J = 1 to J' = 2, etc.) or, in general, from J to J + 1 (involving absorption of energy), the wave numbers of the lines obtained will be

$2B$, $4B$, $6B$, $8B$, … and so on.

The most important feature of the pure rotational spectrum is that every two successive lines have a constant difference of wave number equal to $2B$. This is called ***frequency separation*** (or more strictly ***wave number*** separation). Thus, the various lines in the rotational spectra will be equally spaced as shown in Fig. 21.16.

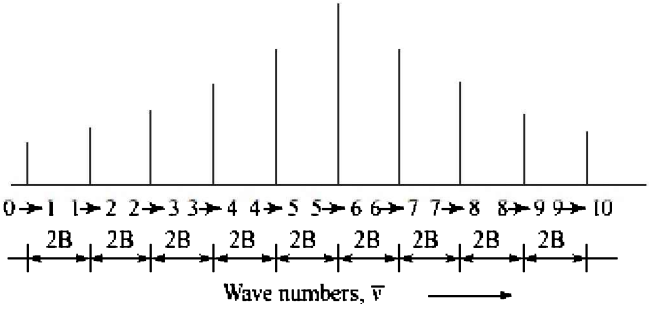


Fig. 21.16 *Appearance of a rotational spectrum.*

Any two successive lines will have the difference in wave numbers given by

$$\Delta\bar{\nu} = 2B = \frac{h}{4\pi^2 Ic}$$

We observe in the spectra that the intensities of different transition are not equal. The intensities increase with increasing J, pass through a maximum and then decreases as J increase further.

21.10.3 Intensities of Rotational Spectra Lines

As explained in Sec. 21.8.2, the relative intensities of the spectra lines will depend upon the relative populations of the energy levels. Greater the population of the energy level, greater is the number of molecules that can be promoted to the next higher level and hence, greater is the intensity of absorption. But the population of a rotational energy level with quantum number J relative to that of the ground level for which J = 0 is given according to Boltzmann's distribution law by equation,

$$\frac{N_J}{N_0} = e^{-E_J/kT} \qquad \ldots(21.24)$$

However, rotational energy levels are degenerate and the degeneracy of any rotational level with quantum number J is given by

$$g_j = 2J + 1 \qquad \ldots(21.25)$$

If we take into consideration degeneracy factor, Eq (21.24) should be replaced by

$$\frac{N_J}{N_0} = g_j e^{-Ej/kT} \qquad \ldots(21.26)$$

From (21.25) and (21.26),

$$\frac{N_J}{N_0} = (2J + 1) e^{-Ej/kT} \qquad \ldots(21.27)$$

$$\text{Intensity} \propto \frac{N_J}{N_0} = (2J + 1) e^{-Ej/kT}$$

Putting $$E_j = h\nu = h\frac{c}{\lambda} = hc\bar{\nu} = hcBJ(J + 1)$$ [(Refer Eq. (21.20)]

We have, $$\frac{N_J}{N_0} = (2J + 1) e^{-hcBJ(J+1)/kT}$$

As J increases, the first factor, viz. $(2J + 1)$, increases whereas the exponential factor decreases slowly in the beginning and then rapidly as the values of J become higher and higher. Hence, the plot of N_J/N_0 versus J for a rigid diatomic molecule is obtained as shown in Fig. 21.17.

The graph clearly shows that relative population and hence, the intensity of transitions first increases, reaches a maximum value and then decreases.

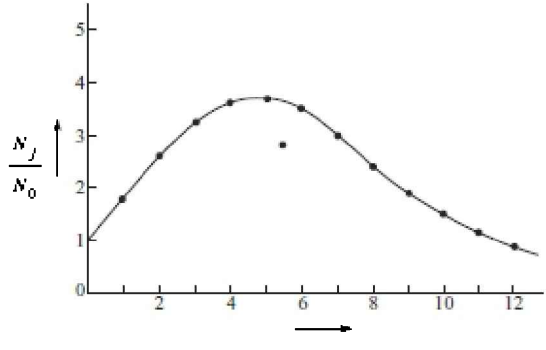


Fig. 21.17 *Plot of relative population of rotational energy levels versus rotational quantum number*

21.10.4 Types of Molecules Showing Rotational Spectra

The condition for obtaining a pure rotational spectrum is that the molecule must have a permanent dipole moment so that it can interact with electromagnetic radiation and absorb or emit photons. Thus, pure rotational spectrum is given only by polar molecules. Consequently, homonuclear diatomic molecules (like H_2, N_2, etc.) and symmetrical linear molecules like CO_2 (or symmetrical molecules like C_6H_6) do not give rotational spectra. Polar molecules life H_2O, NO, N_2O, etc., give pure rotational spectra.

Example 1 *Which of the following molecules show rotational spectra HCl, CO, H_2 and O_2?*

Solution Out of HCl, CO, H_2 and O_2, the first two, namely HCl and CO, will give rotational spectra as they possess a permanent dipole moment. This is a necessary condition for a molecule to show rotational spectra.

21.10.5 Application of Rotational Spectra

By determining the frequency separation $\Delta\bar{v}$, it is possible to calculate the moment of inertia I of the molecule, using the equation $B = h/8\pi^2 Ic$. Then knowing the masses of the atoms present in the diatomic molecule, it is possible to calculate the distance between the atoms, r_0 (i.e. internuclear distance or bond length) using the equation,

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r_0^2$$

Working of Spectrometer The source of radiations is a special type of electronic oscillator ***(called klystron)***. It produces radiations of frequency corresponding to wavelength range of 0.1 to a few hundred centimetres. The energies corresponding to these wavelengths are same as required for rotational transitions. The procedure consists of passing the monochromatic energy of the microwaves through the gaseous sample of the substance being studied and measuring the intensity of the transmitted radiation. By varying the frequency of the oscillator and observing the intensity of the transmitted beams, the frequencies at which absorption take place can be determined from the plot of transmitted intensity versus frequency.

Example 2 *The far infrared spectrum of H1 consist of series of equally spaced lines with $\Delta\bar{v}$ = 12.8 cm^{-1}. What is (a) the moment of inertia, and (b) the internuclear distance?*

Solution: In CGS system,

(a) Here, we are given

$$\Delta v = 12.8 \text{ cm}^{-1}$$

$$I = \frac{h}{4\pi^2 c \Delta\bar{v}} = \frac{6.62 \times 10^{-27}}{4 \times \left[\frac{22}{7}\right]^2 \times (3 \times 10^{10})(12.8)} = 4.36 \times 10^{-40} \text{ g cm}^2$$

(b)

(b) $I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r_0^2$

Here, m_1 (For H atom) $\frac{1.008}{6.022 \times 10^{23}} \text{ g} \quad 1.6739 \times 10^{-24} \text{ g}$

m_2 (For I atom) $\frac{127}{6.022 \times 10^{23}} \text{ g} \quad 2.1089 \times 10^{-22} \text{ g}$

$\therefore \quad r_0^2 = \left(\frac{m_1 + m_2}{m_1 m_2} \right) \times I = \frac{1.6739 \times 10^{-24} + 2.1089 \times 10^{-22}}{1.6739 \times 10^{-24} \times 2.1089 \times 10^{-22}} \times 4.36 \times 10^{-40}$

$\frac{(1.6739 + 210.891) \times 10^{-24} \times 4.36 \times 10^{-40}}{1.6739 \times 2.1089 \times 10^{-46}} \quad 2.6254 \times 10^{-16} \text{ cm}^2$

$\therefore \quad r_0 = 1.62 \times 10^{-8} \text{ cm} \quad 1.62 \text{ Å}$

(a) **In SI units,**

$$\Delta\nu \quad 12.8\ \text{cm}^{-1} \quad 1280\ \text{m}^{-1}$$

$$I \quad \frac{h}{4\pi^2 c \cdot \Delta\bar{\nu}}$$

$$\frac{6.62 \times 10^{-34}}{4\left(\frac{22}{7}\right)^2 \times (3 \times 10^8) \times 1280} \quad 4.36 \times 10^{-47}\ \text{kg m}^2$$

(b)

$$m_1 = 1.6739 \times 10^{-27}\ \text{kg}$$

$$m_2 - 2.1089 \times 10^{-25}\ \text{kg}$$

$$r_0^2 - \left(\frac{m_1 + m_2}{m_1 m_2}\right) \times I = \frac{1.6739 \times 10^{-27} + 2.1089 \times 10^{-25}}{1.6739 \times 10^{-27} \times 2.1089 \times 10^{-25}} \times 4.36 \times 10^{-47}$$

$$= 2.6254 \times 10^{-20}$$

$$\therefore \qquad r - 1.62 \times 10^{-10}\ \text{m} - 0.162\ \text{nm}$$

Example 3 *The pure rotational spectrum of gaseous HCl contains a series of equally spaced lines separated by 20.80 cm^{-1}. Calculate the internuclear distance of the molecule. The atomic masses of H and Cl are 1.673 × 10^{-27} kg and 58.06 × 10^{-27} kg respectively.*

Solution: The spacing between the lines (2B) = 20.80 cm^{-1}

$$B = 10.40\ \text{cm}^{-1}$$

$$B = \frac{h}{8\pi^2 Ic}\ \text{cm}^{-1} \text{ or } I = \frac{h}{8\pi^2 BC}$$

Substituting the values,

$$I = \frac{6.626 \times 10^{-34}}{(8\pi^2)\,(10.40\ \text{cm}^{-1})\,(3 \times 10^{10}\ \text{cm}\,s^{-1})} = 0.2689 \times 10^{-46}\ \text{kg}^2\text{m}^2 \ (J = \text{kg m}^2 s^{-2})$$

The reduced mass is given by the equation

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

where m_1 and m_2 are the atomic masses of H and CI respectively.

Thus,
$$\mu = \frac{(1.673 \times 10^{-27}\,\text{kg})(58.06 \times 10^{-27}\,\text{kg})}{(1.673 - 58.06) \times 10^{-27}\,\text{kg}}$$
$$= \frac{(1.673 \times 58.06) \times 10^{-27}\,\text{kg}}{59.74}$$
$$= 1.626 \times 10^{-27}\,\text{kg}$$
Since
$$I = \mu r^2$$
$$r = \left(\frac{I}{\mu}\right)^{1/2} = \left(\frac{0.2689 \times 10^{-46}\,\text{kg m}^2}{1.626 \times 10^{-27}\,\text{kg}}\right)^{1/2}$$
$$r = 1.29 \times 10^{-10}\,\text{m} = 129\,\text{pm}$$

Example 4 *What is the moment of inertia of a diatomic molecule whose internuclear distance is 150 pm and the reduced mass is 1.5 × 10^{-27} kg?*

Solution: Moment of inertia I of a diatomic molecule is given by the relation
$$I = \frac{m_1 m_2}{m_1 + m_2} \cdot r_0^2$$
where $\frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass and r_0 is the internuclear distance.
In SI units,
Reduced mass = 1.5×10^{-27} kg
$$r_0 = 150\,\text{pm} = 150 \times 10^{-12}\,\text{m}$$
$$I = 1.5 \times 10^{-27} \times (150 \times 10^{-12})^2\,\text{kg m}^2 = 1.5 \times 150 \times 150 \times 10^{-27} \times 10^{-24}$$
$$= 33750 \times 10^{-51} = 3.375 \times 10^{-47}\,\text{kg m}^2$$

Example 5 *The pure rotational spectrum of the gaseous molecule CN has a series of equally spaced lines separated by 3.7978 cm^{-1}. Calculate the internuclear distance of the molecule. The molar masses of C and N are 12.011 and 14.007 g/mol respectively.*

Solution: The spacing between the lines ($2B$) = 3.7978 cm^{-1}
$$B = \frac{3.7978}{2} = 1.8989\,\text{cm}^{-1} \quad \text{or} \quad B = \frac{h}{8\pi^2 Ic}\,\text{cm}^{-1}$$
$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34}\,\text{Js}}{8\pi^2 (1.8989\,\text{cm}^{-1})(3 \times 10^{10}\,\text{cm/s})} = \frac{6.626 \times 10^{-34}\,\text{Js}}{8\pi^2 (189.89\,\text{m}^{-1})(3 \times 10^{8}\,\text{m/s})}$$
$$= 1.4742 \times 10^{-46}\,\text{kg m}^2 \,(J = 1\,\text{kg m}^2\,\text{s}^{-2}) = 1.4742 \times 10^{-46}\,\text{kg m}^2$$

The reduced mass is given by the equation
$$\mu = \frac{m_1 m_2}{(m_1 + m_2)}$$
where N_A is the Avogadro's number and m_1, m_2 are the atomic masses of C and N respectively.

$$\mu = \frac{(12.011\,\text{g mol}^{-1})(14.007\,\text{g mol}^{-1})}{(26.018\,\text{g mol}^{-1})(6.022\times10^{23}\,\text{mol}^{-1})} = 1.073710\times10^{-23}\,\text{g}$$

$$= 1.073710\times10^{-23}\,\text{kg}$$

Thus, $I = \mu r^2$

$$r = \left(\frac{I}{\mu}\right)^{1/2} = \left(\frac{1.474210^{-46}\,\text{kg m}^2}{1.073710^{-26}\,\text{kg}}\right)^{1/2}$$

$$r = 1.1717\times10^{-10}\,\text{m} = 117\,\text{pm}$$

Example 6 *The internuclear distance of the carbon monoxide molecule is 1.13 × 10^{-10} m. Calculate the energy (in joules and eV) of this molecule in the first excited rotational level. The atomic masses of carbon and oxygen are 1.99 × 10^{-26} kg and 2.66 × 10^{-26} kg respectively.*

Solution: We are given, $r = 1.13\times10^{-10}$ m

The reduced mass μ of CO is given by the equation

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.19\times10^{-26}\,\text{kg})(2.66\times10^{-26}\,\text{kg})}{(1.99+2.66)\times10^{-26}\,\text{kg}} = 1.14\times10^{-26}\,\text{kg}$$

Moment of inertia. $I = \mu r^2$

$$= (1.14\times10^{-26}\,\text{kg})\times(1.13\times10^{-10}\,\text{m})^2 = 1.46\times10^{-46}\,\text{kg m}^2$$

The rotational energy levels of a rigid diatomic molecule are given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)\,\text{joule}$$

For the first excited rotational levels, $J = 1$. Here,

$$E_1 = \frac{h^2\times1(1+1)}{8\pi^2 I} = \frac{h^2}{8\pi^2 I}\,\text{joule} = \frac{(6.626\times10^{-34}\,\text{Js})^2}{4\pi^2(1.46\times10^{-46}\,\text{kg m}^2)} = 7.61\times10^{-23}\,\text{joule}$$

Since $1\,\text{eV} = 1.602\times10^{-19}\,\text{J}$

$$E_1 = \frac{7.61\times10^{-23}\,\text{J}}{1.6023\times10^{-19}\,\text{J(eV)}^{-1}} = 4.76\times10^{-4}\,\text{eV}$$

21.11 NONRIGID ROTOR (QUALITATIVE DESCRIPTION)

Frequency of rotation of a rigid rotor is given by

$$\nu = \frac{h}{8\pi^2 I} J(J+1) \qquad \ldots(21.28)$$

We can say from the above equation that the frequency of rotation increases with increase in rotational quantum number J. However, the increase in the frequency of rotation increases the centrifugal force which tends to move the atoms apart. This implies that the bond length of the diatomic molecule increases with increase in the value of J.

Thus, the molecule will no longer behave as a rigid rotor.

Instead, it will behave like a nonrigid rotor.

Wave numbers of the rotational level of a rigid rotor as explained earlier are given by

$$\nu = BJ(J+1) \qquad \ldots(21.29)$$

For a molecule behaving like a nonrigid rotor, the wave numbers of rotational levels are given by

$$\nu = BJ(J+1) - DJ^2(J+1)^2 \qquad \ldots(21.30)$$

where D is called ***centrifugal distortion constant***. When a transition takes place from rotational levels J to $J+1$, the wave number of the line produced, for the molecule behaving like a nonrigid rotor, will be given by

$$\begin{aligned}\Delta\bar{\nu} &= \Delta\bar{\nu}_{J+1} - \bar{\nu}_J \\ &= [B(J+1)(J+2) - D(J+1)^2(J+2)^2] - [BJ(J+1) - DJ^2(J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \\ &= 2(J+1)\{B - 2D(J+1)^2\} \end{aligned} \qquad \ldots(21.31)$$

As J increases, the factor $\{B - 2D\,(J+1)^2\}$ decreases. Hence, $\Delta\bar{\nu}$ decreases with increase in the value of J.

21.12 ISOTOPIC EFFECT

If an atom in a molecule is replaced by its isotope, chemically the new molecule is not different from the original molecule in respect of electron distribution, internuclear distance and dipole moment. But, because of the difference in mass of the isotope, the moment of inertia (I) of the molecule will change. This means that if I increases, B will decrease ($B = h/8\pi^2 Ic$). As the energies or the wave numbers of the rotational levels are directly related to the value of B, the energies of the rotational levels will decrease, i.e. the energy levels will come closer. As the spacing between the adjacent energy levels is equal to $2B$, decrease in the value of B means that the energy levels will come closer.

By studying the rotational spectra with isotopic substitution in molecules, it is possible to calculate not only the atomic masses of the isotopes but also their relative abundances by comparing the absorption intensities.

PROBLEMS FOR PRACTICE

1. The far infrared spectrum of HI consists of a series of equally spaced lines with spacing equal to 12.8 cm^{-1}. Calculate the moment of inertia and the internuclear distance. **[Ans.** 4.37×10^{-47} kg m^2, 0.163 nm]
2. Calculate the relative Boltzmann population of the first four rotational levels of the ground state of HCI^{35} at 300 K. Given the rotational constant is 10.4398 cm^{-1}.

   [Ans. N_J/N_0 for J = 0, 1, 2, 3, 4 are 1.00, 2.71, 3.70, 3.84, 3.31]
3. Calculate the reduced mass and moment of inertia of DCI^{35}, given that internuclear bond distance is 0.1275 nm. **[Ans.** 3.162×10^{-27} kg, 5.141×10^{-47} kg m^2]
4. Calculate the frequency in cm^{-1} and wavelength in cm of the first rotational transition $J = 0 \rightarrow 1$ for DCl^{35} **[Ans.** 10.89 cm^{-1}, 0.9183 cm]
5. Calculate the energy in joules per quantum and joules per mole of photons of wavelength 30 nm.

   [Ans. 6.62×10^{-19} J, 3.98×10^5 J mol^{-1}]

21.13 VIBRATIONAL SPECTRA OF DIATOMIC MOLECULES (INFRARED SPECTRA)

Vibrational Energy Levels of a Simple Harmonic Oscillator A simple harmonic oscillator is the one in which the restoring force is proportional to the displacement in accordance with Hooke's law, i.e.

$$F = -kx \qquad \ldots(21.32)$$

For a diatomic molecule, $x = R - R_e$ where R is the distance to which the atoms have been stretched and R_e is the equilibrium distance between the two atoms. k is called the force constant.

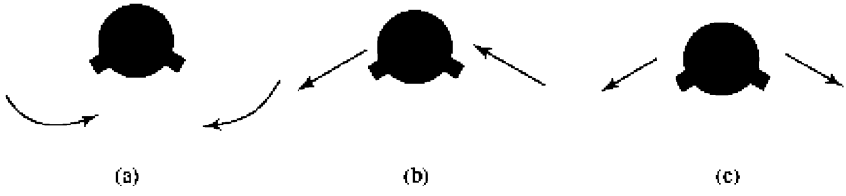


Fig. 21.18 *Vibrational modes of water*

For such an oscillator, the potential energy is given by

$$V = \frac{1}{2} kx^2 \qquad \ldots(21.33)$$

This is the equation for a parabola. Hence, a ***parabolic potential energy curve*** is obtained as shown in Fig. 21.19.

Using the concept of quantum mechanics, it can be shown that if the vibratory motion of the nuclei of diatomic molecule (Fig. 21.20) is taken as equivalent to that of ***simple harmonic oscillator*** then the vibrational energy is obtained using quantum mechanics in the form of Eq. (21.34)

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0 \qquad \ldots(21.34)$$

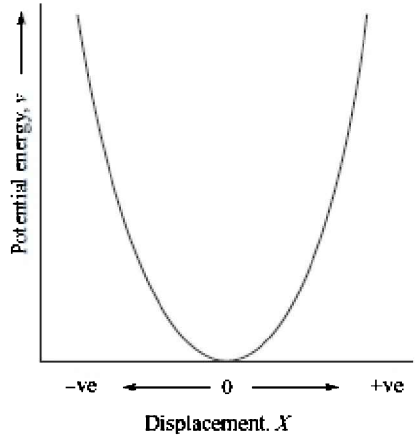


Fig. 21.19 *Parabolic potential energy curve of a harmonic oscillator.*

where v_0 is the frequency of vibration and υ is the vibrational quantum number with allowed values of 0, 1, 2, 3, etc.

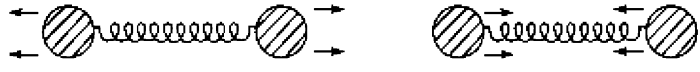


Fig. 21.20 *Vibratory motion of a diatomic molecule.*

Putting $v_0 = \frac{c}{\lambda} = c\bar{v}_e$ or $c\omega_e$ where $\bar{v}_e$ or ω_e represents the equilibrium vibrational frequency in terms of wave numbers, (cm^{-1}), Eq. (21.34) can be written as

$$E_v = \left(v + \frac{1}{2}\right) hc\omega_e \qquad \ldots(21.35)$$

Putting υ = 0, 1, 2, 3, etc., in Eq. (21.35), it may be seen that the vibrational energy levels of a harmonic oscillator are equally spaced. These are shown diagrammatically in Fig. 21.21.

For the lowest vibrational level, υ = 0. The energy for the level will, therefore, be

$$E_0 = \frac{1}{2} hc\omega_e \qquad \ldots(21.36)$$

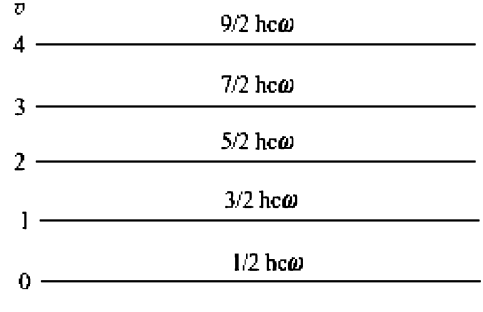


Fig. 21.21 *Equally spread Vibrational energy levels of a harmonic oscillator*

This is called ***zero point energy***. It implies that even ***at absolute zero when all translational and rotational motion ceases in a crystal, the residual energy of vibration E_0 still remains, i.e. the vibrational motion still exists***.

21.13.1 Selection Rules for Vibrational Transitions in a Simple Harmonic Oscillator

The selection rule for a molecular vibration is that the ***electric dipole moment must change when the atoms are displaced***. Here, note that the molecule need not have a permanent dipole. Based on this, the specific selection rule for vibrational transitions is

$$\Delta \upsilon = \pm 1$$

i.e. change in vibrational quantum number should be unity. Transitions for which $\Delta \upsilon = +1$ correspond to absorption and those with $\Delta \upsilon = -1$ correspond to emission.

21.13.2 Vibrational Spectrum for Simple Harmonic Oscillator

As the transitions can take place between vibrational levels whose vibrational quantum numbers differ by unity (i.e. $\Delta \upsilon = \pm 1$), the energy absorbed by a diatomic molecule, when the transition takes place from υ to $\upsilon + 1$, the level will be given by

$$\Delta E_{\upsilon} = \left(\upsilon + 1 + \frac{1}{2}\right) hc\omega_e - \left(\upsilon + \frac{1}{2}\right) hc\omega_e = hc\omega_e$$

or
$$\frac{\Delta E}{hc} = \omega_e$$

i.e.
$$\Delta \bar{\nu}_e = \omega_e$$

Thus, only one absorption line will be obtained in the vibrational spectrum whose wave number is equal to the equilibrium vibrational frequency of the diatomic molecule. Otherwise also, as the vibrational levels are equally spaced (Fig 21.20), any transition from any υ to $\upsilon + 1$ will give rise to the same energy change and hence, only one absorption line is expected. Further, at room temperature, as most of the molecules are in the lowest (ground state) vibrational level with $\upsilon = 0$, therefore, the transitions take place from $\upsilon = 0$ to $\upsilon = 1$. The frequency thus observed is called the fundamental frequency. These spectra are observed in the infrared *(IR)* region.

21.13.3 Types of Molecules Showing Vibrational Spectra

The selection rule for a diatomic molecule to give a vibrational spectrum is that the ***dipole moment of the molecule must change when the atoms are displaced due to vibration***. The condition required is only the change in dipole moment and the molecule need not have a permanent dipole moment. For example, in case of homonuclear diatomic molecules like H_2, O_2, N_2, etc, which have only stretching motion/vibrations and no bending motion/vibrations, the dipole moment does not change during vibration. Hence, these molecules do not give vibrational spectra, i.e. they are said to be ***infrared-inactive***. On the other hand, heteronuclear diatomic molecules like HCI, CO, NO, etc., and polyatomic molecules like CO_2, H_2O, CH_4, C_2H_4, etc., which show change in dipole moment in some mode of vibration give vibrational spectra and are said to be ***infrared-active***.

21.14 VIBRATIONAL ENERGY OF AN ANHARMONIC OSCILLATOR (MORSE EQUATION)

When a molecule is undergoing simple harmonic oscillation, the restoring force of the harmonic vibrations is directly proportional to the displacement and the energy of the harmonic oscillator is

given by the relation

$$E_v = \left(v + \frac{1}{2}\right) hc\omega_e \qquad \ldots(21.37)$$

where υ is the vibrational quantum number, which may be zero or an integer and ω_e is the equilibrium frequency of vibration of the oscillator, i.e. for small displacements. Strictly speaking, the movement of a real oscillator is not perfectly harmonic. This is because as the displacement increases, the restoring force becomes weaker and for large amplitude of vibration, the atoms of the molecule must fall apart, i.e. the molecule must dissociate into atoms. Such a real oscillator is said to be an ***anharmonic oscillator***. P M Morse in 1929 suggested that Eq. (21.37) has to be modified for an anharmonic oscillator by including one additional terms as follows:

$$E_v = \left(v + \frac{1}{2}\right) hc\omega_e - \left(v + \frac{1}{2}\right)^2 hc\, x_e\omega_e \qquad \ldots(21.38)$$

where x_e is called the ***anharmonicity constant***. Putting υ = 0, 1, 2, ... in equations (21.37) and (21.38), the energy levels of the harmonic oscillator and the anharmonic oscillator may be obtained. We observe that whereas the energy levels of a harmonic oscillator are equally spaced, those of the anhar-monic oscillator are not equally spaced but fall more closely together as the quantum number increases.

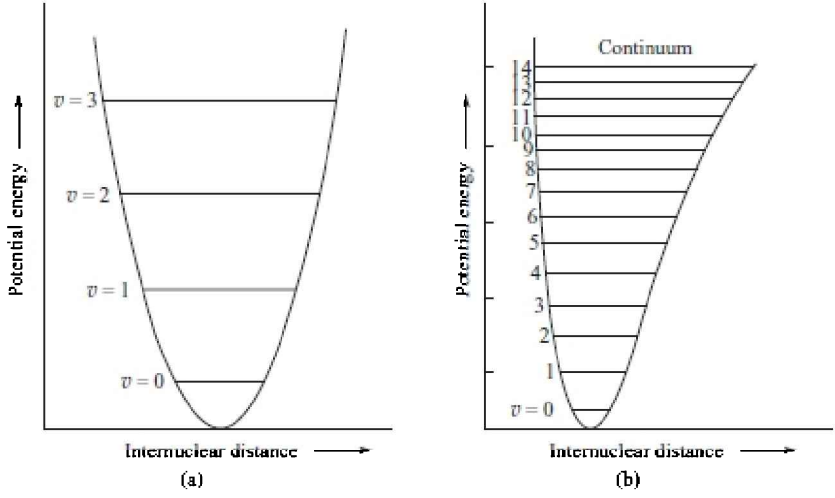


Fig. 21.22 *Potential energy curve and energy levels for (a) harmonic oscillator (b) anharmonic oscillator*

Also, while the potential energy curve for a harmonic oscillator is a parabola [Fig. 21.22 (a)], that of an anharmonic oscillator is different as shown in Fig. 21.22 (b).

Selection Rules for Vibrational Transition of an Anharmonic Oscillator

Selection rules for the anharmonic oscillator are

$$\Delta v = \pm 1, \pm 2, \pm 3, \text{ and so on.}$$

Thus, all types of vibrational transitions are possible. However, the transition from υ = 0 to υ = 1 is found to be almost intense (due to greater population of these energy levels) and is called the ***fundamental absorption***. The transition from υ = 0 to υ = 2 has a very weak intensity and is called

the ***first overtone***. The transition from $\upsilon = 0$ to $\upsilon = 3$ has still weaker intensity and is called the ***second overtone,*** and so on.

21.15 VIBRATIONAL-ROTATIONAL SPECTRA OBTAINED FOR A DIATOMIC MOLECULE TAKING IT AS ANHARMONIC OSCILLATOR

As the energy required for rotation is much less than that required for vibration, the vibrational motion is always accompanied by rotational motion and hence we do not have a pure vibrational spectra; instead we have a vibrational-rotational spectra.

As rotational motion and vibrational motion take place independent of each other, the total energy of the molecule may be taken as the sum of the rotational energy and vibrational energy.

Thus,

$$E_{\text{total}} = E_r + E_v \qquad \ldots(21.39)$$

We may write it as,

$$E_{v,J} = E_J + E_v \qquad \ldots(21.40)$$

Expressing in terms of wave numbers, it can be written as,

$$\bar{\nu}_{v,J} = \bar{\nu}_J + \bar{\nu}_v \qquad \ldots(21.41)$$

But the rotational energy in terms of wave number $\bar{\nu}_J$ and vibrational energy $\bar{\nu}_\upsilon$ are given by following ω two equations :

$$\bar{\nu}_J = BJ(J+1)$$

$$\bar{\nu}_v = \left(\upsilon + \frac{1}{2}\right)\omega_e - \left(\upsilon + \frac{1}{2}\right)^2 x_e\omega_e$$

Substituting these values in Eq. (21.41), we get

$$\bar{\nu}_{v,J} = BJ(J+1) + \left(\upsilon + \frac{1}{2}\right)\omega_e - \left(\upsilon + \frac{1}{2}\right)^2 x_e\omega_e \qquad \ldots(21.42)$$

Here, $\bar{\nu}_{\upsilon,J}$ represents the wave number of a rotational level with quantum number J in the vibrational level with quantum number υ.

From Eq. (21.42), it is clear that in the same vibrational level (so that υ = constant), there will be a number of rotational levels corresponding to $J = 0, 1, 2, 3 \ldots$

When a transition takes place from a level with quantum numbers υ and J to a level with quantum numbers υ' and J', the energy change expressed in terms of wave numbers will be given by

$$\Delta\bar{\nu} = \left[BJ'(J'+1) + \left(\upsilon' + \frac{1}{2}\right)\omega_e - \left(\upsilon' + \frac{1}{2}\right)^2 x_e\omega_e\right] - \left[BJ(J+1) + \left(\upsilon + \frac{1}{2}\right)\omega_e - \left(\upsilon + \frac{1}{2}\right)^2 x_e\omega_e\right] \qquad \ldots(21.43)$$

Restricting to the transition from $\upsilon = 0$ to $\upsilon = 1$, we get

$$\Delta\bar{\nu} = \left[BJ'(J'+1) + \frac{3}{2}\omega_e - \frac{9}{4}x_e\omega_e\right] - \left[BJ(J+1) + \frac{1}{2}\omega_e - \frac{1}{4}x_e\omega_e\right]$$

$$= B[J'(J'+1) - J(J+1)] + \omega_e - 2x_e\omega_e$$

$$= B[(J'-J)(J'+J+1)] + (1-2x_e)\omega_e \qquad \ldots(21.44)$$

Putting $(1 - 2x_e)\,\omega_e = \omega_0$, we can write

$$\Delta\bar{\nu} = \omega_0 + B(J'-J)(J+J'+1) \qquad \ldots(21.45)$$

ω_0 represents the fundamental frequency. This is called the centre of origin of the fundamental band.

1. For transition $\Delta J = +1$, i.e.,

$$J' - J = +1 \text{ or } J' = J + 1$$

$$\Delta\bar{\nu} = \omega_0 + 2B(J+1) \text{ where } J = 0, 1, 2, 3, \ldots \qquad \ldots(21.46)$$

2. For transition $\Delta J = -1$, i.e.

$$J' - J = -1 \text{ or } J = J' + 1$$

$$\Delta\bar{\nu} = \omega_0 - 2B(J'+1) \text{ where } J' = 0, 1, 2, 3, \ldots \qquad \ldots(21.47)$$

Combining equations (21.46) and (21.47), we get

$$\Delta\bar{\nu} = \omega_0 \pm 2Bm \qquad \ldots(21.48)$$

Where $m = J + 1$ in Eq. (21.46) and $m = -(J + 1)$ in Eq. (21.47). As $J = 0, 1, 2, 3, \ldots$, this means that in Eq. (21.48), $m = \pm 1, \pm 2, \pm 3, \ldots$ (+sign for $\Delta J = +1$ and –sign for $\Delta J = -1$)

The nature of the vibration-rotation spectrum can be predicted from Eq. (21.48) as follows.

1. As $m \neq 0$, therefore, line corresponding to the frequency ω_0 will not appear in the spectrum. This wave number is called the ***band centre*** or ***band origin***.
2. As $m = \pm 1, \pm 2, \pm 3, \ldots$, it follows that the spectrum will consist of equally spaced lines on each side of the band centre, with spacing equal to $2B$ between any two adjacent lines.

Keeping in view the selection rule, $\Delta J = \pm 1$, the absorption transitions that can take place from level $\upsilon = 0$ to $\upsilon = 1$ and the corresponding lines obtained in the spectrum may be represented as shown in Fig. 21.23.

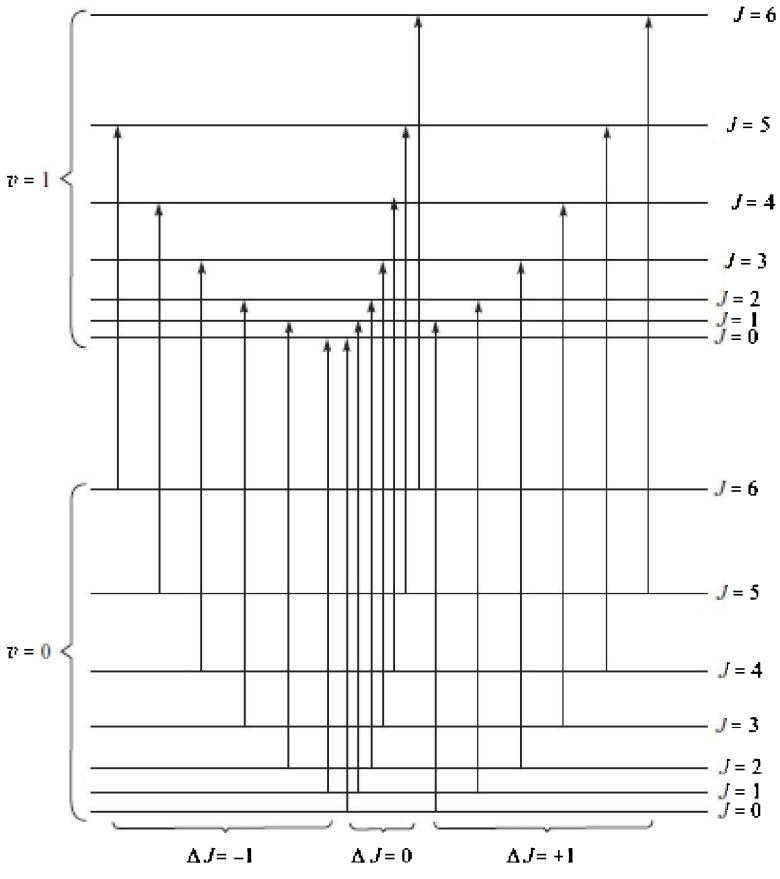


Fig. 21.23 *Vibration-rotation spectrum of a diatomic molecule*

21.15.1 *P, Q* and *R* Branches of Rotational-Vibrational Spectrum

In the case of rotational-vibrational spectrum,

1. For $\Delta J = -1$, lines with frequency lower than the fundamental frequency are obtained. These lines are called ***P-branch*** of the spectrum (Fig. 21.24).

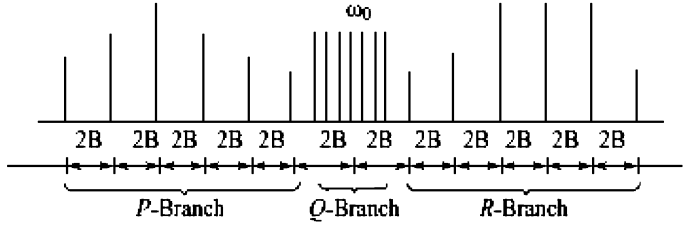


Fig. 21.24 *P, Q* and *R* branches of rotation-vibration spectrum

2. For $\Delta J = +1$, lines with frequency greater than the fundamental frequency are obtained. These lines are called the ***R-branch*** of the spectrum.

3. For $\Delta J = 0$, i.e. when a vibrational transition occurs without being accompanied by rotational transition (e.g. in case of NO),

$$\Delta\bar{v} = \omega_0$$

i.e. a single line is expected at the centre. In actual practice, as the rotational constants of the two vibrational levels are slightly different, a cluster of closely spaced lines appear at the centre. This group of lines is called the ***Q-branch*** of the spectrum. When this type of transition is forbidden (e.g. in case of HCI), a gap appears at the centre.

21.16 APPLICATIONS OF STUDY OF INFRARED SPECTRUM

Various applications of infrared spectrum studied are discussed as under:

1. Calculation of Moment of Inertia and Bond Length The value of B is given by

$$B = \frac{h}{8\pi^2 Ic}$$

$\therefore$ frequency separation,

$$\Delta\bar{v} = 2B = \frac{h}{8\pi^2 Ic}$$

Thus, knowing the frequency separation, the moment of inertia and hence the antinuclear distance i.e. bond length of a diatomic molecule can be calculated.

2. Calculation of Force Constant Taking a simple case where a diatomic molecule may be considered as a simple harmonic oscillator, i.e. an oscillator in which the restoring force (F) is directly proportional to the displacement, in accordance with Hooke's law, we have,

$$F = kx \qquad \ldots(21.49)$$

where x is the displacement and is equal to the distance to which the atoms have been stretched. (R) minus equilibrium distance between the atoms (R_e), i.e. $x = R - R_e$. k in Eq. (21.49) is called force constant. Thus, if $x = 1$ cm, $k = -F$. Hence, ***force constant may be defined as the restoring force per unit displacement (or per cm) of a harmonic oscillator***. It is found to be related to the equilibrium vibrational frequency ω_e (in s^{-1}) according to the equation

$$\omega_e = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} s^{-1} \qquad \ldots(21.50)$$

where μ is the reduced mass of the system.

To convert the frequency ω_e from s^{-1} to cm^{-1}; we divide by velocity of light, c. Thus,

$$\omega_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \text{cm}^{-1} \qquad \ldots(21.51)$$

To calculate k, Eq. (21.51) can be rewritten as follows,

$$k = 4\pi^2 \omega_e^2 \mu$$

or

$$\boxed{k = 4\pi^2 \omega_e^2 \frac{m_1 m_2}{m_1 + m_2}} \qquad \ldots(21.52)$$

where m_1 and m_2 are masses of the oscillating atoms.

Thus, knowing vibration frequency ω_e and the masses of the atoms of the diatomic molecule, the force constant k can be calculated. Note that ω_e is in s^{-1}.

It is found that force constant increases almost directly with the multiplicity of the bond as given below.

Bond	*Force constant (dynes/cm)*
C — C	4.6×10^5
C = C	9.5×10^5
C ≡ C	15.8×10^5

Thus, multiplicity of a bond can be predicted from the value of the force constant. For example, the force constant for C ≡ O in carbon monoxide is 18.6×10^5 dynes/cm, whereas the force constant for C = O in carbon dioxide is 15.2×10^5 dynes/cm. This result confirms that CO_2 has resonating structures containing both carbon oxygen double and triple bonds, i.e. we write

$$O^{\cdot} - C \equiv O \leftrightarrow O = C = O \leftarrow O \equiv C - O^{\cdot}$$

3. Calculation of Equilibrium Dissociation Energy The equilibrium dissociation energy of a diatomic molecule is given by

$$D_e = \frac{\omega_e}{4x_e} \qquad \ldots(21.53)$$

This is the dissociation energy when it is measured from the bottom of the Morse potential energy curve. The true dissociation energy is, however, measured from the ground level ($\upsilon = 0$) and is given by

$$D_0 = \frac{\omega_e}{4x_e} - \frac{1}{2}\omega_e\left(1 - \frac{1}{2}x_e\right) \qquad \ldots(21.54)$$

21.17 VIBRATIONAL FREQUENCIES OF FUNCTIONAL GROUPS

It is observed that skeletal vibrations take place when the absorption of energy is up to 1500 cm^{-1}. They are characteristic of the molecule as a whole whether it is linear, branched or has benzenoid structure. This part of the spectrum is called the ***fingerprint region***. But certain groups of atoms and functional groups, irrespective of the molecule in which they are present, absorb at a particular wave number (>1500 cm^{-1}) to exhibit group vibrations. They give rise to characteristic absorption bonds in the spectrum.

The frequencies (in terms of wave numbers) at which different functional groups show absorption are listed in the table below for some very common functional groups or groups of atoms.

Table 21.1 *Characteristic infrared absorption frequencies*

Bond	Compound (Group)	Type of vibration	Absorption frequency (cm^{-1})
C – H	Alkane	Stretching	2850–2960
	$-CH_3$	Bending	1350–1470

	$-CH_2$	Bending	1465
	Alkenes	Stretching	3000–3100
	Alkynes	Bending out of plane	650–1000
	Aromatics	Stretching	3300
C – C	Alkane, $(CH_3)_3$ C–	Stretching	3050–3150
	$-(CH_2)_n$ ($n > 3$)	Bending out of plane	690–900
C = C	Alkenes	Skeletal	1250
	Aromatics	Skeletal	725
C ≡ C	Alkynes	Stretching	1600–1680
C = O	Aldehydes	Stretching	1475–1600
	Ketones	…	2100–2250
	Carboxylic acids	…	1720–1740
	Esters	…	1705–1725
	Amides	…	1700–1725
	Anhydride	…	1730–1750
	Acid chloride	…	1630–1680
C – O	Alcohols, ethers	…	1760–1810
	Esters, carboxylic	…	1800
	Acids, anhydrides	…	1000–1300
O – H	Alcohols, phenols	…	3600–3650
	Free	…	3200–3400
	H-bonded	…	2400–3400
	Carboxylic acids	Stretching	3100–3500
N – H	Primary amines sec-amines, amides	Bending	1550–1640
C – N	Amines	…	1000–1350
C ≡ N	Nitriles	…	2240–2260
N = O	Nitro (R – NO_2)	…	1350–1550
C – X	Fluoride	…	1000–1400
	Chloride	…	540–785
	Bromide, Iodide	…	< 667

The group absorption frequency ($\Delta\bar{\nu}$) is related to the force constant (k) of the bond and the reduced mass (μ) of the group according to the appropriate relation

$$\Delta\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

i.e. $\Delta\bar{\nu}$ increases with increase in force constant and decreases with increase in reduced mass.

Example 7 *Calculate the force constant for the bond in HCI from the fact that the fundamental vibration frequency is* $8.667 \times 10^{-13}\ s^{-1}$.

Solution:

$$m_1 \text{ (For H atom)} = \frac{1.008}{6.023 \times 10^{23}} = 1.6739 \times 10^{-27}\ \text{kg}$$

$$m_1 \text{ (for Cl atom)} = \frac{35.5}{6.022 \times 10^{23}} = 8.8951 \times 10^{-26}\ \text{kg}$$

∴ Reduced mass

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = 1.6277 \times 10^{-27}\ \text{kg}$$

Also, it is given that

$$\omega = 8.667 \times 10^{13}\ s^{-1} \quad \text{and} \quad k = 4\pi^2\omega^2\mu$$

$$= 4 \times \left(\frac{22}{7}\right)^2 \times (8.677 \times 10^{13})^2 \times (1.6277 \times 10^{-22}\ \text{kg}) = 483.1\ \text{Nm}^{-1}$$

PROBLEMS FOR PRACTICE

1. The hydrogen halides have the following fundamental vibrational frequencies: HF (4141.3 cm^{-1}), HCl^{35} (2988.9 cm^{-1}), HBr^{81} (2649.7 cm^{-1}), HI (2309.5 cm^{-1}). Calculate the force constant of the hydrogen-halogen bonds. **(Ans.** 967 × 516, 412 × 314 Nm^{-1})
2. The antiharmonicity constant of Cl^{35} F^{19} is $\omega_e x_e$ = 9.9 cm^{-1} and the fundamental vibrational frequency is 793.2 cm^{-1}. Calculate the energies of the first three vibrational energy levels.

   (Ans. 1167.52 cm^{-1}, 1921.13 cm^{-1}, 2654.23 cm^{-1})
3. The force constant of HF molecule is 970 Nm^{-1}. Calculate the fundamental vibrational frequency and zero point energy. **(Ans.** 1.247×10^{-14}) s^{-1}, 4.129×10^{-20} J)
4. If the observed fundamental frequency of H_2 is 4159 cm^{-1}, what fraction of the molecules are in $\upsilon = 1$ state at room temperature? **(Ans.** 6.84×10^{-10})
5. Calculate the relative Boltzmann population of the $\upsilon = 1$ and $\upsilon = 0$ vibrational energy levels of a diatomic molecule at 25°C if they are separated by 1000 cm^{-1}. **(Ans.** $N_{\upsilon=1}/N_{\upsilon=0} \approx$ 0008)

RAMAN SPECTRA

21.18 INTRODUCTION

C V Raman of Calcutta University, observed in 1928 that when a substance (gaseous, liquid or solid) is irradiated with monochromatic light of a definite frequency υ the light scattered at right angles to the incident light contained lines not only of incident frequency but also of lower frequency and sometimes of higher frequency as well. The lines with ***lower frequency*** are called ***Stokes lines*** whereas lines with ***higher frequency*** are called ***anti-Stoke's lines***. Line with the same frequency as the incident light is called ***Rayleigh lines***. Raman further observed that the difference between the frequency of the incident light and that of the particular scattered line was constant depending only ***upon the nature*** of the substance being irradiated and was completely independent of the frequency of the incident light. If ν_i is the frequency of the incident light and ν_s, that of the particular scattered line, the difference, $\Delta\nu = \nu_i - \nu_s$ is called ***Raman frequency*** or ***Raman shift***. Raman frequencies observed for a particular substance are characteristic of that substance. The various observations made by Raman are called ***Raman effect*** and the spectrum observed is called ***Raman spectrum***. Raman spectrum is represented by Fig. 21.26.



Fig. 21.25 ***Sir C V Raman*** *was an Indian physicist whose work was influential in the growth of science in India*

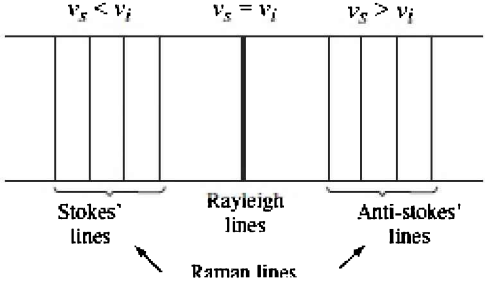


Fig. 21.26 *A simplified representation of Raman spectrum*

21.18.1 Explanation of Rayleigh's Line, Stoke's Lines and Anti-Stokes' Lines in Raman Spectra

When a photon is incident on the molecule, the energy is absorbed by the molecule and it gets excited to some higher energy level. Now, if it returns to the original level, it will emit the same energy as absorbed and thus we have Rayleigh scattering. However, in most cases, the excited molecule does not return to the original level. It may return to a level higher than the original level, thereby emitting less energy than absorbed. This explains the occurrence of Stokes lines. Thus, a part of the energy of the incident photon remains absorbed by the molecule (so that the molecule has

higher energy than before). Alternatively, the excited molecule may return to a level lower than the original level. Thus, more energy is emitted than absorbed. This explains the occurrence of anti-Stokes' lines. In this case, the molecule has less energy than before. The different cases may be represented diagrammatically by Fig. 21.27.

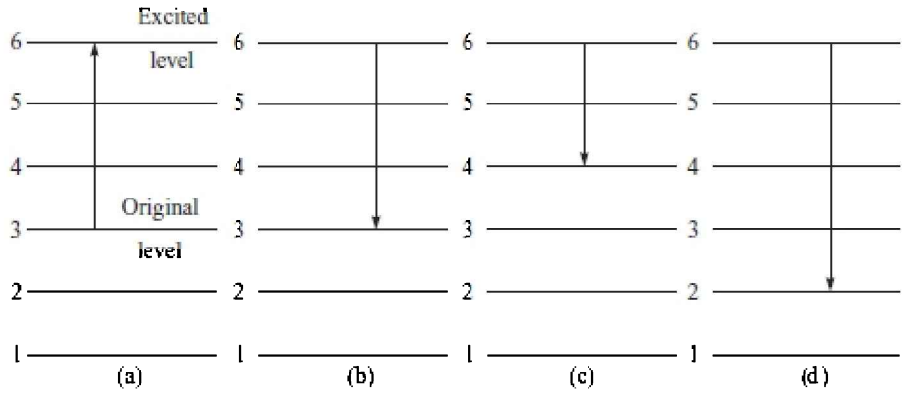


Fig. 21.27 *(a) Energy absorbed by the molecule, (b) Rayleigh scattering, (c) Formation of Stokes' lines (d) Formation of anti-Stokes' line*

21.18.2 Pure Rotational Raman Spectrum Expected for a Diatomic Molecule

The selection rules for pure rotational Raman spectra of diatomic molecules are

$$\Delta J = 0, \pm 2$$

The selection rule $\Delta J = 0$ corresponds to Rayleigh scattering whereas selection rules $\Delta J = \pm 2$ gives rise to Raman lines as explained below:

Energy of a rotational level (in terms of wave number) with quantum number J is given by

$$\bar{\nu} = BJ(J+1) \qquad \ldots(21.55)$$

When transition takes place from a lower rotational level with quantum number J to a higher rotational level with quantum number $(J+1)$, the energy absorbed in terms of the wave numbers will be

$$\Delta\bar{\nu} = BJ'(J'+1) - BJ(J+1) \qquad \ldots(21.56)$$

For the selection rule,

$$\Delta J = +2, \text{ i.e. } J' - J = 2, \text{ we get}$$

$$\Delta\bar{\nu} = B(J+2)(J+3) - BJ(J+1)$$

$$= B(4J+6) \text{ where } J = 0, 1, 2, 3 \qquad \ldots(21.57)$$

Again for the selection rule,

$$\Delta J = -2 \text{ i.e., } J' - J = -2, \text{ we get}$$

$$\Delta\bar{\nu} = BJ'(J'+1) \quad B(J'+2)(J'+3)$$

$$= -B(4J'+6) \text{ where } J' = 0, 1, 2, 3, \ldots \qquad \ldots(21.58)$$

Combining the results of Equations (21.57) and (21.58), the wave numbers of the lines obtained in the Raman will by given by

$$\bar{\nu} - \bar{\nu}_i + \Delta\bar{\nu}$$

or
$$\boxed{\bar{\nu} = \bar{\nu}_i \pm B(4J + 6)} \quad \ldots(21.59)$$

where $J = 0, 1, 2, 3, \ldots$

Here, $\bar{\nu}_i$ represents the wave numbers of Rayleigh line, the plus sign gives lines with higher wave numbers called Antistokes' lines and the minus sign gives lines with lower wave numbers, called Stokes' lines.

From Eq. (21.59), it may be seen that for $J = 0$, $\bar{\nu} = \nu_i + 6B$, i.e. the first Stokes and anti-Stokes' lines will be at a separation of $6B$ from the Rayleigh line. Further, putting $J = 1, 2, 3, \ldots$, the separation between any two adjacent Stoke's lines or anti-Stoke's lines will be $4B$. Thus, the pure rotational Raman spectrum expected for a diatomic molecule may be represented by Fig. 21.28

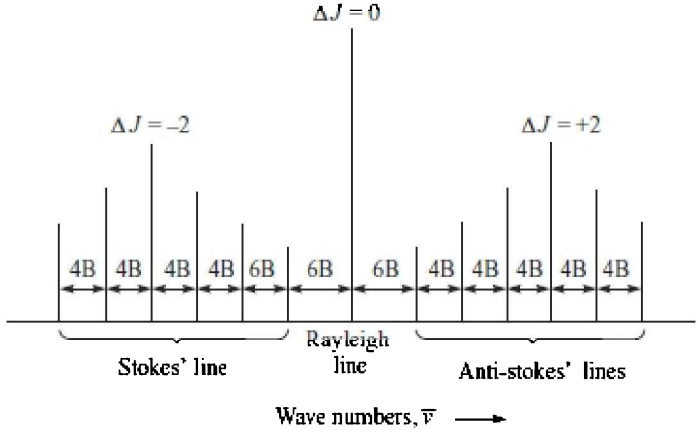


Fig. 21.28 *Pure rotational Raman spectrum expected for a diatomic molecule*

21.19 ROTATIONAL-VIBRATIONAL RAMAN SPECTRA OF DIATOMIC MOLECULES

Diatomic gaseous molecules give rotational-vibrational Raman spectra which are governed by the following selection rules:

$$\Delta v = \pm 1$$
$$\Delta J = 0, \pm 2$$

However, at room temperature, as most of the molecules are in the lowest vibrational levels ($v = 0$), therefore the significant vibrational transition is from $v = 0$ to $v = 1$ (called fundamental vibrational transitions). Restricting to this vibrational transition only, the results obtained are as follows:

For $\Delta J = 0$, $\Delta\bar{\nu} = \omega_e(1 - 2x_e)$ (called Q-branch)

For $\Delta J = +2$, $\Delta\bar{\nu} = \omega_e(1 - 2x_e) + B(4J + 6)$ (called S-branch)

For $\Delta J = -2$, $\Delta\bar{\nu} = \omega_e(1 - 2x_e) + B(4J + 6)$ (called O-branch)

Representing the value of Q, S, and O branch by $\Delta\bar{\nu}_Q$, $\Delta\bar{\nu}_S$ and $\Delta\bar{\nu}_O$ respectively, and the wave number of the exciting radiation by $\bar{\nu}_i$, the wave numbers of the Stokes' lines will be as follows:

$$\bar{\nu}_Q = \bar{\nu}_i - \Delta\bar{\nu}_Q; \quad \bar{\nu}_S = \bar{\nu}_i - \Delta\bar{\nu}_S;$$

$$\Delta\bar{\nu}_O = \bar{\nu}_i - \Delta\bar{\nu}_O$$

We have considered the case for $\Delta\upsilon = +1$ which represents Stokes' lines. The anti-Stokes' lines are those for which $\Delta\upsilon = -1$. They are usually weak because very few molecules are in the excited vibrational state initially.

The rotational transitions accompanying the vibrational transition from $\upsilon = 0$ to $\upsilon = 1$ and the rotational-vibration Raman spectrum obtained may be represented as shown in Fig. 21.29.

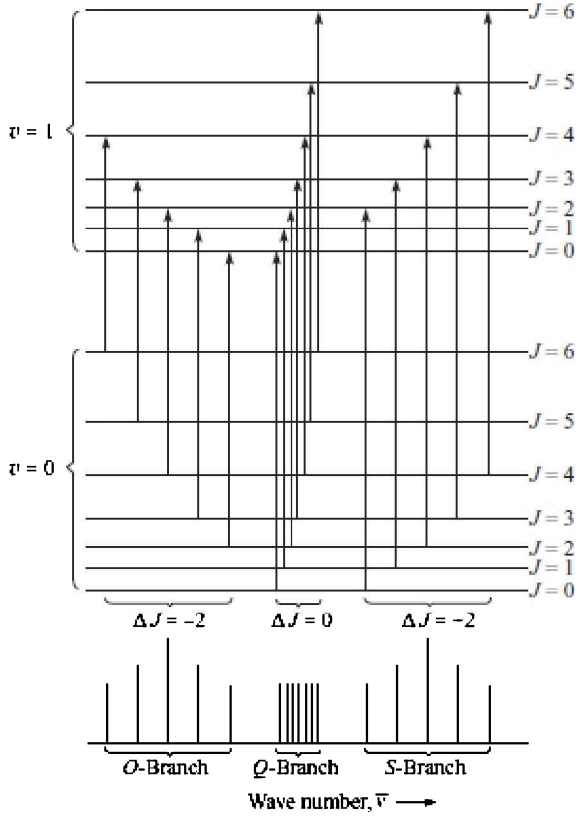


Fig. 21.29 *Rotation-vibration Raman spectrum of a diatomic molecule*

21.19.1 Type of Molecules that give Rotation-Vibration Raman Spectra

The selection rule for a molecule to give rotationvibration Raman spectrum is that the ***polarisation of the molecule must change as the molecule vibrates***. In case of both types of diatomic molecules, i.e. homonuclear as well as heteronuclear, as the molecule vibrates, the control of the nuclei over the electrons varies and hence there is a change in polarisability. That is why both types of diatomic molecules give rotational-vibration Raman spectra, i.e. they are ***vibrational Raman-active***. This is one of the main advantages of Raman spectra over infrared spectra because ho-monuclear diatomic molecules do not give pure vibrational or rotational spectra because they do not possess a permanent dipole moment.

21.19.2 Advantages of Raman Spectroscopy over Infrared Spectroscopy

Raman spectroscopy has a number of advantages over infrared spectroscopy which are discussed here-under:

1. Raman spectra can be obtained not only for gases but even for liquids and solids whereas infrared spectra for liquids and solids are quite diffused.
2. Since Raman frequencies are independent of the frequency of the incident radiation, hence, by suitably adjusting the frequency of the incident radiation, Raman spectra can be obtained in the visible spectrum range where they can be easily observed rather than the more difficult infrared range.
3. Raman spectra can be obtained even for molecules such as O_2, N_2, Cl_2, etc., which have no permanent dipole moment. Such a study is not possible by infra-red spectroscopy.

21.19.3 Experimental Set-up of Raman Spectrophotometer

The experimental arrangement for observing Raman spectra is shown in Fig. 21.30. The fraction of the light scattered is so low that normally very weak Raman lines are observed. Hence, to detect these lines, it is necessary to use a powerful source of incident light. Earlier, mercury vapour lamps were used which gave an intense monochromatic radiation of 435.8 nm wavelength. However, with the development of lasers, which are very powerful source of monochromatic radiation, Raman spectroscopy has undergone radical changes.

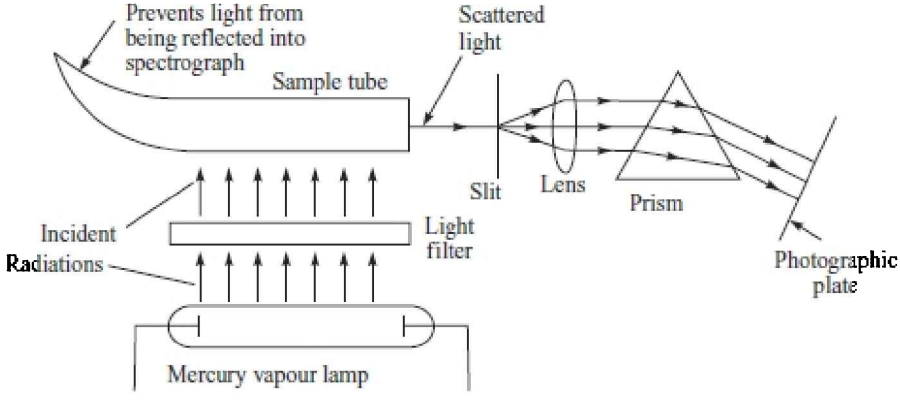


Fig. 21.30 *Raman spectrophotometer*

Example 8 *A sample was irradiated by the 4358 Å line of mercury. A Raman line was observed at 4447 Å. Calculate the Raman shift in* cm^{-1}.

Solution: Since the Raman line is observed at longer wavelength (shorter frequency) than the exciting line, it is evidently a Stokes' line in the Raman spectrum. Raman shift is given by.

$$\Delta\bar{\nu}_{\text{Raman}}(\text{cm}^{-1}) = \frac{10^8}{\lambda_{\text{exc.}}} - \frac{10^8}{\lambda_{\text{Raman}}(\text{Å})}$$

$$= \frac{10^8}{4.358 \times 10^3} - \frac{10^8}{4.447 \times 10^3} = (2.295 - 2.249 \times 10^4)$$

$$\Delta\bar{\nu}_{\text{Raman}}(\text{cm}^{-1}) = 460 \text{ cm}^{-1}$$

PROBLEMS FOR PRACTICE

1. Calculate the Raman line in nm if HCl^{35} is irradiated with 435.8 nm mercury line. Given that the fundamental vibrational frequency of HCl^{35} is 8.667×10^{13} s^{-1} **[Ans.** 498.57 nm]
2. The fundamental vibrational frequencies of SO_2 are 1151.38, 517.69 and 1361.76 cm^{-1}. Account for the absorption bands at 1875.55, 2295.88 and 2499.55 cm^{-1}. **[Ans.**$\bar{\nu}_2 + \bar{\nu}_3$, and $2\bar{\nu}_1$ $\bar{\nu}_1 + \bar{\nu}_3$]
3. The triatomic molecule AB_2 shows three strong infrared absorption bonds. What is the structure of the molecule? **[Ans.** *ABB* bent or *BAB* bent]
4. The infrared and Raman spectra of a triatomic molecule of the type MX_2 show two infrared frequencies and one Raman frequency. Determine the shape of the molecule whether linear or bent.

ELECTRONIC SPECTRA

21.20 INTRODUCTION

Spectra which arises due to electronic transition in a molecule by absorption of radiation falling in the visible and UV range is called electronic spectra. The range of visible region is 12500–25000 cm^{-1} while that of UV region is 25000–70000 cm^{-1}. It is observed that electronic transitions in a molecule are invariably accompanied by vibrational and rotational transitions, thus, making electronic spectra quite complex. Electronic spectra help in the determination of ionisation energies of molecules.

If the light radiation incident on a molecule possesses very high energy, it causes removal of electron from the molecule, i.e. causes ionisation. A beam of photons of known energy is allowed to fall on a sample and the kinetic energy of the ejected electron is measured. The difference between the photon energy and the excess kinetic energy gives the binding energy of the molecule.

21.21 BORN-OPPENHEIMER APPROXIMATION IN RELATION TO ELECTRONIC SPECTRA OF MOLECULES

Electronic spectra of molecules are observed in ultraviolet and visible regions of the electromagnetic spectrum. A transition between two electronic states is almost invariably accompanied by simultaneous transitions between the vibrational and rotational energy levels as well. This is expressed by saying that electronic spectra have ***vibrational fine structure*** and ***rotational fine structure***. According to Born-Oppenheimer approximation, the total energy of a molecule in the

ground state is given by

$$E'' = E''_{el} + E''_{vib} + E''_{rot}$$

Here, E''_{el}, E''_{vib}, and E''_{rot} are the electronic, vibrational and rotational energies respectively. Assuming that the Born-Oppenheimer approximation is valid in the excited state as well, the excited-state energy E' is given by,

$$E' = E'_{el} + E'_{vib} + E'_{rot}$$

The energy change for an electronic transition is given by

$$\begin{aligned}\Delta E &= E' - E'' = (E'_{el} - E''_{el}) + (E'_{vib} - E''_{vib}) + (E'_{rot} - E''_{rot}) \\ &= \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}\end{aligned}$$

It may be understood that

$$\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$$

The frequency of the electronic transition is given by Bohr-Planck relation.

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{\Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}}{hc} \text{ cm}^{-1}$$

21.22 POTENTIAL ENERGY CURVE AND FRANK-CONDON PRINCIPLE

A very useful principle for investigating the vibrational structure of electronic spectra is provided by ***Frank-Condon principle***. It states that ***an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition***. This principle is true since the electrons move so much faster than the nuclei that during the electronic transition, the nuclei do not change their position. An electronic transition may be represented by a vertical line on a plot of potential energy versus the internuclear distance.

Consider Fig. 21.31 where we have shown two potential energy curves for the molecule in the ground electronic state (E_o) and in the first excited electronic state (E_1) Since the bonding in the excited state is weaker than in the ground state, the minimum in the potential energy curve for the excited state occurs at a slightly greater internuclear distance than the corresponding minimum in the ground electronic state. Also quantum mechanically, it is known that the molecule is in the **centre** of the ground vibrational level of the ground electronic state. When a photon falls on the molecule, the most probable electronic transition, according to Frank-Condon principle, takes place from $v' = 0$ to $v' = 2$ (written schematically as $0 \rightarrow 2$). Transitions to other vibrational levels of the excited electronic state occur with smaller probabilities so that their relative intensities are smaller than the intensity of the $0 \rightarrow 2$ transition, as shown in Fig. 21.32.

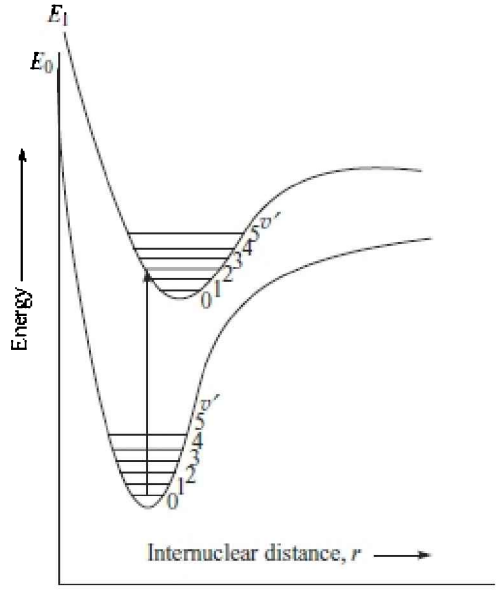


Fig. 21.31 *Electronic transition in a diatomic molecule*

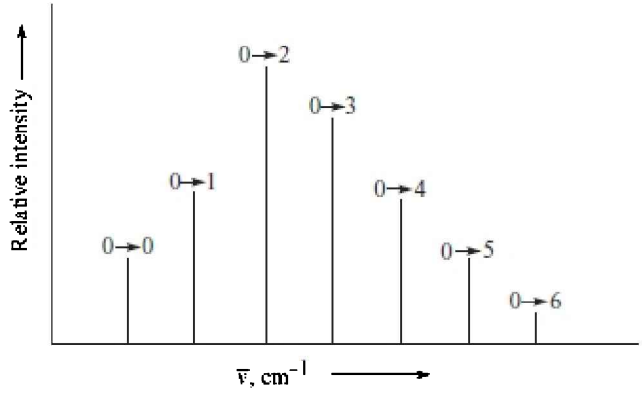


Fig. 21.32 *Electronic spectrum of a diatomic molecule*

Electronic Transitions in Homonuclear Molecules

In molecules such as H_2 and N_2, Highest Occupied Molecular Orbital (HOMO) in the ground state is a Bonding Molecular Orbital (BMO) whereas the Lowest Unoccupied Molecular Orbital (LUMO) is an Anti-Bonding Molecular Orbital (ABMO). The HOMO and LUMO orbitals are collectively referred to as ***Frontier Molecular Orbitals (FMOs)***. The electronic transition, HOMO → LUMO takes place ***when the electron absorbs a photon***. This lies in the UV range. The oxygen molecule O_2 is an exception. It has two unpaired electrons in the ground state which is thus a ***triple state***. The electronic transition occurs from the triple ground state to the triple excited state (rather than to the singlet excited state). The electronic spectrum of O_2 molecule is, of course, complex.

21.23 ELECTRONIC TRANSITION IN *Σ, Π* AND N MOLECULAR ORBITALS

Organic compounds, particularly those containing group like C = C, C = O, –N = N- and extensively conjugated systems, form a special class of polyatomic molecules whose electronic spectra can be easily interpreted even though the investigation of their detailed spectral features may require knowledge of quantum mechanics and group theory. On the basis of Molecular Orbital Theory (MOT), the electrons can be classified as σ, π, or *n* (non-bonding) depending upon the MOs they occupy. For organic carbonyl compounds, the electronic transitions involve promotion of the electrons in *n*, σ and π orbitals in the ground state to the σ* and π* anti-bonding molecular orbitals (ABMOs) in the excited state (Fig. 21.33). Thus, only the transitions of the type σ → σ*, π→π*, and *n* → π* are allowed. Since electrons in the *n* orbitals are not involved in bond formation, there are no ABMOs associated with them.

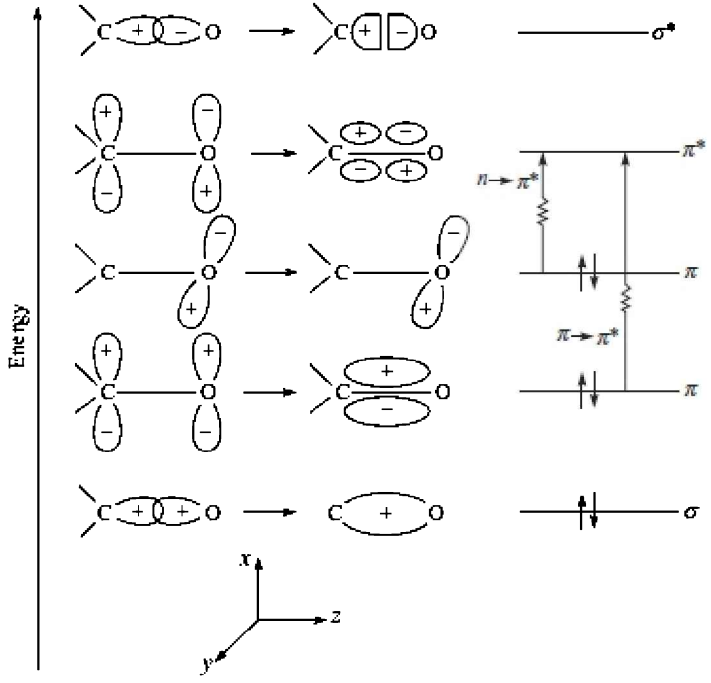


Fig. 21.33 *Localised molecular orbitals and electronic transitions for the carbonyl group*

The σ→σ* transitions occurring in saturated hydrocarbons and other types of compounds in which all valence-shell electrons are involved in single bonds, are found in the far ultraviolet region since they involve very high energy. The π→π* and the *n*→π* transitions, on the other hand, are found either in the UV or visible regions. The unsaturated molecules containing C = C and C = O groups (such as aldehydes and ketones) show *n*→π* and π→π* transitions. For aldehydes and ketones, the more intense band near 180 nm is due to π→π* transition and the weaker band around 285 nm is due to *n*→π* transition. Olefinic hydrocarbons show π→π* transition in the wavelength 160–170 nm. Acetylene shows an absorption near 180 nm.

Molecules such as methyl amine and methyl iodide, which do not contain a π-orbital, show *n*→π* transitions.

In highly conjugated systems, the π-electrons are delocalised over the entire skeletal framework. It is found that the ***absorption bands shift to longer wavelengths as the extent of conjugation increases***. Thus, in the compound $C_6H_5 - (CH = CH)_n - C_6H_5$, the π→π* transition lies in the UV region when n = 1 or 2. As n increases, the electronic transitions shifts to the visible region. This phenomenon is shown schematically in Fig. 21.34.

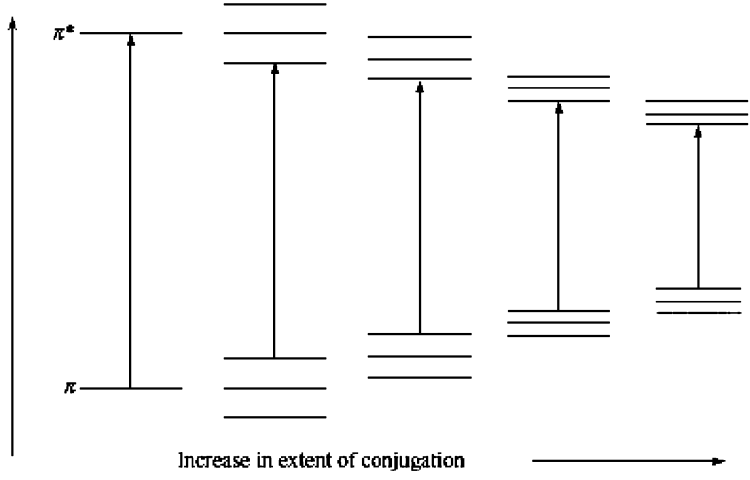


Fig. 21.34 *Energy-level diagram showing that in a conjugated π-electron system, the wavelength of absorption maximum is directly proportional to the extent of conjugation*

The intensity of an electronic band is a function of the extent of overlap of the wave functions of the ground and excited states. As there is very poor overlap of wave functions of the ground in the n→π* transition and there is considerable overlap of the corresponding wave functions in the π→π* transitions, the n→π* transitions are weaker than the π→π* transitions. Again, in strongly acidic media, the n→π* band disappears due to the promotion of lone pair of electrons. In fact, the protonation increases the excitation energy to such an extent that the n→π* transition shifts into the UV region and may not be observed.

The protonation of a functional group introduces major changes in the spectra. The spectrum in such cases is strongly dependent upon the pH. Solvent effects are useful in identifying the nature of these transitions. The n→π* transitions are altered by the solvent effects in cases where the lone pair electrons in oxygen or nitrogen-containing systems interact with polar solvents. The shifts in absorption bonds and their intensity changes are presented as follow:

1. ***Bathochromatic shift*** (or, the ***red shift):*** A shift of λ_{max} to longer wavelengths.
2. ***Hypochromic shift*** (or, the ***blue shift):*** A shift of λ_{max} to shorter wavelengths.
3. ***Hyperchromic shift:*** An increase in the intensity of an absorption band, usually with reference to its molar extinction coefficient E_{max}.
4. ***Hypochromic shift:*** A decrease in the intensity of an absorption band with reference to E_{max}.

PROBLEMS FOR PRACTICE

1. Identify the two geometrical isomers of stilbene $C_6H_5CH{=}CHC_6H_5$ from their λ_{max} values of 294 nm and 278 nm.

Ans. *Cis*-isomer has a higher energy (due to steric hinderance of phenyl groups) and, therefore, shorter λ_{max}. Thus, the 278 nm correspond to *cis*-stilbene.

2. The UV spectrum of acetone shows two peaks at λ_{max} = 280 nm, E_{max} =15 and λ_{max} = 190 nm. E_{max} =100. Identify the electronic transitions for each and compare their intensities.

Ans. (a) $\sigma \rightarrow \sigma^*$ (allowed transition, strong), $n \rightarrow \sigma^*$ (forbidden transition, weak)

(b) $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ (both allowed transitions, strong), $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ (both forbidden transitions, weak)

Hint The longer wave length is associated with smaller energy $n \rightarrow \pi$ transition, $\pi \rightarrow \pi^*$ transition occurs at 190 nm, $\pi \rightarrow \pi^*$ has greater ε_{max} and hence more intense.

3. List all the electronic transitions possible for

(a) CH_4

(b) $H_2C = O$

Ans. [(a) $\sigma \rightarrow \sigma^*$ (b) $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $n \rightarrow \pi^*$]

4. Predict the kind of electronic transitions and intensities in (a) Cl_2, and (b) C = O groups.

Ans. (a) $\sigma \rightarrow \sigma^*$ (allowed transition, strong) $n \rightarrow \sigma^*$ (forbidden transition, weak)

(b) $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ (both allowed transitions strong)

$n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ (both forbidden transitions weak)

Example 9 *Calculate the degrees of freedom of (a) acetylene molecule, and (b) water molecule.*

Solution:

(a) For CH ≡ CH, N = 4, ∴ total degrees of freedom = $3N = 3 \times 4 = 12$

Transitional degrees = 3, Rotational degrees = 2 (Linear molecule)

∴ Vibrational degrees = 12 − 3 − 2 = 7

(b) For H_2O, N =3, ∴ total ssdegrees of freedom =$3 \times 3 = 9$.

Transitional degrees = 3, Rotational degrees = 3 (molecule),

∴ Vibrational degrees = 9 − 3 − 3 = 3.

Example 10 *How does the study of pure rotational spectrum of a diatomic molecule help in the calculation of bond length?*

Solution: The spacing between any two adjacent lines has difference in wave number given by the relation.

$$\Delta\bar{\nu} = 2B = 2 \times \frac{h}{8\pi^2 I c} = \frac{h}{4\pi^2 I c}$$

$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r_0^2$. Knowing the masses m_1 and m_2 of the atoms of the diatomic molecules, r_0, i.e. bond length, can be calculated.

Example 11 *Why is only one absorption line expected in the vibrational spectrum of a diatomic molecule, treating it is a simple harmonic oscillator?*

Solution: For the transition taking place from υ to $\upsilon + 1$, we have the equation,

$$\Delta E_v = \left(v + 1 + \frac{1}{2}\right) hc\omega_e - \left(v + \frac{1}{2}\right) hc\omega_e = hc\omega_e$$

or $$\frac{\Delta E}{hc} = \omega_e \text{ i.e., } \Delta\bar{\nu} = \omega_e$$

Thus, only one absorption line will be obtained.

Alternatively, as the vibrational levels are equally spaced, any transition from any υ to υ + 1 will give rise to same energy change.

Example 12 *Why is electronic spectrum of a molecule called band spectrum?*

Solution: The energy absorbed for electronic transition is very high. It is accompanied by a number of vibrational transitions. Each vibrational transition is further accompanied by a number of rotational transitions which produce a group of closely spaced lines called 'band'. Hence, a number of bands are obtained and, therefore, the spectrum is called band spectrum.

Example 13 *What will be resolving power of first order of a diffraction grating ruled with 500 grooves/mm and having a width of 60 mm? What will be the smallest interval resolved by this grating for sodium light with 5890 Å wavelength?*

Solution: Resolving power of grating (R) = $m \times N$. For resolving power of first order, m = 1

N = Total number of grooves = 500 × 60 = 30,000

Smallest wavelength interval resolved = 5890/30,000 = 0.2 Å

Example 14 *What is the effect on rotational energy of a molecule if an atom is replaced by its heavier isotope (isotopic substitution)?*

Solution: $I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^2$ and spacing between the adjacent lines = $2B$ = $= 2B = \frac{h}{8\pi^2 Ic}$.

Moment of inertia I will increase when an atom is replaced by its heavier isotope. Here, I appears in the denominator.

Thus, if I increases, the spacing between the adjacent energy levels will decrease, i.e. energy levels will come closer.

Example 15 *Write the expression for the energy levels. Comment on the spacing between the levels. What is zero point energy?*

Solution: $E_v = \left(v + \frac{1}{2}\right) hc\omega_e$ (υ = vibrational quantum number)

Putting υ = 0, 1, 2, etc., we find that vibrational energy levels are equally spaced. For the lowest vibrational level υ = 0, the energy for this level will be $E_0 + \frac{1}{2} hc\omega_e$. This is called zero point energy. It means that even at absolute zero when all transitional and rotational motion ceases in a crystal, the residual energy of vibrational E_0 or vibrational motion still exists.

Example 16 *What types of molecules exhibit rotational spectra? Out of CO_2, C_6H_6, H_2O, NO, N_2O, which will exhibit pure rotational spectra?*

Solution: Pure rotational spectrum is obtained for those molecules which have permanent dipole moment so that the molecule can interact with electromagnetic radiation and absorb or emit a photon. Thus, it is given only by polar molecules. As CO_2 and C_6H_6 are symmetrical molecules and nonpolar, they do not give rotational spectra. H_2O, NO, N_2O are polar and hence, give rotational spectra.

Example 17 *In the electronic band spectrum, why are there no simple selection rules for transitions among vibrational levels?*

Solution: According to Frank-Condon principle, electronic transition takes place much faster

than the nuclei can oscillate to change their internuclear distance. Transition can take place from lowest vibrational level of an electronic state to any vibrational level of higher electronic state. That explains why there are no simple selection rules.

Example 18 *Are the lines in the rotational Raman spectra equally spaced? Explain.*

Solution: The lines are not equally spaced. This is because wave numbers of the lines are given by

$$\bar{\nu} = \bar{\nu}_i \pm B(4J + 6)$$

where $\bar{\nu}_i$ represents the wave numbers of Rayleigh line (i.e. equal to that of the incident radiation). Putting $J = 0$, $\bar{\nu} = \bar{\nu}_i \pm 6B$, i.e. first Stokes' and anti-Stokes' line will be separated by 6B from the Rayleigh line. Further, putting $J = 1, 2, 3, \ldots$, the separation between any two adjacent Stokes' lines or anti-Stokes' lines comes out to $4B$.

Example 19 *The selection rules for spectral transitions in atomic spectra are (a) $\Delta n = 1, 2, 3, 4\ldots$. and (b) $\Delta l = \pm 1$. Using these selection rules, determine which of the following transitions are allowed and which are forbidden :*

(a) $1s \rightarrow 2p$

(b) $2p \rightarrow 3s$

(c) $2p \rightarrow 3s$

(d) $4p \rightarrow 5f$

Solution: For forbidden transition, both the selection rules should be obeyed. Transitions (a) and (c) obey the selection rules. Hence, these are allowed transitions.

Transitions (b) and (d) do not obey the selection rules. Hence, these are forbidden transitions.

Example 20 *Arrange the following groups in order of their absorption frequencies: Give justification.*

(a) CF, CCl, CBr, CH

(b) C – C, C = C, C ≡ C

Solution: Group absorption frequencies are related to the force constant (k) of the bond and the reduced mass (μ) of the group by the following equation.

$$\Delta\bar{\nu} - \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

The equation shows that $\Delta\bar{\nu}$ increases with increase in force constant and decreases with increase in reduced mass.

(a) Reduced mass varies in order: CH < CF < CCl < CBr

∴ Absorption frequencies vary in the order: CH > CF > CCl > CBr

(b) Force constants vary as C ≡ C > C = C > C – C

∴ Absorption frequencies vary in the order: C ≡ C > C = C > C – C

Example 21 *Why does the rotational constant B of a diatomic molecule depend upon the electronic state of the molecule?*

Solution: This is because B depends upon the moment of inertia, which in turn depends upon the internuclear distance, r. Internuclear distance, r, is different for different electronic states of a molecule.

Example 22 *In vibrational-rotational spectrum of a diatomic molecule, why does a line not appear at the bond centre ?*

Solution: The wave numbers of the lines obtained in vibration-rotation spectrum are given by $\Delta\bar{\nu} = \omega_0 + 2Bm$ where ω_0 represents the wave number of the line at the band centre and $m = \pm 1, \pm 2,$

etc. As $m \neq 0$, therefore, the line corresponding to ω_0 is not obtained.

Example 23 *Which of the following molecules will show rotational Raman Spectra: HCl, H_2, CO, CH_4, H_2O, NH_3, F_6. Explain.*

Solution: All the molecules except CH_4 and SF_6 give rotational Raman spectra. Rotational Raman spectra are given by a molecule in which the rotation motion takes place with a change in the polariz-ability.

Example 24 *Why is it that the vibrational frequency υ is smaller in the excited state than in the ground state of a molecule?*

Solution: This is because the vibrational frequency is proportional to force constant, *k*. Force constant, *k* is smaller in the excited state.

Example 25 *In the vibration-rotation spectrum of HCl, why is each individual line of the spectrum found to consist of doublets?*

Solution: The splitting takes place due to presence of two isotopes of Cl, viz. ^{35}Cl and ^{37}Cl in HCl. These isotopes with different masses result into different moments of inertia (*I*) and fundamental frequency of vibration (ω_e) for HCl^{35} and HCl^{37}.

Example 26 *Using Heisenberg uncertainty principle, estimate the life of an energy state which gives rise to a line width of (a) 0.1 cm, and (b) 60 MHz.*

Solution: $\tau = \dfrac{1}{4\pi\Delta\nu} = \dfrac{1}{4\pi c\Delta\bar{\nu}}$ (As $\nu = c\bar{\nu}$)

(a) $\Delta\bar{\nu} = 0.1\ \text{cm}^{-1} \therefore \tau = \dfrac{1}{4\pi \times (3\times10^{10}\ \text{cm}\,s^{-1}) \times (0.1\ \text{cm}^{-1})} = 2.5\times10^{-11}\,s$

(b) $\Delta\bar{\nu} = 60\ \text{MHz} \therefore \tau = \dfrac{1}{4\pi \times (60\times10^{6}\,s^{-1})} = 1.35\times10^{-9}\,s$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. Raman and *IR* spectra can tell us whether
   (a) a molecule is linear or non-linear
   (b) a molecule is symmetrical or asymmetrical
   (c) neither of the above
   (d) both of the above
2. The rotational spectra involve
   (a) a very high energy changes
   (b) small energy changes
   (c) no energy changes
   (d) none of these
3. A molecule can be excited to only the next higher rotational level by
   (a) absorption of energy
   (b) release of energy

(c) the electric current

(d) applying magnetic field

4. In the Raman spectrum, the middle line is called

(a) Raman line

(b) Rayleigh line

(c) functional group line

(d) none of these

5. The wave numbers are expressed in

(a) s^{-1}

(b) cm s^{-1}

(c) cm^{-1}

(d) cm^2 s^{-1}

6. The IR spectra of a compound helps in

(a) providing the identify of compounds

(b) showing the presence of certain functional group in the molecules

(c) neither of the above

(d) both of the above

7. The electromagnetic radiation of higher wavelength has____energy.

(a) higher

(b) lower

(c) intermediate

(d) zero.

8. The change in frequency by scattering (Raman effect) occurs due to____of energy between the incident photon and the scattering molecule.

(a) release

(b) absorption

(c) exchange

(d) none of these

9. The spectra caused in the infrared region by the transition in vibrational levels in different modes of vibrations are called

(a) rotational spectra

(b) electronic spectra

(c) vibrational spectra

(d) none of these

10. The electronic spectra consists of

(a) a large number of absorption bands

(b) a large number of closely packed lines

(c) a large number of peaks

(d) none of these

Answers

1. (d)
2. (b)
3. (a)
4. (b)
5. (c)
6. (d)
7. (b)
8. (c)
9. (c)
10. (b)

SHORT-ANSWER QUESTIONS

1. What is Rayleigh's criterion for resolution of two wavelengths λ and $\lambda + d\lambda$?
2. What do you mean by electromagnetic spectrum? List the different types of electromagnetic radiations along with frequency ranges and sources.
3. What do you understand by Doppler broadening (Doppler effect) and lifetime broadening?
4. What do you understand by the terms resolution, linear dispersion and angular dispersion? Explain how resolution depends upon the slit width.
5. What is molecular spectroscopy? How does it differ from atomic spectroscopy? Draw the molecular energy levels of the first two electronic levels. What are vibrational and rotational quantum numbers?
6. Explain the selection rules followed in atomic spectroscopy. Give suitable examples.
7. What do you understand by resolving power of a spectrometer? What is the formula for resolving power of a prism?
8. Briefly explain the terms absorption and emission spectroscopy. Why is absorption spectroscopy preferred? Give its experimental set-up.
9. What are basic components of a spectrometer? Show them diagrammatically.
10. What is the effect of isotopic substitute on rotational spectra?
11. How is rotational spectrum observed experimentally?
12. Explain the relative intensities of the lines obtained in a pure rotational spectrum.
13. What are electromagnetic radiations? List their important characteristics.
14. What are the different types of energies possessed by a molecule.
15. What type of potential energy curve is obtained for a simple harmonic oscillator and why?
16. Why do we get a band spectrum in case of molecules?
17. Write the expression for the rotational energy of a diatomic molecule, taking it as a rigid rotator. Draw the rotational energy-level diagram for such a molecule.
18. What type of molecules exhibit vibrational spectra? Out of H_2, O_2, N_2, HCI, CO, NO, CO_2, H_2O and CH_4, which will give pure vibrational spectra?
19. What do you understand by symmetric, asymmetric, bending, parallel, and perpendicular modes

of vibration? Explain with suitable examples.

20. What are *P*, *Q*, and *R* branches of vibration-rotation spectrum?
21. Why is a diatomic molecule considered as an anharmonic oscillator? Write the Morse equation for the energy of the vibrational levels of an anharmonic oscillator. Compare the potential energy curve of an anharmonic oscillator with that of a harmonic oscillator.
22. What is the most important use of studying pure rotational Raman spectrum?
23. What do you mean by selection rules in spectroscopy. What are gross and specific selection rules?
24. What are the factors which affect the intensity of a spectral line? Explain briefly.
25. Write expression for the vibrational energy of a diatomic molecule, taking it as a simple harmonic oscillator. Represent the vibrational energy level of such a molecule diagrammatically.
26. What type of vibration-rotation spectrum is obtained if the resolving power of the spectrometer is not so high?
27. What are the factors that affect the width of a spectral line?
28. Explain why molecules behave as nonrigid rotors. Write expression for the wave numbers of rotational levels of a non-rigid rotor and hence, derive the expression for the wave numbers of the lines produced.
29. On the basis of polarisability, explain which type of molecules will be rotationally Raman active and which will be inactive.
30. Explain with suitable mathematical equations the type of pure rotational Raman spectrum expected for a diatomic molecule. Mark clearly the separation between the different lines.
31. What structural information is obtained from the study of infrared spectra?
32. What do you mean by 'zero point energy'?
33. What is isotopic effect on vibration-rotation spectrum? Explain with a suitable example.
34. What type of vibrational spectrum is expected for a diatomic molecule taking it as a simple harmonic oscillator?
35. How are infrared spectra helpful in the identification of organic compounds?
36. What are the selection rules for the vibrational transitions in a diatomic molecule, taking it as a simple harmonic oscillator.

GENERAL QUESTIONS

1. Name the different types of molecular spectra. Explain each of them briefly. In which region of the electromagnetic spectrum are they obtained?
2. Explain with suitable derivations what type of rotation-vibration spectrum is obtained for a diatomic molecule, taking it as an anharmonic oscillator.
3. What do you understand by signal-to-noise (S/N) ratio? How can it be enhanced? Briefly explain Fourier transformation for enhancement of S/N ratio. Why is it considered better than the conventional spectroscopy?
4. What do you understand by degree of freedom of motion of a molecule? Briefly explain the different types of degrees of freedom possessed by linear and non-linear molecules.
5. What are selection rules for rotation-vibration Raman spectra of diatomic molecules? Applying these rules explain what type of rotation-vibration Raman spectrum is obtained for a diatomic molecule.
6. Drive expression for the frequency (or wave number) of rotational lines in a pure rotational spectrum. What type of pure rotational spectrum will be observed. How do the intensities of

these lines vary?

7. Explain Raman effect on the basis of polarisability of molecules.
8. What do you understand by 'width' and 'intensity' of a spectral line? Briefly explain the factors on which each of these depend.
9. What is Raman spectrum? Name the different types of lines present in it and explain the reasons for observing these lines? Give the experimental set-up for observing Raman spectra.
10. Write short notes on the following:
    (a) Electromagnetic spectrum
    (b) Molecular energy levels
    (c) Absorption and emission spectroscopy
11. What do you understand by normal modes of vibration of a polyatomic molecule? Show diagrammatically the different normal modes of vibration of CO_2 and H_2O molecules, Give their names and state which of them are inactive in Raman spectra.
12. Briefly explain why the electronic band spectrum obtained is very complex. In spite of its complexity, why is it preferred? How does it help in calculation of dissociation energy of a molecule?
13. Taking the example of carbonyl compounds, represent molecular orbitals and explain the electronic transitions taking place between them.
14. What do you understand by resolving power of a spectrometer? Explain taking the example of a prism as a dispersing element. Also explain how the resolution depends upon the slit width.
15. Explain the formation of electronic bond spectrum on the basis of potential energy curves. How do these curves help in the calculation of the dissociation energy of the molecules?
16. Briefly explain the terms stimulated absorption, stimulated emission and spontaneous emission. Prove that the net absorption is proportional to the population difference of the two states involved in the transition.
17. Considering a diatomic molecule as a rigid rotator, explain the type of rotational (microwave) spectra obtained after deriving the expressions required.



Photochemistry 22

LEARNING OBJECTIVES

- Differentiate between photophysical and photochemical processes
- Differentiate between thermochemical and photochemical reactions
- Study Lambert's law of transmission of light
- Understand the physical significance ofextinction coefficient
- Study Beer's law
- Learn the first and second laws of photochemistry
- Understand quantum efficiency or quantum yield and its determination
- Study luminescence and its differentforms, viz. chemiluminescence, fluorescence and phosphorescence
- Sketch Jablonski diagrams for different electronic transitions
- Understand the phenomenon of photosensitisation
- Learn photochemical equilibrium

22.1 INTRODUCTION

In ordinary thermal reactions, activation energy is obtained from random intermolecular collision on the increase of temperature. In photochemical reactions, on the other hand, activation energy is acquired by the absorption of photons of light of a particular energy. By using light of a particular wavelength in the visible or ultraviolet region, it is possible to excite a particular species in a mixture instantly to an excited state. This is a photochemical reaction, where only a single species can be promoted to excited state independent of the other species in contrast to thermal reactions which do not permit such selectivity.

Photochemistry is defined as that branch of chemistry which deals with the process involving emission or absorption of radiation. Two types of reactions are studied under photochemistry.

1. Photophysical Processes These processes take place in the presence of light but do not involve any chemical reaction. These processes take place due to absorption of light by the substances followed by the emission of the absorbed light. If there is instantaneous emission of the absorbed light, the process is called ***fluorescence.***

If a high amount of energy is absorbed, the electrons may leave the atoms completely. Such a process is called ***photoelectric effect***. Photophysical processes include fluorescence, phosphorescence and photoelectric effect.

2. Photochemical Reactions These are the reactions that take place by absorption of radiations of suitable wavelength. In such processes, the absorbed light energy is first stored in the molecule and then it is further used to bring about the reaction. Examples of photochemical reactions are

(a) Photosynthesis of carbohydrates in plants taking place in presence of chlorophyll, the green colouring matter, present in the leaves

$$\underbrace{6\,CO_2 + 6H_2O}_{\text{From air}} \xrightarrow[\text{(chlorophyll)}]{\text{light}} \underbrace{C_6H_{12}O_6}_{\text{Glucose}} + 6O_2$$

(b)Reaction between hydrogen and chlorine

$$H_2(g) + Cl_2(g) \xrightarrow{\text{light}} 2HCl(g)$$

Experiment to Explain a Photochemical Reaction

A mixture of hydrogen and chlorine remains unchanged with lapse of time. But when exposed to light, the reaction occurs with loud explosion.

$$H_2 + Cl_2 \xrightarrow{\text{Dark}} \text{No reaction}$$

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2HCl$$

A bottle is filled with equimolar amount of hydrogen and chlorine (Fig. 22.2). It is tightly stoppered with a handball. When the lamp is turned on, a beam of light falls on the mixture through the bottom of the bottle. The reaction occurs with an explosion. The ball is expelled with high velocity so that it strikes the opposite wall of the room.

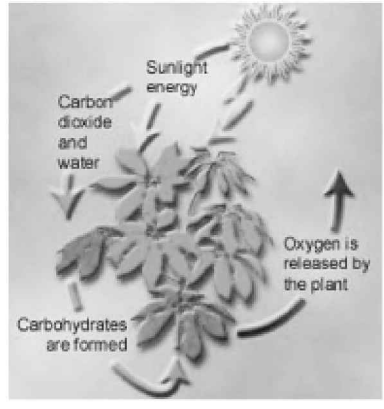


Fig. 22.1 *Photosynthesis of carbohydrates*

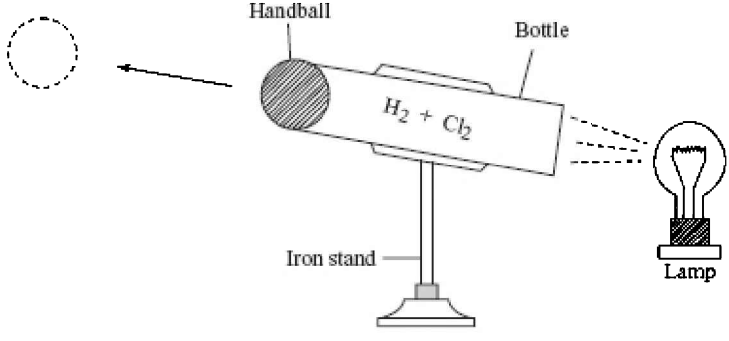


Fig. 22.2 *'HCl cannon' experiment*

Applying Chemistry to Life

Photochemical smog is formed by the reaction of automobile exhaust or the exhaust from chimneys of different industries in the presence of sunlight. The exhausts mainly consist of NO, CO and unburnt hydrocarbons. These gases are called ***primary pollutants.*** Photochemical reactions with these pollutants produce ***secondary pollutants.*** It is these secondary pollutants NO_2, O_3, etc., that cause smog. The reactions are given as under:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ (At high temperatures)

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Sunlight causes photochemical decomposition of NO_2 at $l < 400$ nm

$NO_2(g) + hv - NO(g) + O(g)$

Atomic oxygen is a highly reactive species. It reacts with O_2 to form O_3

$O_2(g) + O + M \rightarrow O_3(g) + M$

where M is an inert substance such as N_2

Ozone reacts with rubber which contains C = C linkage

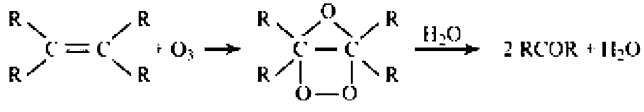




Fig. 22.3 *Photochemical smog*

In industrial areas and cities with high automobile emission, this reaction can cause cracking and bursting of tyres. Such reactions also damage the lung tissues and other biological substances.

Smoke emanating from chimneys causes photochemical smog.

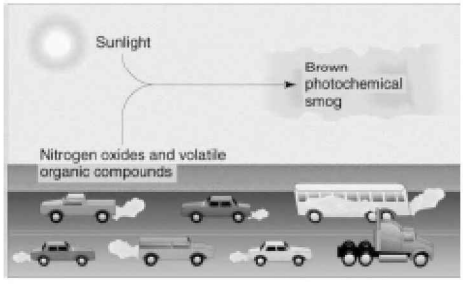


Fig. 22.4 *Automobile exhausts are a major cause of photochemical smog*

22.2 DIFFERENCES BETWEEN THERMOCHEMICAL AND PHOTOCHEMICAL REACTIONS

The main points of difference between the two types of reactions are given in tabular form as under:

Table 22.1 *Difference between thermochemical and photochemical reactions*

Thermochemical reactions	Photochemical reactions
(i) These reactions involve absorption of heat.	(i) These reactions involve absorption or evolution of light.
(ii) Temperature has sufficient effect on the rate of a thermochemical reaction.	(ii) Temperature has very little effect on the rate of photochemical reaction. Instead, the intensity of light has a marked effect on the rate of a photochemical reaction.
(iii) They can take place even in the dark.	(iii) The presence of light is a primary requisite for the reaction to take place.
(iv) The free-energy change (ΔG) of a thermochemical reaction is always negative.	(iv) The free-energy change (ΔG) of a photochemical reaction may not be negative. A few examples of photochemical reactions for which ΔG is positive and still they are spontaneous, are synthesis of carbohydrates in plants and decomposition of HCl into H_2 and Cl_2.

22.3 LAMBERT'S LAW OF TRANSMISSION OF LIGHT

This law put forward by Lambert is stated as under:

When a monochromatic light is passed through a pure homogeneous medium, the decrease in the intensity of light with thickness of the absorbing medium at any point X is proportional to the intensity of the incident light. Mathematically, the law can be put as,

$$-\frac{dI}{dx} \propto I$$

or
$$\frac{dI}{dx} = kI \qquad \ldots(22.1)$$

where dI is the small decrease in intensity of the light on passing through a small thickness dx, I is the intensity of the incident light just before entering the thickness dx and k is the constant of proportionality called ***absorption coefficient.*** It depends upon the nature of the absorbing medium.

The intensity I at any point X at a distance x from the start of the medium can be found in terms of the original intensity I_o as follows:

Equation (22.1) can be rewritten as

$$\frac{dI}{I} = -kdx \qquad \ldots(22.2)$$

when $x = 0, I = I_o$

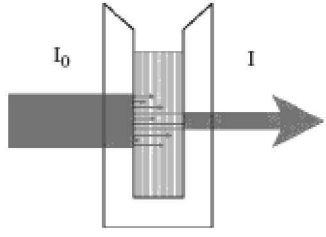


Fig. 22.5 *Illustration of Lambert's law*

Integrating Eq. (22.2) between the limits $x = 0$ to x and $I = I_o$ to I, we get

$$\int_{I_o}^{I} \frac{dI}{I} = \int_{x=0}^{x} -kdx$$

or
$$\ln \frac{I}{I_o} = -kx \qquad \ldots(22.3)$$

or
$$\frac{I}{I_o} = e^{-kx}$$

or
$$I = I_o e^{-kx} \qquad \ldots(22.4)$$

This equation expresses how the original intensity I_o is reduced to the intensity I after passing through a thickness x of the medium.

Equation (22.3) can be written as,

$$2.303 \log \frac{I}{I_o} = -kx \quad \text{or} \quad \log \frac{I}{I_o} = -\frac{k}{2.303} x$$

or
$$\log \frac{I}{I_o} = -k'x \qquad \ldots(22.5)$$

or
$$\frac{I}{I_o} = I_o^{-k'x}$$

or
$$I = I_o\, 10^{-Cx} \qquad \ldots(22.6)$$

where $k' = \dfrac{k}{2.303}$ is called ***extinction coefficient*** of the substance, i.e. the absorbing medium. This quantity is now called ***absorption coefficient*** or ***absorptivity*** of the substance.

$-\log I/I_o$ is called ***absorbance*** of the medium.

Physical Significance of the Extinction Coefficient or Absorptivity

It follows more clearly from Eq. (22.5), which can be rewritten as

$$k' = -\frac{1}{x} \log \frac{I}{I_o} = \frac{1}{x} \log \frac{I_o}{I}$$

If
$$\log \frac{I_o}{I} = 1, \; k' = \frac{1}{x}$$

But
$$\log \frac{I_o}{I} = 1, \text{ means } \frac{I_o}{I} = 10 \text{ i.e., } I = \frac{1}{10} I_o.$$

Hence, extinction coefficient or absorptivity may be defined as follows:

The extinction coefficient or absorptivity is the reciprocal of the thickness (expressed in cm) at which the intensity of the light falls to one-tenth of its original value.

22.4 BEER'S LAW

Beer's law states as under:

When a monochromatic light is passed through a solution, the decrease in the intensity of light with the thickness of the solution is directly proportional not only to the intensity of the incident light but also to the concentration c of the solution. Mathematically, we have

$$-\frac{dI}{dx} \propto I \times c \qquad \ldots(22.7)$$

or
$$-\frac{dI}{dx} = \epsilon Ic \qquad (\epsilon \text{ is 'epsilon'})$$

where ϵ is a constant of proportionality and is called ***molar absorption coefficient.*** Its value depends upon the nature of the absorbing solute and the wavelength of the light used.

Equation (22.7) can be rewritten as,

$$\frac{dI}{I} = -\epsilon c dx$$

Integrating this equation between the limits $x = 0$ to x and $I = I_o$ to I, we get

$$\int_{I_o}^{I} \frac{dI}{I} = \int_{x=0}^{x} -\epsilon c dx$$

or $$\ln \frac{I}{I_o} = -\epsilon cx \qquad \ldots(22.8)$$

or $$\frac{I}{I_o} = e^{-\epsilon cx} \qquad \ldots(22.9)$$

or $$I = I_o e^{-\epsilon cx} \qquad \ldots(22.10)$$

This equation expresses how the intensity of a monochromatic light falls from I_o to I on passing through the thickness x of a solution of concentration c.

$$2.303 \log \frac{I}{I_o} = -\epsilon cx \quad \text{or} \quad \log \frac{I}{I_o} = -\frac{\epsilon}{2.303} cx$$

$$\log \frac{I}{I_o} = -\epsilon' cx \qquad \ldots(22.11)$$

or $$\frac{I}{I_o} = 10^{-\epsilon' cx}$$

or $$I = I_o \times 10^{-\epsilon' cx} \qquad \ldots(22.12)$$

$\epsilon' = \dfrac{\epsilon}{2.303}$ was earlier called *molar extinction coefficient* of the absorbing solution. But now it is called molar absorption coefficient or molar absorptivity of the absorbing medium.

Physical Significance of Molar Extinction Coefficient or Molar Absorptivity It follows from Eq. (22.11), which can be rewritten as

$$\epsilon' = -\frac{1}{cx} \log \frac{I}{I_o} = \frac{1}{cx} \log \frac{I_o}{I}$$

If $$c = 1 \text{ M} \quad \text{and} \quad \log \frac{I_o}{I} = 1$$

then $$\epsilon' = \frac{1}{x}$$

$$\log \frac{I_o}{I} = 1 \text{ means } \frac{I_o}{I} = 10 \text{ i.e., } I = \frac{1}{10} I_o$$

Hence, ***molar extinction coefficient or molar absorptivity may be defined as the reciprocal of that thickness of the solution layer of 1 molar concentration which reduces the intensity of the light passing through it to one-tenth of its original value.***

Example 1 *A certain substance in a cell of length l absorbs 10% of the incident light. What fraction of the incident light will be absorbed in a cell which is five times longer?*

Solution: In the first case, $I_{abs} = 0.10\ I_o$ so that $I_t = 0.90\ I_o$

or $$\frac{I_t}{I_o} = 0.90$$

We have the relation $\log \frac{I_t}{I_o} = -k'x$. Put $x = l$

$$\log \frac{I_t}{I_o} = -k'l \text{ i.e., } \log 0.90 = -k'l \quad \text{or} \quad k' = \frac{0.0458}{l}$$

In the second case, $x = 5l$ so that , $-k \times 5l$

$$\log \frac{I_t}{I_o} = -k \times 5l = \frac{-0.0458}{l} \times 5l = -0.2290$$

or $$\log \frac{I_t}{I_o} = \bar{1}.7710 \quad \text{i.e.,} \quad \frac{I_t}{I_o} = 0.5902 \text{ or } I_t = 0.5902\ I_o$$

$\therefore$ $$I_{abs} = I_o - I_t = I_o - 0.5902\ I_o = 0.4098\ I_o = 40.98\% \text{ of } I_o$$

Example 2 *When an incident beam of 3000 Å wavelength was allowed to pass through 2 mm thick pyrex glass, the intensity of the radiation was reduced to one-tenth of its initial value. What part of the same radiation will be absorbed by 1 mm thick glass?*

Solution: In the first case, it is given that

$$\frac{I_t}{I_o} = \frac{1}{10} \qquad (I_t \text{ denotes transmitted light})$$

$$x = 2 \text{ mm} = 0.2 \text{ cm}$$

Applying Lambert's law, we have

$$\log \frac{I_t}{I_o} = k'x$$

i.e., $$\frac{1}{10} = -k'(0.2) \quad \text{or} \quad k' = \frac{1}{0.2} = 5$$

In the second case, it is given that

$$x = 1 \text{ mm} = 0.1 \text{ cm}$$

As the medium is the same, k' will have the same value, viz. 5.

Applying Lambert's law, we have

$$\log \frac{I_t}{I_o} = -k'x = -5(0.1) = -0.5 \quad \text{or} \quad \frac{I_t}{I_o} = \text{antilog}(-0.5) = \text{antilog}(\bar{1}.5) = 0.3162$$

i.e. $$I_t = 0.3162\ I_o$$

$$I_{abs} = I_o - I_t = I_o - 0.3162\ I_o = 0.6838\ I_o$$

Example 3 *Calculate the transmittance, absorbance and absorption coefficient of a solution which absorbs 90% of a certain wavelength of light beam passed through a 1 cm cell containing a 0.25 M solution.*

Solution: It is given that,

$$I_{abs} = 0.90\ I_o;\ x = 1\ \text{cm};\ c = 0.25\ \text{M}$$

$$I_t = I_o - I_{abs} = I_o - 0.90\ I_o = 0.10\ I_o$$

$\therefore$ Transmittance $\quad T = I_t/I_o = 0.10$

Absorbance $\quad A = \log \dfrac{I_t}{I_o} = \log \dfrac{I_o}{I_t} = \log \dfrac{1}{0.1} = 1$

Applying Beer's law, we have

$$\log \frac{I_t}{I_o} = -\epsilon' cx$$

$$\log 0.10 = \epsilon' \times 0.25 \times 1 \quad \text{or} \quad 1 = \epsilon' \times 0.25$$

$$\epsilon' = \mathbf{0.4\ L\ mol^{-1}\ cm^{-1}}$$

PROBLEMS FOR PRACTICE

1. Light of 256 nm wavelength passing through a 1.0 mm thick cell containing a sample solution reduced to 16% of its initial intensity. Calculate the absorbance and the molar absorption coefficient of the sample. What would be the transmittance through a 2.0 mm cell?

[Ans. $\epsilon = 160\ \text{M cm}^{-1}$, $A = 0.80$, $T = 0.025 = 2.5\%$]

2. A 1 molar solution in a cell of 0.200 mm thickness transmits 10% of a beam of light. Neglecting the absorption by solvent and cell windows, what percentage of the initial intensity will be transmitted by a molar solution in a 0.150 mm thick cell?

[Ans. 3.16%]

[*Hint*. From the first data, calculate ϵ', using the value of ϵ', calculate I_t/I_o from the second data.]

3. The percentage transmittance of an aqueous solution of disodium fumarate at 250 mm and 298 K is 19.2% for a 5×10^{-4} molar solution in a 1 cm cell. Calculate the absorbance A and the molar absorption coefficient ϵ. What will be the percentage transmittance of a 1.75×10^{-5} molar solution in a 10 cm cell?

[Ans. $A = 0.717$, $\epsilon = 1.43 \times 10^3\ L\ \text{mol}^{-1}\ \text{cm}^{-1}$, $T = 56.1\%$]

4. If a 2 mm thick plate of material transmits 70% of the incident light, what percentage will be transmitted by a 0.5 mm thick plate?

[Ans. 91.47%]

22.5 LAWS OF PHOTOCHEMISTRY

1. Grotthus Law (First Law of Photochemistry) The law may be stated as under:

When light falls on a body, a part of it is reflected, a part of it is transmitted and the rest of it is absorbed. It is only the absorbed light which is effective in bringing about chemical reaction.

This law, however, does not imply that the absorbed light must always result into chemical reaction. The absorbed light may simply bring about phenomena such as fluorescence, phosphorescence, etc. Similarly, the absorbed light energy may be simply converted into thermal energy, e.g. in case of potassium permanganate solution, the light energy is absorbed strongly but no chemical effect is produced. Further, in some cases, it is observed that light energy may not be absorbed by the reacting substance directly but may be absorbed by some other substance present along with the reacting substance. The energy thus absorbed is then passed onto the reacting substance which then starts reacting. This process is called ***photosensitisation***. Photosynthesis of carbohydrates in plants where chlorophyll acts as a photosensitiser is a prominent example of photosensitisation.

2. Stark-Einstein Law of Photochemical Equivalence (Second Law of Photochemistry) This law may be stated as under:

Every atom or molecule that takes part in a photochemical reaction absorbs one quantum of the radiation to which the substance is exposed.

If υ is the frequency of the absorbed radiation then the energy absorbed by each reacting atom or molecule is one quantum, i.e., $h\nu$, where h is Planck's constant. The energy absorbed by one mole of the reacting molecules is given by,

$$E = Nh\nu \qquad \ldots(22.13)$$

where N is the Avogadro's number.

$$\text{Putting } \nu = \frac{c}{\lambda}, \text{ we can write} \qquad E = Nh\frac{c}{\lambda} \qquad \ldots(22.14)$$

where c is the velocity of light and λ is the wavelength of the absorbed radiation.

The energy possessed by one mole of photons or the energy absorbed by one mole of the reacting molecules is called one Einstein.

Numerical Value of Einstein Substituting $N = 6.022 \times 10^{23}$ mol^{-1}, in Eq. (22.14) above, we get

$$E = \frac{(6.022 \times 10^{23})(6.626 \times 10^{-27})(3.0 \times 10^{10})}{\lambda}$$

$$= \frac{119.7 \times 10^{6}}{\lambda} \text{ ergs per mole} \quad \text{or} \quad \frac{119.7 \times 10^{6}}{4.184 \times 10^{7}\lambda} \text{ cal per mole}$$

$$\text{or} \quad E = \frac{2.86}{\lambda} \text{ cal per mole (in CGS units)} \qquad \ldots(22.15)$$

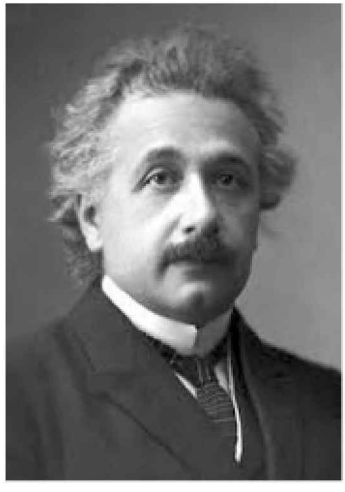


Fig. 22.6 *Albert Einstein was a German born theoretical physicist, best known for his general theory of relativity.*

In this equation, λ is expressed in cm. However, as λ is usually expressed in Angstrom units (Å) and we known that 1 Å = 10^{-8} cm, therefore Eq. (22.14) can be written as

$$E = \frac{2.86}{\lambda} 10^8 \text{ cal per mole} \qquad \ldots(22.16)$$

where λ is in Angstrom units.

Further, putting 10^3 cal = 1 kcal, Eq. (22.16) can be written as

$$E = \frac{2.86 \times 10^5}{\lambda} \text{ kcal per mole} \qquad \ldots(22.17)$$

This equation gives the energy possessed by one mole of photons and is called ***one einstein***. Thus the ***energy per Einstein is inversely proportional to the wavelength of the radiation. Shorter the wavelength of a radiation, greater is the energy per einstein***.

The unit of energy used most frequently in photochemistry is electronvolt (eV).

1 eV = 23.06 kcal/mole

It may be mentioned that 1 eV is the energy acquired by an election when a potential difference of 1 volt is applied to it.

To obtain the equation in **SI units**, we substitute

$$N = 6.022 \times 10^{23} \text{ mol}^{-1}, \quad h = 6.626 \times 10^{-34} \text{ Js}, \quad c = 3.0 \times 10^8 \text{ ms}^{-1}$$

We get,

$$E = \frac{0.1197}{\lambda} \text{ J mol}^{-1} = \frac{11.97 \times 10^{-5}}{\lambda} \text{ kJ mol}^{-1}$$

Example 4 *Calculate the value of einstein of energy for radiation of 4000 Å wavelength.*

Solution

$$E = \frac{2.86 \times 10^5}{\lambda} \text{ kcal/mole} \quad (\lambda \text{ in Å units})$$

$$= \frac{2.86 \times 10^5}{4000} \text{ kcal/mole}$$

$$= \mathbf{71.5 \text{ kcal/mole}}$$

Example 5 *Calculate the energy of one photon of light of 2450 Å wavelength. Will it be able to dissociate a bond in a diatomic molecule which absorbs this photon and has a bond energy equal to 95 kcal per mole?*

Planck's constant (h) = 6.626 × 10^{-27} erg s molecule^{-1}, Velocity of light (c) = 3 × 10^{10} cm s^{-1} Avogadro's number (N) = 6.02 × 10^{23}

Solution

$$\text{Energy of photon} = h\nu = h\frac{c}{\lambda} = \frac{(6.026 \times 10^{-27}) \times (3 \times 10^{10})}{2450 \times 10^{-8}} \text{ ergs}$$

$$= 8.11 \times 10^{-12} \text{ ergsm} = \frac{8.11 \times 10^{-12}}{4.184 \times 10^7} \text{ cal} = 1.938 \times 10^{-19} \text{ cal}$$

Energy required for dissociation of one bond

$$= \frac{95000}{6.02 \times 10^{23}} \text{ cal} = \mathbf{1.578 \times 10^{-19} \text{ cal}}$$

Thus, energy of photon is greater than the energy required to break the bond. Hence, the bond will be dissociated.

Example 6 *If the value of an einstein is 72 kcal, calculate the wavelength of light.*

Solution: Here. E – 72 kcal

From the equation, $$E = \frac{2.86 \times 10^5}{\lambda} \text{ kcal/mole}$$

$$\lambda = \frac{2.86 \times 10^5}{E} \text{ Å} = \frac{2.86 \times 10^5}{72} = \mathbf{3972.2 \text{ Å}}$$

Example 7 *Calculate the value of an einstein of energy in electronvolts for radiation of 3 × 10^{13} s^{-1} frequency.*

Solution: Here, we are given that

$$\nu = 3 \times 10^{13} \text{ s}^{-1}$$

$$\lambda - \frac{c}{\nu} = \frac{3 \times 10^{10} \text{ cms}^{-1}}{3 \times 10^{13} \text{ s}^{-1}} \quad - 10^{-3} \text{ cm} - 10^5 \text{ Å}$$

$$E = \frac{2.86 \times 10^5}{\lambda} \text{ kcal/mole } (\lambda \text{ in Å units}) = \frac{2.86 \times 10^5}{10^5} = 2.86 \text{ kcal/mole}$$

$$- \frac{2.86}{23.06} \text{ eV} - 0.124 \text{ eV}.$$

PROBLEMS FOR PRACTICE

1. What is the energy in kcal of one mole of photons of 2573 Å wavelength?

[Ans. 111.15 kcal]

2. Calculate the energy of one photon of light of 2450 Å wavelength. Will it be able to dissociate a bond in a diatomic molecules which absorbs this photon and has a bond energy equal to 95 kcal per mole?

   Planck's constant (h) = 6.626×10^{-27} erg s molecule^{-1}

   Velocity of light (c) = 3×10^{10} cm s^{-1}

   Avogadro's number (N) = 6.02×10^{23}

   Hint: Calculate the energy of the photon. If this energy is greater than that required to break the bond (bond energy), dissociation of the bond will happen.

[Ans. 1.938×10^{-19} cal, bond will dissociate]

3. Calculate the value of an einstein of energy in electronvolts for a radiation of 3×10^{15} s^{-1} frequency.

[Ans. 12.4 eV]

4. Calculate the value of the einstein corresponding to radiation of 6000 Å wavelength.

[Ans. 47.66 kcal/mol]

5. Find the value of an einstein of energy for radiation of 4240 Å wavelength.

[Ans. 67.45 kcal/mol]

22.6 QUANTUM EFFICIENCY OR QUANTUM YIELD

To relate the number of quanta absorbed with the number of reacting molecules, a term called ***quantum efficiency*** or ***quantum yield*** ϕ has been introduced. It is expressed as

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

$$= \frac{\text{Number of moles reacting in a given time}}{\text{Number of Einsteins of light absorbed in the same time}}$$

Hence, ***quantum efficiency*** may be defined as the ***number of moles reacting per einstein of the light absorbed***.

If Stark–Einstein's law is strictly obeyed in the form already stated, ϕ should be equal to unity. However, it has been experienced that the law is applicable only to the primary processes. Hence, it is sometimes preferred to state it as follows:

Each molecules that gets activated to initiate the reaction absorbs one quantum of light.

22.6.1 Determination of Quantum Yield of a Photochemical Reaction

To determine the quantum yield of any photochemical reaction, we have to measure

- The rate of the chemical reaction in terms of molecules per second
- The quanta absorbed per second

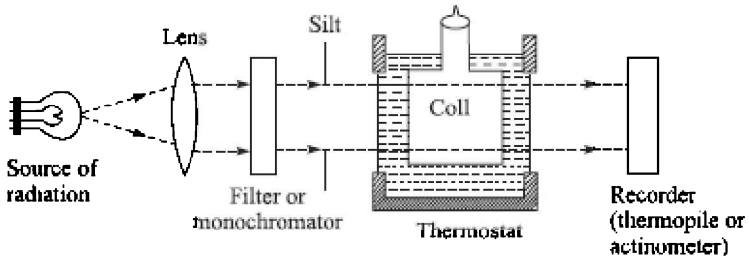


Fig. 22.7 *Apparatus for determination of quantum yield of photochemical reaction*

1. Apparatus The apparatus used for measuring the above two quantities is shown in Fig. 22.7. Various components of the apparatus are described as under:

(a) ***A source of radiation*** emitting radiation of suitable intensity in the desired spectral range. The commonly used sources are filament lamps, carbon and metal arcs and various gas-discharge tubes.

(b) ***Lens of suitable*** focal length.

(c) ***Monochromator*** or ***filter*** which cuts off all radiations except the radiations of the desired wavelength.

(d) ***Slit***.

(e) ***A cell placed in a thermostat*** and containing the reaction mixture. The cell is made of glass or quartz and has optically plane windows for the entrance and exit of light. Glass is used only if the wavelength of light used lies in the visible range. For radiations with wavelength below 3500 Å, a cell completely made of quartz is used.

(f) ***Recorder*** is usually a ***thermopile*** or an ***actinometer*** which is used to measure intensity of radiation. The principle of thermopile and that of an ***actinometer*** are briefly explained below:

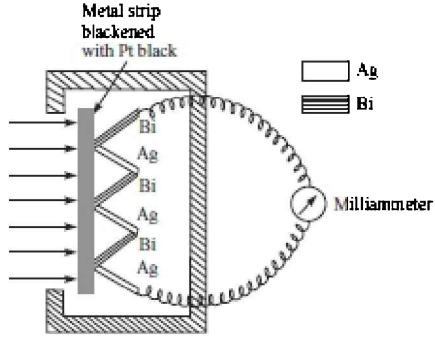


Fig. 22.8 *A thermopile.*

A thermopile is a set of thermocouples. Rods of two different metals (e.g. Ag and Bi) are joined alternately as shown in Fig. 22.8. One set of junction is soldered to a metal strip blackened with platinum or lampblack and the other set of junctions is protected completely from radiation by placing the system in a box. The radiations falling on the blackened metal strip are almost completely absorbed by it. As a result, this set of junctions becomes hot. The temperature difference between the hot end and the cold end produces a current which can be measured by connecting a milliammeter to the thermopile. By calibrating the thermopile with radiations of known intensity,

the desired radiation can be measured.

A ***chemical actinometer*** is a device in which solutions sensitive to light are used. The working of this device is based upon the fact that a definite amount of the radiation absorbed brings about a definite amount of chemical reaction. The most common actinometer is the ulranyl oxalate actinometer which consists of 0.05 molar oxalic acid and 0.01 molar uranyl sulphate (UO_2SO_4) solutions in water. When exposed to light, the following reaction takes place:

$$\begin{matrix}\text{COOH}\\|\\\text{COOH}\end{matrix}\ (aq) \xrightarrow[(UO_2SO_4)]{h\nu} CO_2(g) + CO(g) + H_2O(l)$$

Uranyl sulphate acts as a photosensitiser, i.e. absorbs the light and then passes it onto oxalic acid. The extent of reaction is measured by titrating the oxalic acid solution with potassium permanaganate solution. The actinometer is first calibrated against a thermopile.

2. Procedure It consists of the following two steps

(a) Measurement of the Intensity of Light Absorbed First, the empty cell or the cell filled with the solvent alone (in case of solutions), is placed in the thermostat. The monochromatic radiation is allowed to pass through the cell for a definite time. The reading is taken on the recorder. From this, we get the energy of the incident radiations. Now the reactants are taken in the cell and the radiations are allowed to pass through it for a definite time and the reading is taken again. The difference between the two readings gives the total energy absorbed by the reactants in a given time. From this, the intensity of radiation absorbed I_{abs} is calculated as follows:

$$I_{abs} = \frac{\text{Total energy absorbed}}{\text{Volume of the reation mixture} \times \text{Time in sec.}}$$

(b) Measurement of the Rate of Reaction The rate of reaction can be studied by noting the change in some physical property. Alternatively, samples of the reaction mixtures are removed periodically from the cell and analysed.

Knowing the rate of reaction and intensity of light absorbed, the quantum yield of the reaction can be obtained.

Example 8 *A certain system absorbs 3×10^{18} quanta of light per second. On irradiation for 20 minutes, 0.003 mole of the reactant was found to have reacted. Calculate the quantum yield for the process (Avogadro's number = 6.02×10^{23})*

Solution Number of quanta absorbed per second = 3×10^{18}

Number of ***moles*** reacting in 20 minutes = 0.003

$\therefore$ Number of ***molecules*** reacting in 20 minutes = $0.003 \times 6.022 \times 10^{23}$

Number of ***molecules*** reacting per second

$$= \frac{0.0303 \times 6.022 \times 10^{23}}{20 \times 60}$$

$$= 1.506 \times 10^{18}$$

$\therefore$ $$\text{Quantum yield } (\phi) = \frac{\text{Number of molecules reacting per second}}{\text{Number of quanta absorbed per second}}$$

$$= \frac{1.506 \times 10^{18}}{3 \times 10^{18}} = 0.5$$

Example 9 *A uranyl oxalate acinometer is irradiated for 15 minutes with light of 4350 Å. At the end of this time, it is found that oxalic acid equivalent to 12.0 ml of 0.001 molar $KMnO_4$ solution*

has been decomposed by light. At this wavelength, the quantum efficiency of the actinometer is 0.58. Find the average intensity of the light used in (a) ergs per second, and (b) quanta per second.

Solution Oxalic acid decomposes in 15 minutes

$$= 12.0 \text{ ml of } 0.001 \text{ molar} = \frac{0.001}{1000} \times 12 \text{ moles}$$

$$= \frac{0.001}{1000} \times 12 \times 6.022 \times 10^{23} \text{ molecules} = 7.23 \times 10^{18} \text{ molecules}$$

∴ Number of molecules decomposed per second

$$= \frac{7.23 \times 10^{18}}{15 \times 60} = 8 \times 10^{15}$$

∴ Number of quanta absorbed per second

$$= \frac{\text{Number of molecules reacting/sec}}{\text{quantum efficiency}} = \frac{8 \times 10^{15}}{0.58} = 1.38 \times 10^{16}$$

Further, wavelength of light absorbed = 4350 Å = 43500×10^{-8} cm

$$\therefore \quad \text{Energy of one quantum} = h\nu = \frac{hc}{\lambda} = \frac{(6.62 \times 10^{-27}) \times (3 \times 10^{10})}{4350 \times 10^{-8}}$$

$$= 4.57 \times 10^{-12} \text{ ergs}$$

∴ Energy absorbed per second

$$= (1.38 \times 10^{16}) \times (4.57 \times 10^{-12}) \text{ ergs} = \mathbf{6.31 \times 10^4 \text{ ergs}}$$

Example 10 *For the photochemical reaction A → B, 1.0×10^{-5} moles of B ere formed on absorption of 6.0×10^7 ergs at 3600 Å. Calculate the quantum efficiency.*

$N = 6.02 \times 10^{23}$, $h = 6.0 \times 10^{-27}$ erg sec, $c = 3 \times 10^{18}$ cm/sec

Solution Wavelength of the light absorbed = 3600 Å = 3600×10^{-8} cm

∴ Energy of one quantum

$$h\nu = h\frac{c}{\lambda} = \frac{(6 \times 10^{-27})(3 \times 10^{10})}{3600 \times 10^{-8}} \text{ ergs} = 5.0 \times 10^{-12} \text{ ergs}$$

Total energy absorbed.

$$= 6.0 \times 10^7 \text{ ergs (Given)}$$

∴ Number of quanta absorbed

$$= \frac{6.0 \times 10^7}{5.0 \times 10^{-12}} = 1.2 \times 10^{19}$$

Number of moles reacting = 1.0×10^{-5}

Number of molecules reacting = $1.0 \times 10^{-5} \times 6.02 \times 10^{23} = 6.02 \times 10^{18}$

$$\text{Quantum efficiency } (\phi) = \frac{\text{Number of molecules reacting}}{\text{Number of quanta absorbed}} = \frac{6.02 \times 10^{18}}{1.2 \times 10^{19}} \cong \mathbf{0.5}$$

Example 11 *In the photobromination of cinhamic acid using blue light of 4358 Å at 30.6°C, an*

intensity of 14000 ergs per second produced a decrease of 0.0075 millimoles of Br_2 during an exposure of 1105 seconds. The solution absorbed 80.1% of the light passing through it. Calculate the quantum yield for the photoreaction of bromine.

Solution Intensity of incident light = 1400 ergs per second

$$\text{Energy of one quantum} = \frac{hc}{\lambda} \frac{(6.62 \times 10^{-27}) \times (3 \times 10^{10})}{4358 \times 10^{-8}} \text{ ergs} = 4.56 \times 10^{-12} \text{ erg}$$

$$\therefore \text{Number of quanta/second} = \frac{14000}{4.56 \times 10^{-12}} = 3.07 \times 10^{15}$$

As the light absorbed is 80.1%

$$\text{Number of quanta absorbed/second} = 3.07 \times 10^{15} \times \frac{80.1}{100} = 2.46 \times 10^{15}$$

Amount of substance reacting = 0.075 millimole = 0.000075 moles

$$\text{Number of molecules reacting/second} = \frac{0.000075 \times 6.023 \times 10^{23}}{110^5} = 4.09 \times 10^{16}$$

$$\text{Quantum yield } (\phi) = \frac{4.09 \quad 10^{16}}{2.46 \times 10^{15}} = \textbf{16.6 molecules/quanta}$$

PROBLEMS FOR PRACTICE

1. When gaseous HI is irradiated with radiation of 2350 Å wavelength, it is observed that 1.85×10^{-2} mole decomposes per 1000 cal of radiant energy absorbed. Calculate the quantum efficiency of the reaction

[Ans. 1.9]

2. A certain system absorbs 3.0×10^{16} quanta of light per second. On irradiation for 20 minutes, 0.002 mole of the reactant was found to have reacted. Calculate the quantum efficiency of the process.

[Ans. 0.669]

Example 12 *What are the reasons for very high and very low quantum yields in photochemical reactions?*

Solution The reason for very high or very low quantum yield is found in the fact that a photochemical reaction takes place in two steps:

(a) *Primary Process* This involves the activation of certain molecules by absorption of light (one quantum per molecule), i.e.

$$AB + h\nu \longrightarrow AB^*$$

or the dissociation of certain molecules to produce active atoms or free radicals, i.e.

$$AB + h\nu \longrightarrow A + B^*$$

Active or excited atom

(b) *Secondary Process* This involves the reaction of the activated molecules or the products of a primary process with other molecules or the deactivation of the activated molecules. Actually, a number of reactions are involved in the secondary process.

Some of these are endothermic reactions and thus take place slowly, thereby affecting the

overall reaction. Some of these are exothermic reactions and the heat evolved decomposes the products, again affecting the overall reaction. The effect of these factors brings about sudden rise or fall of quantum yield.

22.7 SOME EXAMPLES OF PHOTOCHEMICAL REACTIONS

22.7.1 Photosynthesis of HCl from Hydrogen and Chlorine

This reaction whose quantum yield is very high, i.e. 10^4 to 10^6, may be represented as

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

The high quantum yield of this reaction is explained by the chain mechanism. The different steps involved are as follows:

1. Primary Process

$$Cl_2 + h\nu \rightarrow 2\dot{Cl} \qquad \text{Chain-initiating step}$$

Thus, a chlorine molecule absorbs one quantum of light and dissociates to give Cl atoms.

2. Secondary Processes

(a) $\dot{Cl} + H_2 \xrightarrow{\text{Exo}} HCl + \dot{H}$

(b) $\dot{H} + Cl_2 \longrightarrow HCl + \dot{Cl}$

Chain-propogating steps

(c) $\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$ Chain terminating step

The H atoms produced in the reaction (a) attacks Cl_2 according to the reaction (b) producing HCl and Cl atoms. The Cl atom thus produced attacks more of H_2 according to the reaction (a) producing the H atom again. In this way, the reactions (a) and (b) repeat over and again till almost whole of H_2 and Cl_2 have reacted to form HCl. The reaction stops when the Cl atoms left off combine with each other to form Cl_2, according to the reaction (c). ***This reaction takes place on the walls of the reaction vessel.***

In this reaction, the reaction (a) of the secondary processes which immediately follow the primary process is ***exothermic*** and, therefore, takes place very easily and consequently, the chain reaction is set up easily. In the photosynthesis of HBr, the reaction (a) of the secondary process is ***endothermic*** and thus, has very little tendency to take place.

The quantum yield of the above reaction decreases if the reaction vessel contains small traces of oxygen. This is explained on the basis that oxygen brings about chain termination by the following reactions:

$$H + O_2 \longrightarrow HO_2$$

$$Cl + O_2 + HCl \longrightarrow HO_2 + Cl_2$$

22.7.2 Photosynthesis of HBr from Hydrogen and Bromine

The reaction may be represented as

$$H_2 + Br_2 \xrightarrow{h\nu} 2HBr$$

The quantum efficiency of this reaction is very low, i.e. about 0.01 at ordinary temperature. This is explained by proposing the following mechanism for the above reaction.

1. Primary Process

$$Br_2 + h\nu \longrightarrow 2Br$$

2. Secondary Processes

(a) $Br + H_2 \xrightarrow{Endo} HBr + H$ (b) $H + Br \longrightarrow HBr + Br$

(c) $H + HBr \longrightarrow H_2 + Br$ (d) $Br + Br \longrightarrow Br_2$

The H atom produced in the reaction (a) attacks Br_2 according to the reaction (b) producing HBr and Br atoms. The Br atom, thus, produced, attacks more of H_2 according to the reaction (a) producing H-atoms again. As a result, reactions (a) and (b) should repeat over and again, i.e. a chain reaction should be set up and the quantum yield of the reaction should be very high. But actually, the quantum yield is very low. This is explained as follows:

Reaction (a) is endothermic and, hence, takes place slowly or almost does not tend to take place. The reactions (b) and (c) depend upon the formation of H atoms in the reaction (a). Consequently, reactions (b) and (c) are very slow. So the only important reaction in the secondary processes is the reaction (d). This is just the reverse of the primary process. Thus, the Br atoms formed in the primary process do not combine to form HBr; instead, they combine together to give back Br_2. As a result, the quantum yield of the reaction is very low at ordinary temperatures.

The quantum yield of the above reaction increases with increase of temperature. This is obviously because of the fact that the reaction (a) which is endothermic and requires high energy of activation becomes faster at high temperatures because the required energy of activation becomes available at higher temperatures. This reaction produces more H atoms thereby increasing the rate of reactions (b) and (c) also.

22.7.3 Photochemical Decomposition of Hydrogen Iodide

The photolysis of HI to give H_2 and I_2 has been studied in the wavelength range of 2070-2820 Å and the quantum yield of the reaction has been found to be approximately 2. The mechanism for the photolysis of HI has been proposed as under:

1. Primary Process

$$HI + h\nu \longrightarrow H + I^*$$

i.e. a molecule of HI absorbs one photon of light and dissociates to give a normal hydrogen atom and an excited iodine atom.

2. Secondary Processes The products of primary process then take part in the secondary processes as follows:

(a) $H + HI \longrightarrow H_2 + I$ (b) $I^* + HI \xrightarrow{Endo} H + I_2$

(c) $H + H \xrightarrow{Exo} H_2$ (d) $I + I \longrightarrow I_2$

(e) $H + I \xrightarrow{Exo} HI$

All these secondary processes may not be important. The reactions (c) and (e) are highly exothermic and the heat produced causes the dissociation of the products of these reactions. Reaction (b) is endothermic and hence, takes place slowly. Thus, the only secondary processes of importance are the reactions (a) and (d). Rewriting the reaction of primary process and the two important reactions, viz. (a) and (d) of secondary processes, we have

$HI + h\nu \longrightarrow H + I^*$ } Reaction of the primary process

$H + HI \longrightarrow H_2 + I$
$I + I \longrightarrow I_2$
} The only important reactions of the secondary processes

Adding these three equations, we get the overall reaction:

$$2HI + h\nu \rightarrow H_2 + I_2$$

Thus, for every one quantum of light absorbed, two molecules of HI are decomposed. Hence, the

quantum yield value of 2 is explained.

22.7.4 Photolysis (Photochemical Decomposition) of HBr

The quantum yield of this reaction is found to be 2. Mechanism of this reaction is suggested to be similar to that of photolysis of HI. Use HBr in place of HI, Br_2 in place of I_2, and Br in place of I.

22.7.5 Photolysis of Acetone

The reaction may be represented as

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{h\nu} \underset{\text{Ethane}}{C_2H_6} + \underset{\text{Carbon monoxide}}{CO}$$

The major products of the photolysis of acetone are ethane and carbon monoxide but small amounts of methane (CH_4) and appreciable amounts of diacetyl, $(CH_3CO)_2$, are also found to be present. The quantum yield of the reaction is found to be nearly unity. All these observations suggest the following probable mechanism for the photolysis of acetone.

1. Primary Process

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{h\nu} \underset{\substack{\text{Methyl}\\\text{free radical}}}{\dot{C}H_3} + \underset{\substack{\text{Acetyl}\\\text{free radical}}}{CH_3\dot{C}O}$$

2. Secondary Processes A number of secondary reactions are possible. A few of these are as under:

(a) $CH_3\dot{C}O \longrightarrow \dot{C}H_3 + CO$

(b) $\dot{C}H_3 + CH_3\dot{C}O \longrightarrow C_2H_6 + CO$

(c) $CH_3\dot{C}O + CH_3\dot{C}O \longrightarrow (CH_3CO)_2$

Thus, no chain reaction is set up. The free radicals formed in the primary process simply react with each other. Hence, the quantum efficiency of the reaction is unity.

22.7.6 Photolysis of Ammonia

This is an example of a photochemical reaction whose quantum yield is very low, i.e. about 0.25 at ordinary temperatures and pressures. The probable mechanism is as follows:

1. Primary Process

$$NH_3 + h\nu \rightarrow \dot{N}H_2 + \dot{H}$$

The presence of H atoms has been established.

2. Secondary Processes The ultimate products of the photolysis of ammonia have been found to be nitrogen, hydrogen and hydrazine. Hence, the following probable secondary reactions have been proposed.

(a) $\dot{N}H_2 + \dot{N}H_2 \longrightarrow N_2 + 2H_2$

(b) $\dot{N}H_2 + \dot{N}H_2 \longrightarrow N_2H_4$

(c) $\dot{H} + \dot{H} \longrightarrow H_2$

(d) $\dot{N}H_2 + \dot{H} \longrightarrow NH_3$

Since the quantum yield of the reaction is very low, we assume that the reactions (a) to (c) take place only to a very small extent. The important secondary reaction is the reaction (d) only which involves the reversal of the primary process leading to decline in the value of (ϕ).

The glow produced by a body, without the involvement of heat is called luminescence. Luminescence is also called ***cold light.*** We know when a block of iron is heated, it first becomes red hot and eventually becomes white and begins to glow. But this will not be called luminescence. Luminescence does not occur by the action of heat. It can occur, for example, when the electrons excited to higher levels by the absorption of radiation return to original levels. Luminescence is of the following three types:

1. Chemiluminescence When a photochemical reaction takes place, light is absorbed. However, there are certain reactions in which light is produced. The emission of light in chemical reactions at ordinary temperatures is called chemiluminescence. The chemiluminscence is just the reverse of a photochemical reaction.

A few examples of chemiluminescence are as given below:

(a) The light emitted by glow worms is due to the oxidation of the protein, ***luciferin, present in glow worms***.

(b) The oxidation of yellow phosphorus in oxygen or air to give P_2O_5 at ordinary temperatures (–10 to 40°C) is accompanied by the emission of visible greenish-white luminescence. In the above cases, a part or whole of the energy emitted during the reaction, is used up for the excitation of electrons. When they jump back to the inner orbits, the emission of light takes place.

2. Fluorescence There are certain substances which when exposed to light of certain radiations absorb the energy and then immediately or instantaneously start re-emitting the energy. Such substances are called fluorescent substances and the phenomenon is called fluorescence. Obviously, the absorption of energy results into the excitation of the electrons followed immediately by jumping back of the excitated electrons to the lower levels. As a result, the absorbed energy is emitted back.

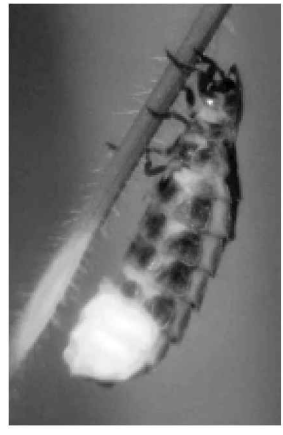


Fig. 22.9 *A glow worm emits light due to chemiluminescence.*

Fluorescence starts as soon as the substance is exposed to light and it stops as soon as the light is cut off.

A few examples of the substances showing the phenomenon of fluorescence are given below:

(a) Fluorite, CaF_2

(b) Certain organic dyes such as eosin, fluorescein, etc.

(c) Certain inorganic compounds such as uranyl sulphate, UO_2SO_4

Notably in the phenomenon of fluorescence, the wavelength of the emitted light is usually greater than that of the absorbed light. This is explained on the basis that the charge absorbed raises the electron to a sufficiently higher level but the return of the excited electron to the original level takes place in steps, through the intermediate levels. The energy thus produced in every jump is smaller and hence, the wavelength of the light emitted is larger than that of the absorbed light.

3. Phosphorescence There are certain substances which continue to glow for some time even after the external light is cut off. Such substances are called phosphors or phosphorescent substances and the phenomenon is called phosphorescence. Thus, in a way, phosphorescence is slow fluorescence. It is found mostly in solids, because the molecules have least freedom of motion. The excited electrons thus keep on jumping back slowly for quite some time.

Some examples of the substances exhibiting phosphorescence are ***zinc sulphide*** and ***sulphides of the alkaline earth metals.*** It has been found that fluorescent substances become phosphorescent if fixed by suitable methods, e.g. by fusion with other substances, etc. For example, many dyes show fluorescence when dissolved in fused boric acid or glycerol and when cooled to rigid mass become phosphorescent.

Chemiluminescence, fluorescence and phosphorescence together are called ***luminescence*** as mentioned earlier.

22.9 EXCITATION OF ELECTRONS (JABLONSKI DIAGRAM)

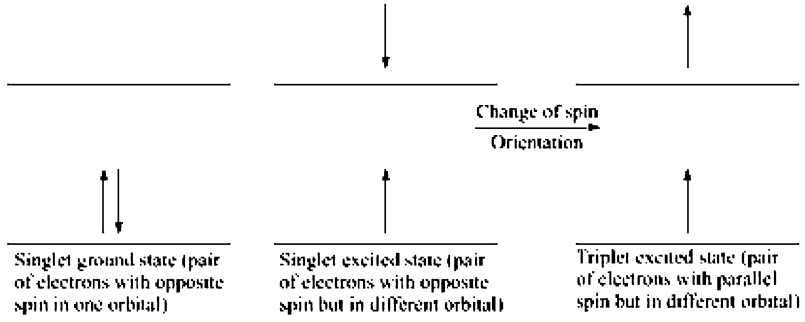
When radiations are incident on certain substances, some of the electrons may absorb energy and jump to higher levels. The electrons may return to the ground state or may bring about a chemical change.

The electronic spins are expressed in terms of ***spin multiplicity*** which is equal to $2S + 1$, where S is the total electron spin. Taking $+\frac{1}{2}$ and $-\frac{1}{2}$ as spin values of electrons spinning clockwise and anticlockwise, we can say if a molecule contains all the paired electrons, their spins will neutralise so that $S = 0$ and spin multiplicity will be $2S + 1$, i.e. 1. This is ***singlet excited state*** of the molecules.

If after excitation of electrons, the electrons occupy different orbitals with similar spins $S = \frac{1}{2} + \frac{1}{2} = 1$ and spin multiplicity will be $2S + 1 = 3$. The molecule is said to be in ***triplet excited state***.

Ground singlet state is denoted by S_0 and successive singlet excited states are denoted by S_1, S_2, S_3, etc.

Corresponding triplet excited states are denoted by T_1, T_2, T_3, etc. Excitation of electrons in the molecules can be represented as under:



Any singlet excited state possesses higher energy than the corresponding triplet excited state. Thus,

$$E_{S_1} > E_{T_1} > E_{S_2} > E_{T_2}, \text{ and so on.}$$

Excited molecules return to the original (ground) state by emitting energy in a number of ways as shown in Fig. 22.10. This is known as ***Jablonski diagram***.

In the first step of reverting to ground state, transition from higher excited singlet states (S_2, S_2, etc.) to lowest excited singlet state S_1 occurs. This is called Internal Conversion (IC). Loss of energy takes place only in the form of heat, no radiations are emitted. Therefore, this step is called ***non-radiative*** or ***radiationless*** transition. From the first excited singlet state, the molecules return to the ground state through one of the following paths.

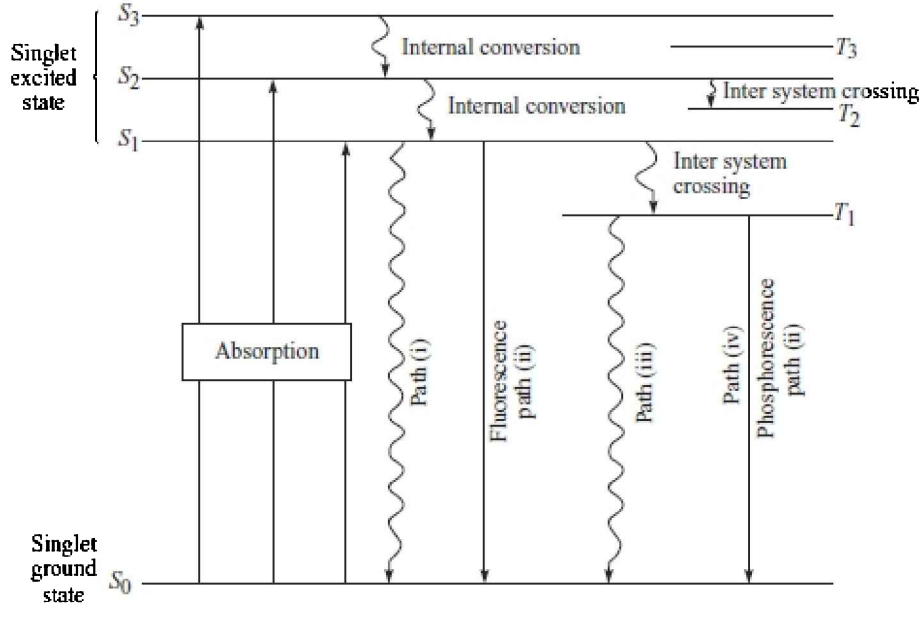


Fig. 22.10 *Jablonski diagram showing excitation of molecules and their return to the ground state by different paths*

Path I If the molecule emits rest of the energy also in the form of heat, the whole process becomes non-radiative. This is shown by a wavy line in the figure.

Path II If the molecule loses energy in the form of radiation to reach the ground state, it is radiative transition. This transition represents ***fluorescence*** and is shown by a straight line in the figure.

Path III It may sometimes so happens that some energy is lost in moving from first excited singlet state to the first excited triplet state, i.e. from S_1 to T_1 in the form of heat. This is called ***Intersystem Crossing*** *(ISC)* and is a non-radiative step. Further transition from first excited triplet state to the ground state again in the form of loss of heat. Thus, the path III is completely non-radiative.

Path IV After reaching first excited triplet state from first excited singlet state, further transition to the ground state may occur in the form of emission of radiations, thus the path IV is a radiative step. It represents the phenomenon of phosphorescence.

Triplet states have much longer lifetime than singlet state. Therefore, phosphorescence continues even after the absorbed radiation is removed.

22.10 | PHOTOSENSITISATION

There are substances which do not react directly when exposed to light. On adding another substance, the photochemical reaction starts. The substance thus added itself does not undergo any chemical change.

The substances added merely absorbs the light energy and thus passes it on to one of the reactants. ***Such a substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change is called photosensitiser and the process is called photosensitisation.*** Thus a photosensitiser simply acts as a carrier of energy.

At the first instance, it appears that a photosensitiser is similar to a catalyst. However, this is not so as it acts by a different mechanism.

Examples *A few well-known examples of the photosensitised reactions are briefly described as under:*

1. Dissociation of Hydrogen Molecules in Presence of Mercury Vapour Hydrogen molecules do not dissociate when exposed to ultraviolet light. However, when hydrogen gas is mixed with mercury vapour and then exposed to ultraviolet light, hydrogen molecules dissociate to give hydrogen atoms through the following reactions:

$$Hg + h\nu \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow Hg + 2H$$

where Hg* represents the activated mercury atom. Thus, in the above reaction, mercury acts as a photosensitiser.

The hydrogen atom being highly reactive can easily reduce metallic oxides, nitrous oxide, carbon monoxide, etc.

2. Photosynthesis of Carbohydrates in Plants Carbon dioxide and water vapour present in the air do not absorb the visible light emitted by the sun. However, the green colouring matter, namely ***chlorophyll*** present in the plants, can absorb the visible light. After absorption, if passes on the energy to carbon dioxide and water molecules which then combine to form carbohydrates along with the evolution of oxygen.

$$\underbrace{CO_2 + H_2O}_{\text{from air}} + \underbrace{h\nu}_{\text{from sunlight}} \xrightarrow{\text{chlorophyll}} \underbrace{\frac{1}{6}(C_6H_{12}O_6)}_{\text{Glucose}} + O_2$$

Thus, chlorophyll acts as a photosensitiser in the above reaction.

3. Decomposition of Oxalic Acid in Presence of Uranyl Sulphate This reaction forms the basis of the actinometer used to measure the intensity of radiation. The coloured uranyl ions absorb the light and then pass it on to the colourless oxalic acid which then undergoes decomposition, the extent of decomposition depending upon the light energy absorbed.

$$UO_2^{2+} + h\nu \rightarrow UO_2^{2+*}$$

$$UO_2^{2+*} + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \rightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The uranyl ions acts as photosensitisers.

Photo-inhibitors Presence of certain substances considerably reduces the quantum yield of some photochemical reactions. For example, in the photosynthesis of HCl, the presence of traces of oxygen reduces the quantum yield of the reaction. Substances like nitric oxide, sulphur dioxide, propylene, etc., also show similar effects. ***Such substances which reduce the quantum yield of photochemical reactions are called photo-inhibitors.*** It is believed that such substances react with the chain-propogating atoms or radicals resulting into the chain termination. The chain termination is the photosynthesis of HCl by the presence of traces of oxygen taking place as follows:

$$\dot{H} + O_2 \rightarrow HO_2$$

$$\dot{Cl} + O_2 + HCl \rightarrow HO_2 + Cl_2$$

22.11 PHOTOCHEMICALEQUILIBRIUM

Suppose a substance A changes into the substance B by the absorption of light. If the reverse reaction can also occur either as ***photochemical reaction*** or as ***thermal reaction (dark reaction).*** The situation may be represented as

$$A \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} B$$

$$A \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} B$$

A stage may reach when the rate of forward reaction may become equal to the rate of the backward reaction. Now further absorption of light produces no chemical change. The reaction is then said to have attained a ***photochemical equilibrium.***

Examples

(i) **Photochemical decomposition of sulphur trioxide**

$$2SO_3 \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} 2SO_2 + O_2$$

(ii) **Photochemical decomposition of nitrogen dioxide**

$$2NO_2 \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} 2NO + O_2$$

Equilibrium Constant The equilibrium constant of a photochemical equilibrium is different from that of the ordinary chemical equilibrium. This is because the rate of a photochemical reaction does not depend upon the concentration of the reactants but it depends upon the intensity of the light absorbed. Thus, for the reaction.

$$A \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} B$$

Rate of forward reaction $\propto I_{abs} = k_1 I_{abs}$

Rate of backward reaction $\propto [B] = k_2[B]$

When the reaction is in equilibrium,

Rate of forward reaction = Rate of backward reaction

i.e. $k_1 I_{abs} = k_2[B]$

or $$\frac{k_2}{k_1} = \frac{I_{abs}}{[B]} \quad \ldots(22.18)$$

or $$K = \frac{I_{abs}}{[B]} \quad \ldots(22.19)$$

where, $K = \frac{k_2}{k_1}$ is the ***photochemical equilibrium constant***

From Eq. (22.19), it is clear that the photochemical equilibrium constant depends upon the intensity of the light absorbed.

Further Eq. (22.18) may be written as

$$[B] = \frac{k_2}{k_1} I_{abs}$$

It follows that the concentration of the products formed at equilibrium is directly proportional to the intensity of the light absorbed.

Example 13 *What do you understand by the following terms?*

(a) Radiative and nonradioactive (radiationless) transitions.

(b) Internal conversion and intersystem crossing

Solution

(a) In a transition when energy is lost only in the form of heat due to collision with other molecules, it is called nonradiative (radiationless) transition. When energy is lost in the form of light or ultraviolet radiation, etc., it is called radiative transition.

(b) The transition from higher excited singlet states (S_2, S_3, etc.) to the lowest singlet excited state (S_1) accompanied by loss of energy in the form of heat is called ***internal conversion.*** The transition from an excited singlet state to the corresponding excited triplet state ($S_1 \rightarrow T_1$), ($S_2 \rightarrow T_2$), etc., accompanied by loss of energy in the form of heat is called ***intersystem crossing***.

Example 14 *What types of transitions are involved in fluorescence and in phosphorescence? Comment on the wavelength of radiation emitted in these phenomena as compared to that of the light absorbed for excitation.*

Solution Fluorescence involves a radioactive transition between two states of same multiplicity (usually two singlets) whereas phosphorescence is due to radiative transition between two states of different multiplicity (usually triplet to singlet). The energy emitted during these phenomena is less than the energy absorbed because a part of internal energy is lost as heat in internal conversion or intersystem crossing. Hence, frequencies emitted are smaller or wavelengths are longer.

Example 15 *Comment on the free-energy change of the photochemical reaction giving reasons.*

Solution The free-energy change (ΔG) of a photochemical reaction may not be negative. There are many photochemical reactions for which ΔG is positive (e.g. photosynthesis of carbohydrates in plants, ozonization of oxygen, etc.) The reason for increase of free energy is that a part of the light energy absorbed by the reactants is converted into free energy of products.

Example 16 *What is the physical significance of extinction coefficient of absorptivity?*

Solution According to Lambert's law, $I = I_o e^{-kx}$ or $\ln \frac{I}{I_o} = -kx$

$$\text{or } \log \text{ or } \log \frac{I}{I_o} = -\frac{k}{2.303} x = -k'x \quad \text{where} \quad k' = \frac{k}{2.303}$$

is called extinction coefficient. We can rewrite it as,

$$\log \frac{I_o}{I} = k'x \quad \text{or} \quad k' = \frac{1}{x} \log \frac{I_o}{I}.$$

If $$\frac{I_o}{I} = 10, \quad \text{i.e.} \quad I = \frac{1}{10} I_o, \; k' = \frac{1}{x}$$

Hence, extinction coefficient is the reciprocal of that layer of thickness at which the intensity of light falls to 1/10th of its original value.

Example 17 *Why does quantum yield of photosynthesis of HCl decrease if (a) the reaction is carried out in capillary tubes, and (b) small traces of oxygen are present?*

Solution

(a)This is because a capillary tube is very narrow. The chain reaction taking place through Cl and H atoms gets terminated on the walls of the capillary tube.

(b)This is because oxygen leads to chain termination through the following reactions.

$$H + O_2 \rightarrow HO_2, \; Cl + O_2 + HCl \rightarrow HO_2 + Cl_2$$

Example 18 *What is the difference between fluorescence and phosphorescence?*

Solution: When certain substances like calcium fluorite are exposed to light, they immediately start emitting the light. The phenomenon is called fluorescence. The fluorescence stops as soon as the source of external light is removed. However, there are certain substances (e.g. ZnS) which continue to glow for some time even after the external light is cut off. This phenomenon is called phosphorescence.

Example 19 *What type of plot is obtained when optical density (D) or absorbance (A) is plotted against the concentration of the solution?*

Solution: According to Beer's law, $\log \frac{I}{I_o} = -\log T = D(\text{or } A) = \epsilon cx$

Hence, a plot of optical density *(D)* or absorbance *(A)* versus concentration will be a straight line passing through the origin.

SUMMARY

1. A process that takes place in the presence of light but does not involve a chemical reaction is called *photophysical* reaction.
2. A process that is initiated by light and also involves a chemical reaction is called *photochemical reaction.*
3. *Lambert's law:* When a monochromatic light is passed through a pure homogeneous medium, the decrease in the intensity of light with thickness of the absorbing medium at any point *X* is proportional to the intensity of the incident light.
4. The *extinction coefficient or absorptivity* is the reciprocal of the thickness (expressed in cm) at which the intensity of the light falls to one-tenth of its original value.
5. *Beer's law:* When a monochromatic light passes through a solution, the decrease in the intensity of light with the thickness of the solution, is directly proportional not only to the intensity of incident light but also to the concentration *c* of the solution.

6. *First law of photochemistry (Grotthus law):* When light falls on a body, a part of it is reflected, a part of it is transmitted and the rest of it is absorbed. It is only the absorbed light which is effective in bringing about a chemical reaction.
7. *Second law of photochemistry (Stark-Einstein law):* Every atom or molecule that takes part in a photochemical reaction absorbs one quantum of the radiation to which the substance is exposed.
8. *Quantum efficiency* of a reaction may be defined as the number of moles reacting per einstein of the light absorbed
9. The glow produced by a body without the involvement of heat is called *luminescence*. Luminescence is also called cold light.
10. The emission of light in chemical reactions at ordinary temperature is called *chemiluminescence*.
11. There are certain substances which when exposed to light or radiations absorb the energy and then immediately start re-emitting energy. This phenomenon is called *fluorescence*.
12. There are some substances which continue to glow for some time even after the external light is cut off. This phenomenon is called *phosphorescence*.
13. *Photosensitisation* is a phenomenon by which a substance when added to a reaction mixture helps to start the photochemical reaction, but itself does not undergo any chemical change.

KEY RELATIONS

Lambert's law:

$$I = I_0 e^{-kx}$$

$$I = I_0 10^{-k'x}$$

Beer's law:

$$I = I_0 e^{-\epsilon cx}$$

$$I = I_0 10^{-\epsilon' cx}$$

Energy per einstein: $E = \dfrac{0.1197}{\lambda} \text{ J mol}^{-1} = \dfrac{11.97 \times 10^{-5}}{\lambda} \text{ kJ mol}^{-1}$

Quantum efficiency: $\phi = \dfrac{\text{No. of molecules reacting in a given time}}{\text{No. of einsteins of light absorbed in the same time}}$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. Which of the following statements is true?
   (a) It is the secondary reaction in which absorption of radiation takes place.
   (b) It is the primary reaction in which absorption of radiation takes place.
   (c) The absorption of radiation takes place in both the primary and secondary reactions.
   (d) None of the above.
2. "It is only the absorbed light radiations that are effective in producing a chemical reactions." This is the statement of

(a) Lambert law

(b) Lambert-Beer law

(c) Grotthus-Draper law

(d) Stark-Einstein law

3. "In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products."

This is the statement of

(a) Lambert-Beer's law

(b) Grotthus-Draper law

(c) Stark-Einstein law

(d) Lambert's law

4. The equation for Lambert's law is

(a) $\ln\left(\frac{I_o}{I}\right) = -bx$

(b) $\ln\left(\frac{I}{I_o}\right) = bx$

(c) $\ln\left(\frac{I}{I_o}\right) = \epsilon cx$

(d) $\ln\left(\frac{I}{I_o}\right) = \epsilon cx$

5. One einstein of energy is

(a) $E = \frac{2.859}{\lambda} \times 10^5 \text{ cal mol}^{-1}$

(b) $E = \frac{2.859}{\lambda} \times 10^5 \text{ kcal mol}^{-1}$

(c) $E = \frac{2.859}{\lambda} \times 10^5 \text{ J mol}^{-1}$

(d) $E = \frac{2.859}{\lambda} \times 10^5 \text{ kJ mol}^{-1}$

6. In some photochemical reactions, low quantum yield is obtained. It is due to

(a) deactivation of reacting reaction

(b) occurrence of reverse primary reaction

(c) recombination of dissociated fragments

(d) all of these

7. One einstein is given by (N is Avogadro's number)

(a) $E = \frac{Nhc^2}{\lambda}$

(b) $E = \frac{Nhc}{\lambda^2}$

(c) $E - \frac{Nhc}{\lambda}$

(d) $E - \frac{Nh}{c\lambda}$

8. "Only the fraction of incident light that is absorbed by the substance can bring about a chemical change." This is the
   (a) first law of photochemistry
   (b) second law of photochemistry
   (c) third law of photochemistry
   (d) none of these
9. The light emitted in a chemiluminescent reaction is also called
   (a) cold light
   (b) hot light
   (c) bright light
   (d) none of these
10. The number of molecules reacted or formed per photon of light absorbed is called
   (a) yield of the reaction
   (b) quantum efficiency
   (c) quantum yield
   (d) quantum productivity

Answers

1. (b)
2. (c)
3. (c)
4. (b)
5. (b)
6. (d)
7. (c)
8. (a)
9. (a)
10. (c)

SHORT-ANSWER QUESTIONS

1. State and explain first and second laws of photochemistry.
2. Define 'photochemistry'. Give two examples ofphotophysical processes and two examples

ofphotochemical reactions.

3. Write short notes on 'fluorescence' and 'phosphorescence'. What is the difference between them?
4. 'What are photo-inhibitors'? How do they work?
5. Why is it that in certain cases, quantum yield is lower then that expected from einstein law of photochemical equivalence? Give two examples to support your point.
6. What is meant by primary and second processes in photochemistry?
7. How do you explain that in fluorescence, the wavelength of the light emitted is usually greater than that of the light absorbed?
8. How do you explain that photochemical yield of the reaction between hydrogen and chlorine is very high?
9. Briefly explain the following terms:

   Transmittance, Absorbance or optical density, Molar extinction coefficient.
10. What is a chemical actinometer? Briefly explain the working of a uranyl oxalate actinometer.
11. Briefly explain fluorescence and phophorescence using Tablonski diagram.
12. What is photosensitisation? Explain with two suitable examples.
13. Define Stark-Einstein's law of photochemical equivalence. What is one einstein of energy? How is it calculated in kT mol^{-1}?
14. On the basis of mechanism, how can you justify that quantum yield of photolysis of HI is 2?
15. What do you understand by quantum yield of a photochemical reaction? Why do some reactions have high quantum yield whereas some others have very low value? What is the modified defination of Stark-Einstein law?
16. State and explain Lambert's law.
17. Give at least three points in which photochemical reactions differ from thermochemical reactions.
18. Give one example of photochemical reaction in which the quantum yield is very high. Briefly explain the reasons for the same.
19. Write a short note on 'photosensitisation'.
20. What mechanism has been proposed to explain photolysis of acetone?
21. State and explain Beer's law.
22. Give the photolysis of ammonia. What is the quantum yield of the process? Give reasons for your answers.
23. What is quenching in fluorescence? What do you mean by internal quenching and external quenching? Write the various steps from activation to deactivation in the process.

GENERAL QUESTIONS

1. State and explain the first and second laws of photochemistry (Grotthus-Draper law and Stark-Einstein's law of photochemical equivalence). What do you understand by 'one einstein' of energy? How is its value calculated in CGS units and in SI units?
2. What do you mean by quantum yield of a photochemical reaction? Explain why photosynthesis of HCl has very high quantum yield while photosynthesis of HBr has very low. What happens to the quantum yield of photosynthesis of HCl if the vessel contains small traces of oxygen? Explain with reasons.

3. What do you understand by photochemical equilibrium? Give two examples. Show that for the reaction.



the concentration of the product at equilibrium is proportional to the intensity of the light absorbed.

4. What are photochemical reactions? Give at least five examples of photochemical reactions. List the main points of difference between a photochemical reaction and thermochemical reaction.

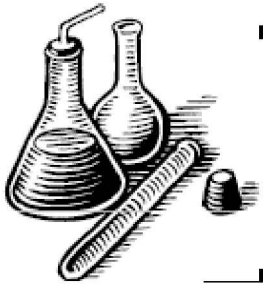
5. What do you understand by 'quantum yield' or 'quantum efficiency' of a photochemical reaction? How is it determined experimentally?

6. Explain the term "photosensitisation" with at least three examples along with their mechanisms.

7. State and explain Lambert's law and Beer's law governing absorption of light by a sample. What are the limitations of Beer's law?

8. Draw Tablonski diagram. Depict the nonradiative (radiationless) and radiative transitions, internal conversion and intersystem crossing fluorescence and phosphorescence. What should be the type of multiplicity for fluorescence and for phosphorescence? What should be the type of excited state for a chemical reaction to occur and why?

9. What do you understand by the terms *spin multiplicity, singlet states* and *triplet states?* Explain the phenomenon of fluorescence and phosphorescence using a Tablonski diagram.



Physical Properties and Molecular Structure

23

LEARNING OBJECTIVES

- Differentiate between additive property and constitutive property
- Acquaint yourself with the phenomenon of optical activity and learn the terms like plane polarised light and specific rotation
- Know the cause of optical activity and follow internal compensation and external compensation
- Define dipole moment and understand induced polarization
- Learn Clausius-Mosotti equation and measure dipole moment using vapour-temperature method, refraction method and dilute solution method
- Appreciate the importance of dipole moment studies in the determination of structure of molecules
- Learn magnetic susceptibility and its measurement
- Understand the utility of magnetic susceptibility in the determination of molecular structure
- Explain the phenomenon ofdiamagnetism and paramagnetism
- Follow the relationship between magnetic moment and number of unpaired electrons
- Learn the applications of magnetic susceptibility measurement

23.1 INTRODUCTION

Physical properties of a substance depend upon the structure of the molecules and the intermolecular forces in the substance. Determination of physical properties can guide us to the structure of molecules. Various physical properties that support the determination of molecular structure are

1. Molar refraction (Rheochor)
2. Surface tension (Parachor)
3. Optical rotation
4. Dipole moment
5. Magnetic susceptibility

It is observed that these properties are additive as well as constitutive. This fact makes the study of the above physical properties useful for the determination of structures of compounds.

An ***additive property*** is defined as the property, the aggregate value of which is the sum of values of its constituents.

A ***constitutive property*** is defined as the property which depends upon the constitution or structure of the molecule-like arrangement of atoms within the molecule, multiple bonds and rings, etc. The properties that we shall discuss here are optical rotation, dipole moment and magnetic susceptibility. Molar refraction and surface tension have been discussed in the chapter "The Liquid State."

23.2 | OPTICAL ACTIVITY

1. Plane Polarised Light If a ray of light travels in any direction, it has vibrations in all directions at right angles to the path of propogation (Fig. 23.1). If this light is passed through a Nicol prism then the light which emerges out of the prism is found to have vibrations only in one plane. This light is called 'plane polarised light'. The Nicol prism used here is called a polariser. In place of a Nicol prism, a polaroid consisting of a film of cellulose acetate mounted between two glass plates can also be used.

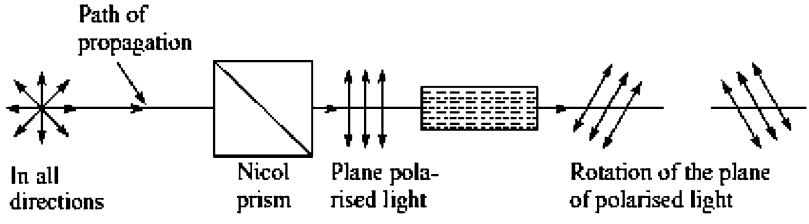


Fig. 23.1 *Plane polarised light and its rotation*

2. Optical Activity If the plane polarised light is passed a through a solution of sugar, it is found that the plane of polarised light gets rotated when it comes out of the solution. The substances like quartz, sugar, etc., which rotate the plane of polarised light are called optically active substances and the property of a substance to rotate the plane of the polarised light is called optical activity. The substances which rotate the plane of the polarised light to the right are called dextro-rotatory and those which rotate the plane of polarised light to the right are called dextro-rotatory and those which rotate the plane of polarised light to the left are called laevo-rotatory.

3. Specific Rotation The angle (in degrees) through which the plane of the polarised light is rotated on passing through the solution of an optically active substance depends upon the following factors:

(a) Nature of the optically active substance

(b) Concentration of the solution (in g/ml)

(c) Length of the solution, i.e. the length of the tube through which the light passes (in decimeters).

(d) Wavelength of the light used

(e) Temperature of the solution

Thus, if m grams of the substance are dissolved in v ml of the solution (so that the concentration of the solution is m/v g/ml), l is the length of the tube (in decimetres) and α is the angle of rotation (in degrees) then it is found that

$$\alpha \propto (\text{concentration in g/ml}) \times (\text{length of the tube in dm})$$

i.e. $$\alpha \propto \frac{m}{v} \times l$$

or $$\alpha = [\alpha]^t_\lambda \frac{m \times l}{v} \quad \ldots(23.1)$$

where $[\alpha]_\lambda^t$ is a constant. It depends upon the nature of the substance, the wavelength of light used (λ) and the temperature of the solution (t°C). If D line of the sodium light is used and the temperature of the solution is 25°C then it is written as $[\alpha]_D^{25^\circ}$. This constant is called 'specific rotation' of the substance.

Thus, from Eq. (23.1),

$$[\alpha]^t_\lambda = \frac{v \times \alpha}{l \times m} \quad \ldots(23.2)$$

If $m = 1$, $v = 1$ ml and $l = 1$ dm

Then $[\alpha]^t_\lambda = \alpha$

Hence, ***specific rotation of a substance may be defined as the angle of rotation produced when one gram of the substance is dissolved in one ml of the solution (i.e. concentration of the solution is 1 g/ml) and the length of the solution through which light passes is 1 dm.***

If it is given that c grams of the substance are dissolved in 100 ml of the solution, then we may put $m = c$ and $v = 100$. Equation (23.1) reduces to

$$\boxed{[\alpha]^t_\lambda = \frac{100 \times \alpha}{l \times c}} \quad \ldots(23.3)$$

If instead of solution, the substance taken is a pure liquid or a solid then m/v is replaced by density d of the pure substance. Equation (23.2) changes to

$$\boxed{[\alpha]^t_\lambda = \frac{\alpha}{l \times d}}, \text{ for pure liquids or solids} \quad \ldots(23.4)$$

4. Molar Rotation If we multiply the specific rotation with the molecular mass of the substance and divide the result by 100, we obtain molar rotation. It is represented by $[M]_\lambda^t$.

Thus, $$[M]^t_\lambda = \frac{M\,[\alpha]^t_\lambda}{100}$$

23.3 MEASUREMENT OF OPTICAL ACTIVITY

The instrument used for the measurement of the amount of rotation caused by an optically active substance to the plane of the polarised light is called a ***polarimeter.*** It consists of two Nicol prisms, one of which is called the ***analyser.*** Both of these are fitted on the opposite ends of the same metal tube. However, the polariser is fixed but the analyser can be rotated about the axis of the tube. In between the polariser and the analyser, there is space for keeping the glass tube containing the solution. The glass tube is normally 10 for 25 cm in length and has glass windows on both the ends. A circular scale is fixed on the metal tube near the analyser, as shown in Fig. 23.2.

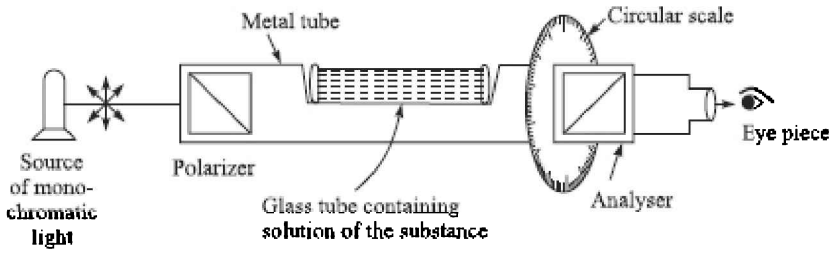


Fig. 23.2 *Working of a Polarimeter.*

Procedure Monochromatic light from a suitable source (usually sodium vapour lamp) is passed through the instrument, without the liquid or the solution. The light emerging out of the analyser is viewed through the eyepiece. The analyser is then rotated slowly till the field of view is completely dark. This gives the initial reading of the instrument. Next, the tube is fitted with the liquid or the solution and the shutter is closed. On seeing through the eyepiece, the field of view is no longer found to be dark. The analyser is rotated slowly till the field of view becomes completely dark again. This gives the final reading. The difference between the final reading and the initial reading gives the angle of rotation 'α'. If it comes out to be positive, the substance is dextro-rotatory and if negative, it is laevo-rotatory.

23.4 CAUSE OF OPTICAL ACTIVITY IN A COMPOUND

As mentioned earlier, optical activity is a ***constitutive*** property, i.e. it depends upon the arrangement of atoms within the molecule. Organic compounds, which are found to be optically active, contain at least one carbon atom to which four different atoms or groups are attached. Such a carbon atom is called an ***asymmetric carbon*** atom and is usually shown by putting an asterisk over it. A very simple example of such a compound is lactic acid, as represented below.

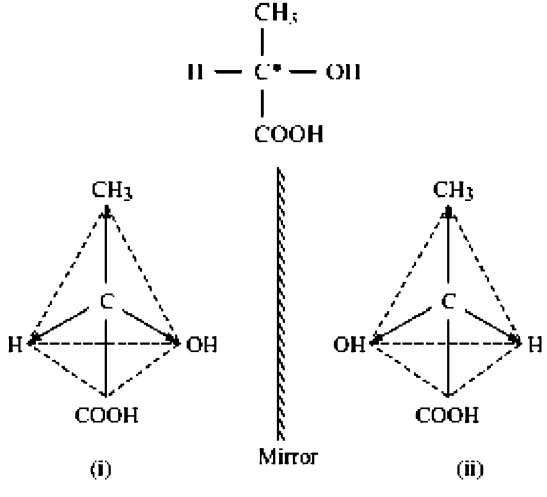


Fig. 23.3 *Spatial difference in d and l forms of lactic acid*

Such a compound exists in two forms, one of which rotates the plane of the polarised light to the right and is called ***dextro-rotatory*** (*d* form or '+' form) and the other which rotates the plane of the polarized light to the left and is called ***laevo-rotatory*** (*l*-form or '–' form). The two forms have the same constitution but differ in the arrangement of atoms or groups in space. Thus, the two forms are called ***optical isomers***.

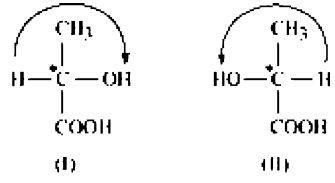
Le Bel and van't Hoff explained the differences in the two forms by suggesting that in case of such molecules, the asymmetric carbon atom is present in the centre of a regular tetrahedron and the four atoms of groups attached to it are present at the corners of a tetrahedron. This gives rise to two different spatial arrangements which are mirror images of each other, as shown in Fig. 23.3.

The two configurations are different in the sense that they are not superimposable over each other. The above two forms may be represented in a simplified way as follows:

In Form I, the arrangement from H to OH is clockwise and in Form (II), the arrangement from H to OH is anticlockwise. Hence, if one of the them is dextro-rotatory, the other is laevo-rotatory. However, by merely looking at the configurations, it is not possible to predict as to which form is dextro or laevo. The two forms are also said to be ***enantiomorphs.***

External Compensation and Internal Compensation

(a) External Compensation If equimolar quantities of *d*- and *l*-forms are mixed together, the mixture obtained is optically inactive. This is obviously due to the fact that the rotation caused by one form to the right is compensated by the equal rotation caused by the second form to the left. This process is called ***external compensation***, and the mixtures thus, obtained are called ***racemic mixtures*** (or *dl* forms or ± form). This form can be separated into *d* and *l* forms by suitable methods.



(b) Internal Compensation In case of compounds containing two asymmetric carbon atoms (e.g. tartaric acid, Fig. 23.5), another form is also found to exist. In this form, the rotation caused by half the molecule is compensated by the other half within the molecule. Thus, the molecule is optically inactive. This is a case of ***internal compensation.*** This form which is optically inactive due to ***internal compensation*** is called ***meso form.***

Certain compounds may not contain asymmetric atoms but still show optical activity. This is because such a molecule as a whole is asymmetric. In other words, the molecule cannot be divided into two equal halves with a plane. We can, therefore, conclude that ***optical activity is a property related to the asymmetry of the molecule.***

Example 1 *A solution of a certain optically active substance in water contains 1.56 g in 100 ml rotated polarised light by 4.91° in apolarimeter which has a cell 20 cm long. The D line of sodium was used as a light source. Calculate the specific rotation.*



Fig. 23.4 *Mirror images in nature provide an interesting example ofoptical activity*

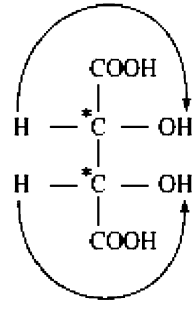


Fig. 23.5 *Meso form of tartaric acid*

Solution Here, we are given

$$c = 1.56 \text{ g}/100 \text{ ml}$$
$$\alpha = 4.91°$$
$$l = 20 \text{ cm} = 2 \text{ dm}$$

$$[\alpha]_{\lambda}^{t} = \frac{100 \times \alpha}{l \times c} = \frac{100 \times 4.91}{2 \times 1.56} = 157.37°$$

Example 2 *When α-D glucose ($[\alpha]_D^{20}$ = +112.2°) is dissolved in water, the optical rotation decreases as β-D glucose is formed until at equilibrium, $[\alpha]_D^{20}$ = +52.7°. As expected, when β-D glucose ($[\alpha]_D^{20}$ = +18.7°) is dissolved in water, the optical rotation increases unit $[\alpha]_D^{20}$ = +52.7 is obtained. Calculate the percentage of β-form in the equilibrium mixture.*

Solution Suppose x is the fraction of *D*-glucose in β form.

The fraction of α-form = $1 - x$

$$\therefore \quad x(+18.7) + (1 - x)(+112.2) = 52.7$$
$$x = 0.636 \text{ or Amount of } \beta\text{-form} = 63.6\%$$
$$1 - x = 0.364 \text{ or Amount of } \alpha\text{-form} = 36.4\%$$

Example 3 *The value of $[\alpha]_D^{20}$ for lactose is 55.4°. What is the concentration in grams per*

litre of a solution of lactose which gives a rotation of 7.24° in a 10 cm cell at 20° with sodium D light?

Solution Here, we are given

$$[\alpha]_D^{20} = 55.4°$$
$$\alpha = 7.2°$$
$$l = 10 \text{ cm} = 1 \text{ dm}$$

Putting the values in the formula,

$$[\alpha]_\lambda^t = \frac{100 \times \alpha}{l \times c} \quad \text{or} \quad 55.4 = \frac{100 \times 7.2}{l \times c}$$
$$C = 13.0 \text{ g/100 ml} = 130.0 \text{ g/litre}$$

PROBLEMS FOR PRACTICE

1. A 13 per cent aqueous solution of maltose showed a rotation = 17° in a 10 cm tube for D-line of sodium at 25°C. Another solution of maltose under identical conditions gave a rotation of 35°. Calculate the strength of this maltose solution in grams per litre. **[Ans.** 267.6 g/litre]

2. When α-*D*-mannose ($[\alpha]_D^{20} = +29.3°$) is dissolved in water, the optical rotation decreases as β-*D*-mannose is formed until at equilibrium, $[\alpha]_D^{20} = +14.2°$. As expected, when β-*D*-mannose ($[\alpha]_D^{20} = -17.0°$) is dissolved in water, the optical rotation increases until $[\alpha]_D^{20} = +14.2°$ is obtained. Calculate the percentage of α-form in the equilibrium mixture. **[Ans.** 67.4%]

3. Calculate the specific rotation of a substance, the solution of which contains 5 g of the substance dissolved in 25 ml of water and shows a rotation of 5° when introduced in 20 cm long polarimeter tube.

[Ans. 12.5°]

23.5 DIPOLE MOMENT

1. Polar and Nonpolar Covalent Bonds The pair of electrons shared by two identical atoms in a bond is situated exactly in the middle of the two atoms. Such a bond has no separation of charges and the bond formed between the two atoms is called nonpolar covalent bond.

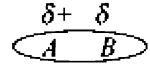
However, if the atoms involved in a covalent bond are different having different electronegativities, the pair of electrons is not situated in the middle. It is tilted towards the more electronegative atom. This causes separation of charges, one atom gaining partial negative charge and the other atom gaining partial positive charge. This is illustrated as under for the two types of covalent bonds.

H × H	H × Cl
↑	↑
Exactly in the centre (nonpolar covalent bond)	Tilted towards chlorine (polar covalent bond)



Fig. 23.6 *BF_3 dipoles*

The molecule containing polar covalent bond is called a dipole (two poles), having a positive pole and a negative pole. In general, a dipole *AB* can be represented as



It may be realised that the charges on the poles are not unit charges (+1 and –1) because complete transference of electrons from one atom to the other does not take place. Only a partial polarity is produced on the two poles.

2. Dipole Moment of a Diatomic Molecule The extent of polarity of a molecule is expressed in terms of dipole moment which is defined as follows:

The dipole moment of a polar diatomic molecule is the product of the charge on each end of the molecule and the average distance between the centre of their nuclei, i.e. the bond length.

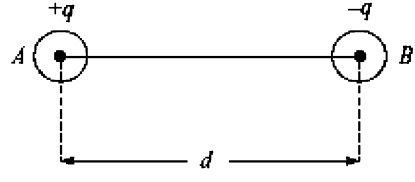


Fig. 23.7 *Dipole moment of a diatomic molecule*

For a polar diatomic molecule *AB* in which the atom *B* is more electronegative than *A*, if $+q$ is the average on the end *A* and $-q$ on the end *B* of the molecule and *d* is the average distance between the centre of their nuclei then the dipole moment of the molecule *AB* is given by

$$\mu = q \times d$$

Obviously, if the molecule is nonpolar, $q = 0$ and hence, $\mu = 0$.

The charge present on the ends of the molecule is usually of the order 10^{-10} esu and the distance between the atoms (i.e. bond length) is usually of the order of 10^{-8} cm (i.e. Å units). Therefore, μ must be of the order of $10^{-10} \times 10^{-8} = 10^{-18}$ esu cm. This value is called 1 debye. Thus,

$$1 \text{ debye} = 10^{-18} \text{ esu cm}$$

The dipole moment is a vector quantity, i.e. it has both magnitude as well as direction. It is, therefore, represented by an arrow pointing from the +ve end to the –ve end of the molecule, i.e.

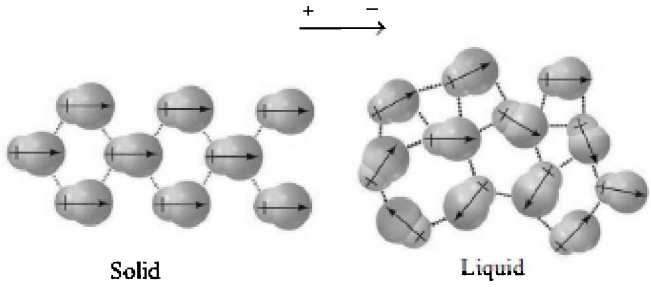


Fig. 23.8 *Dipole moments in solids and liquids*

3. Dipole Moment of Polyatomic Molecules In a polyatomic molecule every two bonded atoms have their dipole moment. This is called the bond moment. The net dipole moment of a polyatomic molecule is the resultant of the different bond moments.

The resultant will depend upon the direction of the bonds. Thus, if a molecule AB_2 contains two *A*-*B* bonds at an angle θ and μ_{AB} is the value of each bond moment then the dipole moment of the molecule will be

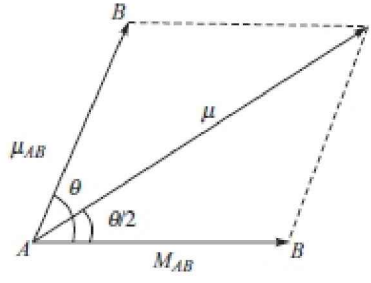


Fig. 23.9 *Dipole moment of a polyatomic molecule*

$$\mu = 2\mu_{AB} \cos \frac{\theta}{2}$$

For a more general molecule *ABC* with two bonds *AB* and *AC* having bond moments μ_1 and μ_2 and inclined at an angle θ, the dipole moment of the molecule (by parallelogram law) will be

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

As μ is known from experiments, therefore, knowing the value of θ, the method is usually used for the calculation of bond moments. Alternatively, knowing the value of μ and μ_{AB}, the method can be used for the calculation of θ and hence, for predicting the shapes of molecules.

Observed values of dipole moments of certain substances and calculated moments of certain bonds are given in Table 23.1 and 23.2 respectively.

Table 23.1 *Observed values ofdipole moments ofsome substances*

Inorganic molecules		Organic molecule	
	Dipole moment		Dipole moment

Molecule	(Debye)	Molecule	(Debye)
H_2, Cl_2, Br_2, I_2, N_2	0	CH_4, C_2H_6, C_2H_4, C_2H_2	0
CO_2, CS_2, $SnCl_4$, SnI_4	0	CCl_4, CBr_4	0
HCl	1.03	CH_3Cl	1.86
HBr	0.78	CH_3Br	1.80
HI	0.38	C_2H_5Br	2.03
H_2O	1.84	CH_3OH	1.78
NH_3	1.46	C_2H_5OH	1.85
H_2S	1.10	CH_3NH_2	1.24
SO_2	1.63	CH_3COOH	1.74
N_2O	0.17	C_6H_5Cl	1.73
CO	0.12	C_6H_5Br	1.71
PH_3	0.55	C_6H_5I	1.20
PCl_3	0.78	$C_6H_5NO_2$	4.23
HCN	2.93	$C_6H_5NH_2$	1.56
		C_6H_5OH	1.70
		$C_6H_4Cl_2$	0
		M-$C_6H_4Cl_2$	1.72
		O-$C_6H_4Cl_2$	2.50

Table 23.2 *Bond moments (in debye units) ofsome common bonds (atoms on the right-hand side are more electronegative than on the left-hand side)*

Bond	Bond Moment	Bond	Bond Moment	Bond	Bond Moment
H-C	0.2		(2.0)*	C-O	0.9
H-N	1.5			C=O	2.5

H-O	1.6	H–F	1.03	C≡O	5.3
H-F	(2.0)*	H–Cl	0.78	C-N	0.4
		H–Br			
		H–I	0.38		
			1.7	C-S	1.2
H-P	0.55	C–Cl		C=S	3.2
H-S	0.8	C–Br	1.6		
		C–I	1.4		
				N-O	1.9
H-Cl	1.03	P–Cl	1.8		
		P–Br	1.6		

*Arbitrarily fixed value

The dipole moment of some groups like $-NO_2$, $-NH_2$, $-CH_3$, etc., have also been reported. These are called ***group moments.*** The value depends upon whether the group is present in an aliphatic compound or aromatic compound. The values of a few groups are given below.

Group *(X)*	$-NO_2$	–CN	$-CH_3$	$-NH_2$
Group moment (in Alk – *X)*	–3.05	–3.46	0	+1.23
Group moment (in Ar – *X*)	–3.93	–3.99	+0.45	+1.55

A negative value of group moment means that the group is net electron withdrawing, i.e. more electronegative and a positive value means that the group is net electron repelling, or less electronegative than the alkyl or aryl radical. Based on these values, we can predict the course of electrons involving compounds with such groups and propose a mechanism of the reaction.

23.6 | POLARISATION OF MOLECULES (INDUCED POLARISATION)

Every molecule is made up of a positively charged nuclei and negatively charged electron cloud as shown in Fig. 23.10(a). The centre of positive charge and centre of negative charge coincide. When such a molecule is introduced between the two plates of an electric field, the positively charged nuclei and, hence, the centre of the positive charge is attracted towards the negative plate, whereas the negatively charged electron cloud is attracted towards the positive plate of the electric field. As a result, the molecule gets distorted, as shown in Fig. 23.10(b). This is called ***polarisation*** of the molecule and the distorted molecule with positive and negative ends is called an ***electric dipole.*** The molecule remains polarised so long as it is under the influence of an electric field but goes back to the original state as soon as the electric field is switched off. That is why this type of polarisation is called ***induced polarisation*** and the electric dipole formed is called ***induced dipole.***

Even after polarisation, the molecule is neutral as a whole, this means that the positive charge on one end must be equal to the negative charge on the other. Suppose this charge is **q.** If **d** is the distance of separation between the charges then the dipole moment of the induced dipole μ_i will be given by,

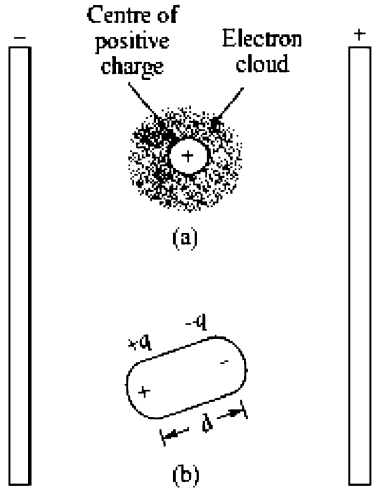


Fig. 23.10 *Polarisation ofmolecule of an electric field: (a) original state (b) polarised state.*

Evidently, the value of μ_i depends upon the nature of the molecule and the strength of the electric field, say X. Thus,

$$\mu_i = q \times d \qquad \ldots(23.5)$$

where, α is a constant called the ***polarisability*** of the given molecule.

$$\mu_i = \alpha \times X \qquad \ldots(23.6)$$

α is found to be related to the dielectric constant 'D' of the medium present between the plates, i.e. the molecules being studied, according to the equation given Clausius and Mossotti (derivation given in the next section):

$$\left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha \qquad \ldots(23.7)$$

where M is molecular mass of the molecules,
ρ is the density of the molecules, and
N is Avogadro's number.

23.6.1 Clausius-MosottiEquation

Suppose an electrostatic field is applied to two plates so that they are charged. Let the strength of the uniform electric field produced between them be equal to E_o.

Now, if a nonpolar substance is placed between the plates, the strength of the electric field will be reduced to E because the induced dipole (called dielectrics) acts against the applied field and hence, partially neutralises the charges of the plates as shown in Fig. 23.11. The ratio E_o/E is called the ***dielectric constant D of the medium.*** From electrostatics, we have the relation,

$$E_o = E + 4\pi I \qquad \ldots(23.8)$$

where I is the induced dipole moment per unit volume, i.e. $I = \mu_i \times n$ where μ_i is induced dipole moments in a single molecule and n is the number of molecules per cc.

Dividing both sides of Eq. (23.8) by E and putting $E_o/E = D$, we get

$$D = 1 + \frac{4\pi I}{E} \quad \text{or} \quad (D-1)E = 4\pi I \qquad \ldots(23.9)$$

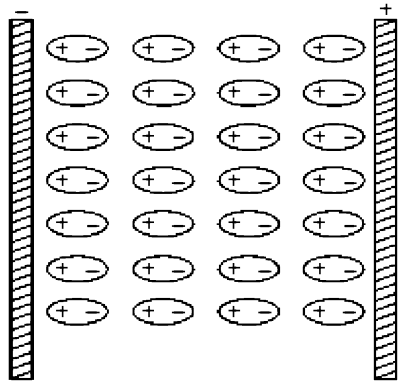


Fig. 23.11 *Partial neutralisation of the charges on the plates by the induced electric dipole (dielectrics)*

The intensity of the electric field strength X acting on each molecule is calculated by supposing that a unit charge is enclosed in a small spherical cavity which is large as compared with the size of the molecule but small in comparison with the distance between the plates. The electric intensity X then has the contribution of the following quantities.

(a) The field strength of the charges on the plates = E_o

(b) The charges induced on the surfaces of the dielectrics in contact with the plates = $-4\pi I$

(c) The charge induced on the surface of the spherical cavity = $\frac{+4}{3}\pi I$

$$X = E_o + \frac{4}{3}\pi I - 4\pi I \qquad \ldots(23.10)$$

Substituting the value of E_o from Eq. (23.8), we get

$$X = (E + 4\pi I) + \frac{4}{3}\pi I - 4\pi I \qquad \ldots(23.11)$$

Substituting the value of $4\pi I$ from Eq. (23.9), it becomes

$$X = E + \left(\frac{D-1}{3}\right)E = \left(1 + \frac{D-1}{3}\right)E$$

or $$X \quad \left(\frac{D+2}{3}\right)E \qquad \ldots(23.12)$$

From Eqs (23.11) and (23.12), we have

$$E + \frac{4}{3}\pi I = \left(\frac{D+2}{3}\right)E \quad \text{or} \quad \left(\frac{D+2}{3} - 1\right)E = \frac{4}{3}\pi I$$

or
$$\left(\frac{D-1}{3}\right)E = \frac{4}{3}\pi I \qquad \ldots(23.13)$$

Putting
$$I = \mu_i \times n$$
$$= \alpha X \times n \qquad (\because \mu_i = \alpha X)$$
$$= \alpha\left(\frac{D+2}{3}\right)E \times n \qquad \left(\because X = \left(\frac{D+2}{3}\right)E \text{ from Eq. (23.12)}\right)$$

Equation (23.13) becomes

$$\left(\frac{D-1}{3}\right)E = \frac{4}{3}\pi\alpha\left(\frac{D+2}{3}\right)E \times n$$

or
$$\left(\frac{D-1}{D+2}\right) = \frac{4}{3}\pi n\alpha \qquad \ldots(23.14)$$

If ρ is the density of the substance placed between the charged plates and M is its molecular mass then molar volume of the substance $= \frac{M}{\rho}$. If N represents Avogadro's number, the number of molecules per unit volume will be

$$n = \frac{N}{M/\rho} = \frac{N\rho}{M} \qquad \ldots(23.15)$$

Substituting this value in Eq. (23.14), we get

$$\left(\frac{D-1}{D+2}\right) = \frac{4}{3}\pi\frac{N\rho}{M}\alpha$$

or
$$\left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha \qquad \ldots(23.16)$$

All quantities on the right-hand side of Eq. (23.16) are constant (α being constant for a substance) independent of temperature, therefore, the quantity on the left hand-side of Eq. (23.16) must also be constant, independent of temperature and depending only upon the nature of the molecules. This quantity is called ***induced molar polarisation*** and is represented by P_i. Thus,

$$P_i = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} \qquad \ldots(23.17)$$

Induced molar polarisation is defined as the amount of polarisation produced in 1 mole of the substance when placed between the plates of an electric field of unit strength.

Expression (23.17) gives the relationship between dielectric constant and polarisability of a substance and is called Clausius-Mosotti equation.

Study of Certain Substances Using Eq. (23.17), the values of molar polarisation have been determined for a number of substances. It is found that whereas molar polarisation values of a number of substances such as O_2, CO_2, N_2 and CH_4 are constant and independent of temperature, the polarisation values for some other substances such as HCl, $CHCl_3$, $C_6H_5NO_2$ and CH_3Cl do not come out to be constant but decrease with increase of temperature.

In case of molecules such as HCl, $CHCl_3$, etc., the centre of positive and negative charges do not coincide with each other. Thus, they possess some dipole moment even in the absence of an electric field.

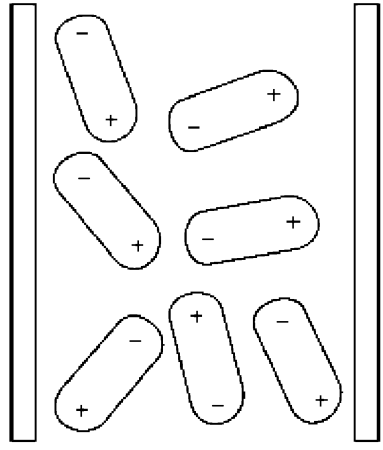


Fig. 23.12 *Permanent dipoles oriented in a random manner in the absence of an electric field*

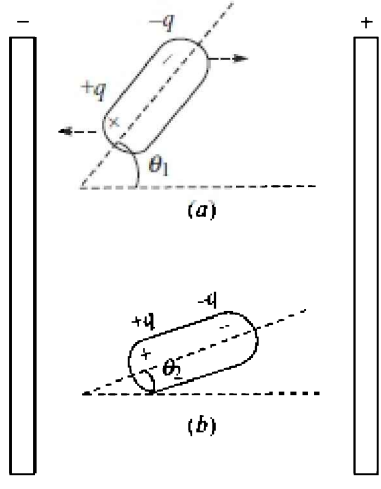


Fig. 23.13 *(a) Original state of a permanent dipole: (b) Final state after polarization and orientation*

The dipole moment thus possessed by molecules is called ***permanent dipole moment.*** In the absence of electric field, these permanent dipoles are oriented in a random manner as shown in Fig. 23.12. However, in the presence of an electric field (Fig. 23.13), two disturbing effects take place. These are:

1. The electric field will tend to rotate and orient these dipoles in the direction of the field.
2. The electric field will tend to polarise the molecules.

If the molecules were stationary, the dipoles would have been oriented perfectly parallel to the electric field, i.e. at right angles to the plates of the electric field. However, due to thermal agitation, they take up a position in between that of the original state and the perfectly parallel state, as shown in Fig. 23.13 (b) for any one permanent dipole.

Thus, in case of molecules possessing permanent dipoles, the right-hand side of Eq. (23.17) will give the total polarisation (P_t) which will be the sum of the induced molar polarisation (P_t) and the ***orientation molar polarisation*** (P_o),

i.e.
$$P_t = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = P_i + P_o \qquad \ldots(23.18)$$

And the induced polarisation is given by Eq. (23.7)

$$P_i = \frac{4}{3}\pi N\alpha \qquad \ldots(23.19)$$

The orientation molar polarisation is given by the equation put forward by Debye, viz.

$$P_o = \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \ldots(23.20)$$

where μ is the ***permanent dipole moment*** of the molecule, k is Boltzmann's constant (= R/N) and T is the temperature.

Substituting the values of P_i and P_o from equations (23.19) and (23.20) in Eq. (23.18), we get

$$P_t = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \ldots(23.21)$$

23.6.2 Measurement of Dipole Moment

1. Vapour-temperature Method Equation (23.21) can be written in the form

$$P_t = A + \frac{B}{T} \qquad \ldots(23.22)$$

where $A = \frac{4}{3}\pi N\alpha$ and $B = \frac{4\pi N\mu^2}{9k}$ are constant for the given substance.

Thus, if P_t is plotted against $1/T$, a straight-line graph will be obtained, if the molecules possessed permanent dipoles. The slope of the plot is given by

$$B = \frac{4\pi N\mu^2}{9k} \qquad \ldots(23.23)$$

From this equation, the permanent dipole moment of the molecule can be calculated, as all other quantities are constants whose values are known.

Solving Eq. (23.23) by putting the values of the various constants, we get

$$\mu = 0.0128\sqrt{B} \times 10^{-18}$$

Figure 23.14 gives the plots for a few polar and nonpolar substances. We observe that P_t varies with temperature for substances with permanent dipoles (for example, HCl, CH_3Cl, etc). But there is no effect of temperature on nonpolar substances such as CH_4, CCl_4, etc. not having permanent dipoles. These substances possess only induced molar polarisation. The basic

equation for the determination of dipole moment is

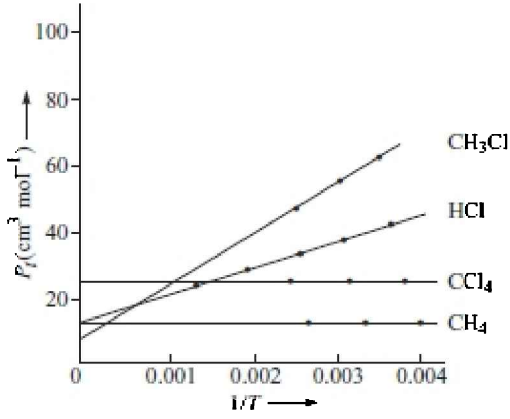


Fig. 23.14 *Plots of P_t vs 1/T for polar and non-polar molecules*

$$P_t = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = A + \frac{B}{T} \qquad \ldots(23.24)$$

where A and B are constants with

$$B = \frac{4\pi N\mu^2}{9K}$$

The experiment involves the determination of the dielectric constant D and the density ρ at different temperatures T. The values of P_t are then calculated and plotted against $1/T$. If P_t is found to vary linearly with $1/T$, the substance possesses a permanent dipole moment and the value of the dipole moment (μ) is calculated from the slope of the line. On the other hand, if P_t is found to be independent of temperature, the substance does not possess any permanent dipole moment (i.e. it is nonpolar).

The dielectric constant required in the above equation is determined by first measuring the capacity of a condenser in vacuum between the plates (C_o) and then measuring the capacity of the same condenser when filled with the given substance (C). The dielectric constant of the given substance is then given by the relation, as mentioned earlier also.

$$D = \frac{C}{C_o} \qquad \ldots(23.25)$$

2. Refraction Method According to Clausius-Mosotti equation, the induced molar polarisation (P_i) of the molecules is given by,

$$P_i = \frac{D-1}{D+2}\cdot\frac{M}{\rho} = \frac{4}{3}\pi N\alpha \qquad \ldots(23.26)$$

As D is a pure number, molar polarisation P is simply the molar volume of the material. Further, it has already been proved that it is independent of temperature if the substance is nonpolar and does not have a permanent dipole moment. For such molecules, the dielectric constant of a substance is related to its refractive index for light of long wavelength according to the equation,

$$D = n_\infty^2 \qquad \ldots(23.27)$$

Equation (23.27) was derived by JC Maxwell,

Substituting this value in Eq. (23.26) above, we have

$$P_i = \frac{n_\infty^2 - 1}{n_\infty^2 + 2}\frac{M}{\rho} = \frac{4}{3}\pi N\alpha \qquad \ldots(23.28)$$

However, n_∞^2 cannot be found by extrapolating the values of refractive indices measured with visible light to infinite wavelength. This is because visible light can displace only electrons whereas the positively charged nuclei remain unaffected. Thus, the induced polarisation can be considered to be sum of ***electron polarisation*** *(P_E)* and ***atom polarisation*** *(P_A)*, i.e.

$$P_i = P_E + P_A$$

To find total value of P_i, it is, therefore, necessary to measure the refractive index using infrared rays because they can displace the heavy atomic nuclei as well as electrons but measurement of refractive index with infrared radiations is difficult. This problem is solved by finding electron polarisation by measuring the refractive index *(n)* using visible light *(D*-line), i.e.

$$P_E = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} \qquad \ldots(23.29)$$

5% of this value is added to it to account for P_A to get the total value of P_i. This serves as satisfactory approximation.

Total polarisation (P_t) of a molecule possessing a permanent dipole moment is the sum of two terms, the first called ***induced polarisation*** *(P_i)* and the second called the ***orientation polarisation*** *(P_o)* due to permanent moment possessed by the molecule. Hence, we can write

$$P_t = P_i + P_o \qquad \ldots(23.30)$$

Substituting the value of P_o from Debye equation, viz.

$$P_o = \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \ldots(23.31)$$

Equation (23.30) becomes,

$$P_t = P_i + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \ldots(23.32)$$

Substituting the values of the constants and simplifying, we can write

$$\mu = 0.0128\sqrt{(P_t - P_i)T} \qquad \ldots(23.33)$$

P_t can be determined by finding the dielectric constant of the vapour at temperature T and P_i can be found either by measuring the refractive index using infrared radiation or by approximation method explained above.

3. *Dilute Solution Method* The equation $P_t = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho}$ is applicable to gases and vapours only.

For substances which are not gaseous, the following procedure is followed.

(a) A ***dilute*** solution of the given substance is prepared in a ***nonpolar*** solvent such as

benzene, CCl_4, CS_2, etc. The density and dielectric constant of a solution are determined at different temperatures.

(b) For each temperature, the molar polarisation of the solution P_S is calculated using the relation

$$P_S = \left(\frac{D-1}{D+2}\right)\left(\frac{x_1M_1 + x_2M_2}{\rho}\right) \quad \ldots(23.34)$$

where x_1 and x_2 are the mole fractions of the solvent and the solute in the solution. M_1 and M_2 are their respective molecular masses and ρ is the density of the solution.

(c) The molar polarisation of the solution is related to the molar polarisation of the solvent (x_1) and of the solute (x_2) as it is an additive property.

$$P_S = x_1P_1 + x_2P_2 \quad \ldots(23.35)$$

Thus, knowing the values of x_1, x_2 and P_1, the value of P_2, i.e. molar polarisation of the substance can be calculated. The values of P_2 obtained for different temperatures are plotted against $1/T$. The value of μ is obtained from the slope of the line.

23.7 | DIPOLE MOMENT AND STRUCTURE OF MOLECULES

Dipole moment studies help in elucidating the structure of compounds as follows:

1. In Calculating the Percentage Ionic Character of a Polar Covalent Bond For example, the dipole moment of HCl is 1.03 *D*. If the bond were 100% ions, each end would acquire full one unit charge, i.e. $4.8 = 10^{-10}$esu.

The bond distance in HCl is taken to be 1.275 Å, i.e. 1.275×10^{-8} cm.

Hence, if HCl were 100% ionic, the dipole moment would have been

$$= (48 \times 10^{-10}) \times (1.275 \times 10^{-8}) \text{ esu cm}$$

$$= 6.11 \times 10^{-18} \text{esu cm} = 6.11\ D$$

Actual value of dipole moment of HCl = 1.03 *D*

$\therefore$ Percentage ionic character H-Cl bond = $= \frac{1.03}{6.11} \times 100 = 17\%$ approx approx

2. In Comparing Relative Properties of Molecules The dipole moments of HF, HCl, HBr, HI are 2.0, 1.03, 0.78 and 0.38 debye respectively. This shows that the polar character of the molecules decreases as we move from HF to HI.

3. In Predicting the Shapes of the Molecules The fact that the dipole moment is a vector quantity and that a particular bond has almost a constant value of bond moment is very useful in predicting the shapes of molecules. A few cases are discussed below:

(a) Triatomic Molecules In triatomic molecules of the type AB_2 there are two possibilities.

(i) The dipole moment of the molecule may be zero as in case of CO_2 and CS_2. This shows that in these molecules, one bond moment is equal and opposite to the other. Hence, the molecules must be linear, as shown below:

$$\delta \leftarrow \delta' \rightarrow \delta \qquad\qquad \delta \leftarrow \delta' \rightarrow \delta$$
$$O=C=O \qquad\qquad S=C=S$$
$$\mu = 0 \qquad\qquad \mu = 0$$

(ii) The molecule may have a definite value of dipole moment (e.g. μ for H_2O = 1.84 D, μ for SO_2 = 1.63 D). Obviously, in these cases, the possibility of linear shape is ruled out. The two bonds must have a definite angle between them which can be, calculated, if we know the bond moments. For example, the bond moment for H-O is 1.6 D, the bond angle is calculated to be nearly 105°. Thus, H_2O may be represented as shown in the figure.

Such molecules are called ***bent molecules*** and the shape is called ***V-shape.***

(b) Tetratomic Molecules In tetratomic molecules of the type AB_3, the two simple possibilities are the following:

(i) Dipole Moment of the Molecule May be Zero as in BF_3 In such a case, all the four atoms must be in one plane and the angles between the bonds must be equal. Such a shape is called ***planar trigonal.***

(ii) The Molecule May have Some Definite Value of Dipole, (e.g. NH_3_ PCl_3, PF_3) This indicates that one atom lies out of plane of rest of the atoms. For example, the molecule of NH_3 may be represented as shown in the figure. Such a shape is called ***pyramidal shape.***

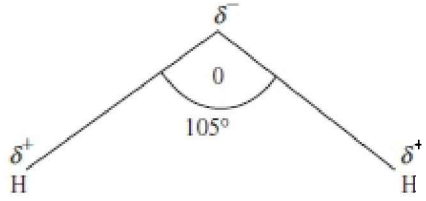
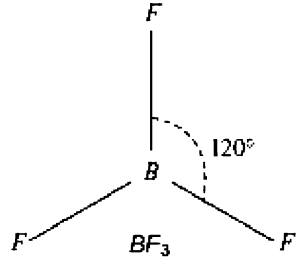


Fig. 23.15 *H_2O, triatomic molecule*



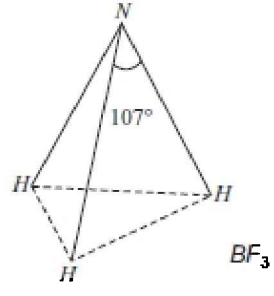


Fig. 23.16 *Molecules triatomic molecule*

(c) Penta-atomic Molecules The penta-atomic molecules of the type AB_4 which we commonly come across are CH_4, CCl_4, $SiCl_4$, $SnCl_4$, etc. The dipole moments of all these molecules is found to be zero. This is possible only if these molecules have symmetrical or regular geometry so that the different bond moments cancel out one another. The experimental facts confirm that these molecule have ***tetrahedral*** shape as represented below:

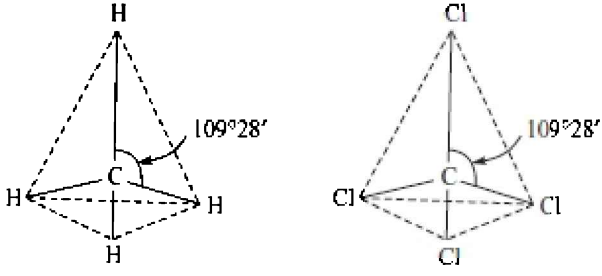


Fig. 23.17 *Penta-atomic molecules*

4. In Differentiating between o, m and p Isomers As benzene is a regular hexagon its dipole moment is zero, therefore, on substituting two atoms or groups in the ortho, meta or para positions, the disubstituted derivative will have different dipole moments for the *o*, *m* and *p* positions, as shown below:

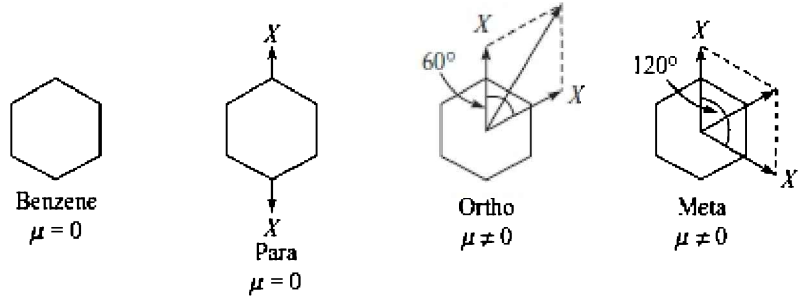


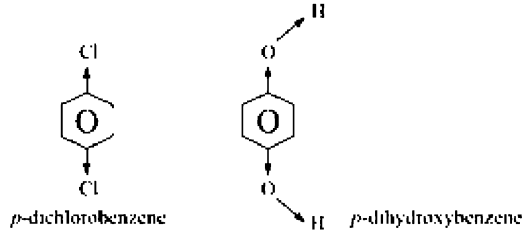
Fig. 23.18 *o, m and p isomers*

Obviously, para will have zero dipole moment, and meta will have less dipole moment than ortho compound.

Example 4 *Explain how p-chlorobenzene has zero dipole moment while p-dihydroxybenzene has a definite value.*

Solution The structures of *p*-dichlorobenzene and *p*-dihydroxybenzene are given below:

It is clear from the structures of the two compounds that the dipole moments of two C-Cl bonds will cancel each other, so that the net dipole moment of the molecule will be zero.



This cancellation of dipole moments of two C-O-H groups in *p*-dihydroxybenzene is not possible. Hence, it shows a definite value of dipole moment.

Example 5 *The bond length of H–I bond is 1.60 Å. Which of the following is the correct value for its dipole moment (in deby units), if it were present in the completely ionic form (charge on the electron = 4.8 × 10^{-10}esu). 3.00, 3.20, 7.68, 0.33, 6.40, 2.77, 9.28.*

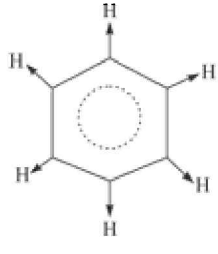
Solution For H-I, we are given that

$$d = 1.60 \text{ Å} = 1.60 \times 10^{-8} \text{ cm}$$
$$q = 4.8 \times 10^{-10} \text{esu}$$
$$\mu = q \times d = (4.8 \times 10^{-10})(1.60 \times 10^{-8})$$
$$= 7.68 \times 10^{-18} \text{esu cm} = 7.68 \, D$$

Example 6 *How can you establish the planar nature of benzene using dipole moment measurement?*

Solution Dipole moment of benzene molecule is zero, i.e. $\mu = 0$. This is possible only if benzene has a planar structure as represented in the figure. In this structure, dipole moments of six C-H bonds cancel one another and the net dipole moment of the benzene molecule is zero.

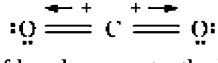
Had the structure not been planar, molecule would have shown a net di-pole moment which is not the case.



Example 7 *How will you arrive at the structure of (a) carbon dioxide, and (b) water from dipole moment studies?*

Solution

(a) *Carbon dioxide.* The dipole moment of carbon dioxide (μ_{CO_2}) is zero, although C = O bond moment $\mu_{C=O}$) is 2.5 D. This implies that the two C = O bond moments nullify each other, acting in opposite directions.



Using the parallelogram law of bond moments, the bond angle θ for a triatomic molecule

is calculated as follows:

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta \quad \text{or} \quad \cos\theta = \frac{\mu^2 - (\mu_1^2 + \mu_2^2)}{2\mu_1\mu_2}$$

where μ_1, μ_2 are the bond moments of bonds and μ is the dipole moment of the molecule. For carbon dioxide, the above equation becomes

$$\cos\theta = \frac{\mu_{CO_2}^2 - 2\mu_{CO}^2}{2\mu_{CO}^2} \quad (\because \mu_1 = \mu_2) \quad \text{or} \quad \cos\theta = \frac{0 - 2\mu_{CO}^2}{2\mu_{CO}^2} = -1$$

$$\theta = \cos^{-1}(-1) = 180°$$

That is the carbon dioxide molecule is linear.

(b) *Water.* The bond moment, $\mu_{O\text{-}H}$ and the dipole moment μ_{H_2O} are found to be 1.505 *D* and 1.84 *D* respectively. Again, using parallelogram law of bond moments, we can calculate the bond angle θ.

$$\cos\theta = \frac{\mu_{H_2O}^2}{2\mu_{O-H}^2} = -1 \quad \text{or} \quad \cos\theta = \frac{(1.84)^2}{2(1.505)^2} - 1 = -0.2520$$

$$\theta = \cos^{-1}(-0.2520) = 104°36'$$

Thus, water molecule has ***bent (or V) shape.***

Example 8 *The bond length of H-I bond is 1.60Å and its dipole moment is 0.38 D. Calculate the percentage ionic character of H-I bond.*

Solution Assuming H-I to be 100% ionic bond, each end would acquire full one charge, i.e. $q = 4.8 \times 10^{-10}$esu

$$\mu = q \times d$$

$$= (4.8 \times 10^{-10}\text{ esu})(1.60 \times 10^{-8}\text{ cm}) = 7.68 \times 10^{18}\text{ esu cm} = 7.68\ D$$

Observed $\mu = 0.38\ D$ (Given)

$$\% \text{ ionic character} = \frac{0.38}{7.68} \times 100 = 4.95\%$$

23.8 MAGNETIC SUSCEPTIBILITY

1. Magnetic Permeability If two magnetic poles of strength m_1 and m_2 are separated by a distance r, then the force F acting between them is given by,

$$F = \frac{1}{\mu}\frac{m_1 \times m_2}{r^2}$$

The quantity μ in the above expression is called the magnetic permeability of the medium between the poles. ***It is defined as the relative tendency of the magnetic lines of force to pass through the medium as compared to that in the vacuum.*** For vacuum, μ is taken as equal to 1. Similarly, for air, μ is taken as approximately equal to 1.

2. Diamagnetic, Paramagnetic and Ferromagnetic Substances For media other than vacuum

or air, μ can be less than or greater than 1. If μ is less than 1 then the magnetic lines of force prefer to pass through the vacuum rather than through the substance comprising the medium. In other words, the magnetic lines of force are repelled away from the substance. Such substances are said to be diamag-netic. On the other hand, if μ is greater than 1, then the magnetic lines of force have greater tendency to pass through the substance rather than through the vacuum. In other words, the magnetic lines of force are attracted towards the substance. Such substances are called paramagnetic. If μ is very high (i.e. of the order of 10^3 or more), the tendency of the substance to attract the magnetic lines of force is very high. Such substances are said to be ferromagnetic. Ferromagnetism is exhibited mainly by iron, cobalt, nickel and their alloys. The behaviour of diamagnetic and paramagnetic substances in a magnetic field is shown diagrammatically in Fig. 23.19.

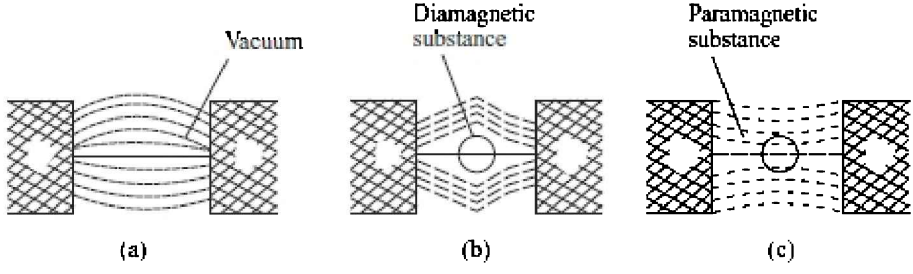


Fig. 23.19 *(a) Magnetic lines of force passing through vacuum (b) Magnetic lines of force pushed away by the magnetic substance (c) Magnetic lines offorce drawn in by the paramagnetic material.*

3. Magnetic Susceptibility If a material is placed in a magnetic field, the strength of the magnetic field in the material is called magnetic induction. Mathematically,

if H is the strength of the applied magnetic field and $B$is the magnetic induction in the given material then

$$B = H + 4\pi I \qquad \ldots(23.36)$$

where I represents the magnetic moment per volume in the material and is called ***intensity of magnetisation.*** It may be positive or negative depending upon whether the material is paramagnetic or diamagnetic.

The intensity of magnetisation produced per unit strength of the applied magnetic field is called ***specific magnetic susceptibility.*** It is usually represented by χ. Thus mathematically,

$$\chi = \frac{I}{H} \qquad \ldots(23.37)$$

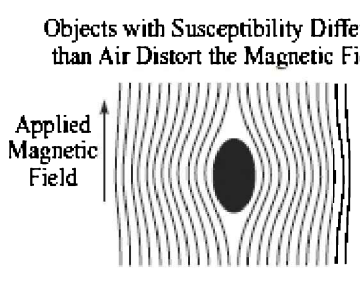


Fig. 23.20 *Magnetic susceptibility*

This quantity is usually measured experimentally in the study of magnetic properties of different materials.

Multiplying the specific magnetic susceptibility with molar volume (M/ρ) of the material, we get magnetic susceptibility per mole or ***molar magnetic susceptibility.*** It is usually represented by χ_M. Mathematically,

$$\chi_M = \frac{M}{\rho} \cdot \frac{I}{H} \qquad \ldots(23.38)$$

Thus, ***molar magnetic susceptibility may be defined as the intensity of magnetisation induced per mole of the material by the unit field strength.***

Quite often, it is more convenient to deal with the quantity χ_M in place of χ

Further, the magnetic induction B is related to the strength of the applied magnetic field H according to the equation,

$$B = \mu H \qquad \ldots(23.39)$$

where μ is the magnetic permeability of the medium (i.e. the material placed between the poles).

$$I = \chi H \qquad \ldots(23.40)$$

Substituting the values of B and I from Eqs (23.39) and (23.40) in Eq. (23.36), we get,

$$\mu H = H + 4\pi\chi H$$

$$\mu = 1 + 4\pi\chi \qquad \ldots(23.41)$$

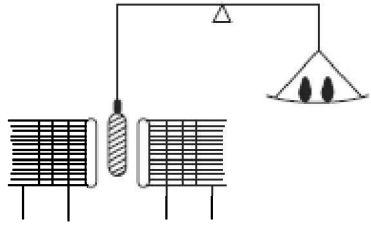


Fig. 23.21 *Gouy's method for measurement of magnetic susceptibilities.*

Determination of Magnetic Susceptibility (Gouy's Method) The Gouy method for magnetic susceptibility measurement is illustrated as under:

The material under examination is taken in a thin cylinder or a tube which is then suspended vertically with a wire from one arm of the balance between the two poles of an electromagnet such that the lower end of the cylinder is nearly in the middle of the poles of the electromagnet (Fig. 23.21). The cylinder is now counterbalanced in this position by placing weights in the other pan of the balance. The current is now switched on into the electromagnet. If the substance is paramagnetic, the cylinder will be pulled down (so that more magnetic lines of force can pass through it). On the other hand, if the substance is diamagnetic, the cylinder will be pushed upward (so that less magnetic lines of force may pass through it). In the first case, some extra weights will have to be added into the pan, whereas in the second case, some weights will have to be removed from the pan to restore the balance.

The change in weight is equal to the magnetic force acting on the material. Therefore, if Δm is the change in the mass then we have the relation

$$\Delta mg = \frac{1}{2}(\chi - \chi_a)AH^2 \qquad \ldots(23.42)$$

where g is the acceleration due to gravity so that Δmg gives the change in weight. The right-hand side is the magnetic force acting on the material of volume susceptibility (magnetic susceptibility) χ, when A is the area of cross section of the specimen, H is the field strength and χ_a is the volume susceptibility of the air.

Value of $\chi_a = 0.03 \times 10^{-6}$. Thus, using Eq (23.42), the value of χ can be calculated.

In the above calculations, the absolute value of the field strength H is also required. However, the necessity of measuring H and A can be eliminated if the experiment is first performed with a substance of known susceptibility using the same magnetic field and the same cylinder for taking this substance. Usually, water is taken as the standard substance for this purpose. Then evidently we have the following relation:

$$\frac{\Delta m_s}{\Delta m_w} = \frac{\chi_s - \chi_a}{\chi_w - \chi_a} \qquad \ldots(23.43)$$

where Δm_s is the change in mass when the sample under examination is placed in the magnetic field and Δm_w is the change in mass when water is taken in the same cylinder and placed in the same magnetic field. χ_s is the magnetic susceptibility (volume susceptibility) of the sample, and χ_w and χ_a are those of water and air respectively. We can, thus, eliminate the use of H.

4. Magnetic Susceptibility and Molecular Structure It has been revealed that molar magnetic susceptibility (χ_M) is an *additive* as well as a *constitutive* property. The values assigned to the various atoms and to the structural factors (i.e., double bond, triple bond, rings etc.) can be obtained from the experimentally determined values for a large number of elements and compounds. The values of magnetic susceptibility for some of the atoms and structural groups are given in Table 23.3 below.

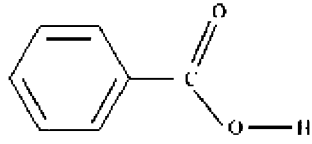
Table 23.3 Atomic and structural susceptibilities

Atom	Magnetic susceptibility	Structural factor	Magnetic susceptibility
	$\times 10^{-6}$		$\times 10^{-6}$
H	-2.93	C = C double bond	+5.4
C	-6.00	N = N double bond	+1.9
O (in alcohols and ethers)	-4.61	N = N double bond	+1.9
O (in ketones)	+1.73	C = N double bond	+8.2
O (in esters and acids)	-3.36	C ≡ C triple bond	+0.8
N (in open chain)	-5.57	C ≡ N triple bond	-0.8
N (in ring)	-4.61	Benzene ring	-1.5
N (in a mines)	-1.54		

F	-11.5	**Note:** For an aromatic compound, the value of benzene ring has been added, no value has been added for C = C double bond.
Cl	-20.1	
Br	-30.6	

The calculation of molar magnetic susceptibility of a compound for the atomic and structural values help us to decide between the possible structures for a compound or to confirm the structure of the compound by comparing the calculated value with the experimental value.

Example 9 *Confirm that the structure of benzoic acid is*



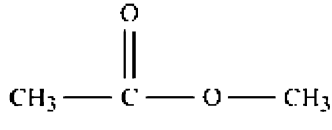
Given that the magnetic susceptibility of a compound is measured as –70.3 × 10^{-6}.

Solution The magnetic susceptibility contributions are due to various atoms and structural factors and hence, the total value for χ_M can be calculated as follows:

$$\begin{aligned}
7\text{C atom} &= 7 \times (-6.00 \times 10^{-6}) = -42.00 \times 10^{-6} \\
6\text{H atom} &= 6 \times (-2.93 \times 10^{-6}) = -17.58 \times 10^{-6} \\
1\text{O atom (alcohol)} &= 1 \times (-4.61 \times 10^{-6}) = -4.61 \times 10^{-6} \\
1\text{O (acid)} &= 1 \times (-3.36 \times 10^{-6}) = -3.36 \times 10^{-6} \\
1 \text{ benzene ring} &= 1 \times (-1.5 \times 10^{-6}) = -1.50 \times 10^{-6} \\
\text{Total calculated value} &= -69.05 \times 10^{-5} \\
\text{Observed value} &= -70.3 \times 10^{-6}
\end{aligned}$$

As the calculated value is very close to the observed value, the given structure is correct.

Example 10 *Establish that the structure of methyl acetate is*



Given that the magnetic susceptibility of the compound is found to be – 70.3 × 10^{-6}.

Solution The value for χ_M for this structure can be calculated as follows:

$$\begin{aligned}
3\text{C atom} &= 3 \times (-6.00 \times 10^{-6}) = -18.00 \times 10^{-6} \\
6\text{H atom} &= 6 \times (-2.93 \times 10^{-6}) = -17.58 \times 10^{-6} \\
1\text{O atom (ether)} &= 1 \times (-4.61 \times 10^{-6}) = -4.61 \times 10^{-6}
\end{aligned}$$

$$1O\ (\text{ester}) = 1 \times (-3.36 \times 10^{-6}) = -3.36 \times 10^{-6}$$

$$\text{Total calculated value} = -43.55 \times 10^{-6}$$

$$\text{Observed value} = -43.6 \times 10^{-6}$$

23.9 | EXPLANATION OF DIAMAGNETISM AND PARAMAGNETISM

The study of atomic structure supports that an electron is associated with orbital motion and spin motion. Movement of a charged particle produces a small magnetic field and we obtain a definite value of magnetic moment. An electron spinning clockwise will give magnetic moment in a direction opposite to that spinning anticlockwise.

Thus, if all the electrons in a molecule are paired, they will give the net value of magnetic moment as zero. If such a substance is placed in a magnetic field, it is ***repelled*** by the magnetic field because a small magnetic moment is induced in the substance which works against the external magnetic field.

We can, therefore, say that ***diamagnetism is the property of substances containing paired electrons only.***

On the contrary, if the molecule (substance) contains some electrons which are unpaired, each of them will possess magnetic moment which will not get cancelled. Hence, such a substance will possess a definite value of magnetic moment which will not get cancelled. If such a substance is placed in a magnetic field, we shall find that the molecules will arrange themselves parallel to the external magnetic field. In such a case, the induced magnetic moment of the substance is too small to overcome the permanent magnetic moment of the substance. Such substances get attracted by the magnetic field, and are known as paramagnetic substances.

We can say that ***paramagnetism is the property of substances containing a certain number of unpaired electrons.***

Table 23.4 gives the expected magnetic moments and molar magnetic susceptibilities for different number of unpaired electrons.

Table 23.4 Expected magnetic moments and molar magnetic susceptibilities for different number of unpaired electrons

No. of unpaired electrons *(n)*	Spin magnetic moment (B.M.)	Molar magnetic susceptibility at 298 K
	$\mu_M = \sqrt{n(n+2)}$	$\chi_M = \frac{N}{3kT}[n(n+2)]$
1	1.73	1260×10^{-6}
2	2.83	3360×10^{-6}
3	3.83	6290×10^{-6}

4	4.90	10100×10^{-6}
5	5.92	14700×10^{-6}

Further, greater the number of unpaired electrons, greater is the magnetic property associated. If the number of unpaired electrons is more than 4 (like in Fe, Co, Ni), the substance has a high value of magnetic moment and is called ***ferromagnetic.***

1. Molecular Interpretation of Diamagnetism The classical theory of diamagnetism and paramagnetism was put forward by Langevin in 1905.

According to Langevin, ***diamagnetism results from the orbital motion of the atoms and molecules.***

According to Lenz's law, which states that when a current flows through a wire in a magnetic field, the magnetic field induces current in a coil in such a manner that it opposes the applied field. Similarly, the applied magnetic field perturbs the orbital motion, thereby inducing a magnetic field which opposes its own direction. In a multi-electron atom, the orbits are spatially oriented at random relative to the field.

The molar diamagnetic susceptibility χ_M^d is given by

$$\chi_M^d = -\frac{ZNe^2}{6mc^2}\sum \overline{r_i^2} \qquad 2.832 \times 10^{10} \sum \overline{r_i^2} \qquad \text{(after substituting for various quantities)}$$

where $\overline{r_i^2}$ = Mean square distance of the i^{th} orbit from the nucleus.

Z Atomic number, e Charge on electron,

m = Mass of electron, and c = Velocity of light

Diamagnetism is a common property of all atoms of all matter whether it possesses a permanent dipole moment or not.

2. Molecular Interpretation of Paramagnetism According to Langevin's theory of paramagnetism, each atom or molecule behaves as a small bar magnet with magnetic moment μ. The magnetic moment may either be due to orbital motion of an electron or due to unpaired electron spin. The molar paramagnetic susceptibility due to permanent magnetic moment is given by

$$\chi_M^p = \frac{N\mu_m^2}{3kT} = \frac{\text{constant}}{T} \qquad (\mu_m = \text{Magnetic moment})$$

i.e. χ_M^p varies inversely with absolute temperature T. This is known as ***Curie's law,*** which holds over a limited range of temperature.

In case the system is distorted by the external field, the molar paramagnetic susceptibility is more correctly given by

$$\chi_M^p = \frac{N\mu_m^2}{3kT} - \alpha_m$$

where α_m is the magnetic polarisability of the system.

As all substances exhibit diamagnetic behaviour, the total molar magnetic susceptibility is the sum of χ_M^p and χ_M^p However, the diamagnetic contribution is negligibly small as compared to paramagnetic contribution.

23.10 | DETERMINATION OF THE MAGNETIC MOMENT

OF A PARAMAGNETIC SUBSTANCE

Each atom, ion or molecule of a paramagnetic substance behaves like a micromagnet with a definite inherent magnetic moment of magnitude μ_m: When such a substance is placed in the external magnetic field, micromagnets tend to arrange themselves parallel to the applied field. However, this tendency is opposed by the thermal motion of the particles. Hence, the actual arrangement taken up will depend upon the temperature. Langevin, in 1905, put forward the following relationship between molar magnetic susceptibility χ_M, magnetic moment μ_M and temperature T.

$$\chi_M = \alpha_m + \frac{\mu_m^2 N}{3kT} \qquad \ldots(23.44)$$

where N is Avogadro's number, k is Boltzmann's constant and α_M is a constant for the given substance.

It represents the diamagnetic molar susceptibility of the substance induced by the applied magnetic field.

In Eq. (23.44), all quantities are constant except χ_M and T. Thus, determining χ_M for the given substance at different temperatures T, and then plotting χ_M vs $\frac{1}{T}$, a straight-line graph will be obtained, the slope of which will be equal to $\frac{\mu_m^2 N}{3k}$. Hence, μ_m can be calculated.

Magnetic moment is usually expressed in Bohr Magneton (BM)

$$\text{BM} = eh/4\pi mc$$

where h is Planck's constant, c is the velocity of light, e is the charge on electron and m is its mass. Substituting various values, we have

$$1 \text{ BM} = 9.2732 \times 10^{-21} \text{ ergs gauss}^{-1}$$

1. Relationship between Magnetic Moment And Number of Unpaired Electrons The total magnetic moment of any atom, ion or molecule is the sum of the following two values:

(a) Magnetic moment due to the ***orbital motion*** of the electron. It is equal to $\sqrt{l(l+1)}$ BM where l is the azimuthal or orbital quantum number for that electron.

(b) Magnetic moment due to ***spin motion*** of the electron. It is equal to $2\sqrt{s(s+1)}$ BM where s is the spin quantum number having value equal to 1/2.

If ions or molecules are considered instead of free atoms, it is expected that the orbital motions of the electrons are tied into the nuclear configuration of the molecule or the ion so tightly that they are unaffected by applied magnetic field. Hence, the orbital motion contribution to the magnetic-moment is negligible. Thus, the magnetic moment of the molecule or the ion is mainly due to the spin motion of the electrons. (Hence, it is called spin magnetic moment.) Thus, we have,

$$\mu_m = 2\sqrt{s(s+1)} \text{ BM} \qquad \ldots(23.45a)$$

Here, s represents spin quantum number for one unpaired electron. For a molecule or ion containing a number of unpaired electrons, the expression is usually written as

$$\mu_m = 2\sqrt{S(S+1)} \text{ BM} \qquad \ldots(23.45b)$$

where S represents the total spin quantum number.

Thus, for one unpaired electron, $S = \frac{1}{2}$

For two unpaired electrons, $S = \frac{2}{2}$

For three unpaired electrons, $S = \frac{3}{2}$, and so on.

In general, for n unpaired electrons, $S = \frac{n}{2}$, hence Eq. (23.45b) becomes

$$\mu_m = 2\sqrt{\frac{n}{2}\left(\frac{n}{2}+1\right)}$$

$$\boxed{\mu_m = \sqrt{n(n+2)}\ \text{BM}} \qquad \ldots(23.46)$$

Knowing the number of unpaired electrons present, the magnetic moment (μ_m) can be calculated or vice versa.

2. Relationship between Molar Susceptibility and the Number of Unpaired Electrons Taking α_m as constant, Eq. (23.44) can be written as

$$\chi_M = \frac{\mu_m^2 N}{3kT} \qquad \ldots(23.47)$$

where χ_M and μ_m are the magnetic susceptibility and magnetic moment respectively.

Substituting the value of μ_m in Eq. (23.47), we get

$$\boxed{\chi_M = \frac{N}{3kT}[n(n+2)]} \qquad \ldots(23.48)$$

The expected value of spin magnetic moments and magnetic susceptibilities for different values of n are given in Table 23.4.

23.11 | APPLICATIONS OF MAGNETIC SUSCEPTIBILITY MEASUREMENT

Some important applications of magnetic susceptibility measurement are given below:

1. In Calculation of the Number of Unpaired Electrons in a Molecule or Ion Knowing the molar magnetic susceptibility χ_M, which can be easily determined experimentally, the number of unpaired electrons present in a molecule or an ion can be calculated. This has helped in understanding the electronic structures of a number of molecules. For example, the molar magnetic susceptibility of oxygen has been found to be 3400×10^{-6} which shows that it must contain two unpaired electrons. Thus, the structure of oxygen molecule should be represented as



It is a paramagnetic molecule.

2. In Establishing the Formulas of Certain Compounds For example, it has been shown that the formula of hypophosphoric acid is $H_4P_2O_6$ and not H_2PO_3. This is because if the latter formula were correct, sodium and silver salts, $NaHPO_3$ and Ag_2PO_3, would contain an odd number of electrons and should be paramagnetic while actually they are paramagnetic. Hence their salts must have the formulas $Na_2H_2P_2O_6$ and $Ag_4P_2O_6$ respectively. Similarly, the formula of mercurous chloride is Hg_2Cl_2 and not HgCl. Dimerisation leads to spin neutralisation of electrons.

3. In Confirming the Structure of a Given Molecule The use of molar magnetic susceptibilities in confirming the structure of a given molecule is based upon the fact that magnetic susceptibility is an additive as well as constitutive property.

4. In Explaining the Existence of Odd Electron Molecules The compounds containing odd electrons are expected to be paramagnetic. This is actually found to be so for a few gaseous compounds, namely nitric oxide, nitrogen dioxide and chlorine dioxide. Moreover, their magnetic susceptibilities show that they contain one unpaired electron in each case.

5. In the Study of Coordination Compounds An important application of magnetic susceptibility in chemistry has been in the study of coordination compounds of transition elements. Measurement of magnetic susceptibility helps us know the number of unpaired electrons present in the complex which in turn helps to assign the correct structure to the complex ion in some cases. For example, the magnetic susceptibility values of the complexes $[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$ (though each has the same coordination number, i.e. 6) suggest that there is one unpaired electron present in the former whereas there are five unpaired electrons present in the latter. These are explained by suggesting the following electronic structure to these complexes. (Fig. 22)

$$Fe = 26 = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$$
$$Fe^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$$

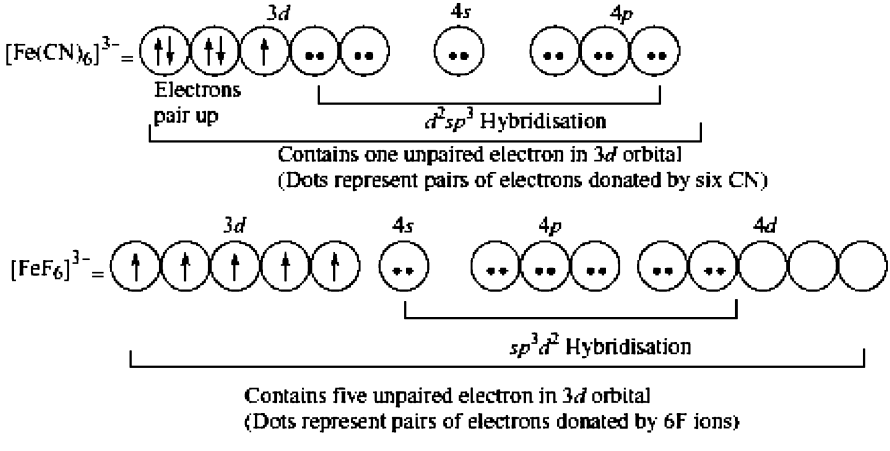


Fig. 23.22 Structure of $[Fe(CN)_6]^{3-}$ and (ii) $[FeF_6]^{3-}$

Example 11 *Write the Clausius-Mosotti equation. What important result do you draw from it for nonpolar molecules?*

Solution The induced polarisation P_i in a nonpolar molecule is given by

$$P_i = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha$$

where D = Dielectric constant of the medium (substance)
M = Molecular mass, ρ = Density, N = Avogadro's number
α = Constant for given substance

All quantities on the RHS of the equation are constants and also independent of temperature.

Therefore, P_i for nonpolar substances like O_2, N_2, CH_4, CCl_4, etc., is constant independent of temperature.

Example 12 *For polar molecules with permanent dipole moment, write the expression for the total polarisation. What is the most important use of this expression?*

Solution For polar molecules with permanent dipole moment, total polarisation is given by the sum of induced polarisation and orientation polarisation, i.e.

$$P_t = P_i + P_o = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right)$$

It can be written in the form

$$P_t = A + \frac{B}{T}$$

where $A = \frac{4}{3}\pi N\alpha$ and $B = \frac{4\pi N\mu^2}{9k}$

Thus, a plot of P_t versus $1/T$ will give a straight-line whose slope is

$$B = \frac{4\pi N\mu^2}{9k} \quad \text{or} \quad \mu = \sqrt{\frac{9k}{4\pi N}}\, B = 0.0128\sqrt{B} \times 10^{-18} \text{ esu cm}$$

Thus, permanent dipole moment μ of the molecule can be calculated.

Example 13 *Comment on the value of magnetic permeability μ for diamagnetic, paramagnetic and ferromagnetic substances.*

Solution For a diamagnetic substance, $\mu < 1$

For paramagnetic substances, $\mu > 1$

For ferromagnetic substances, $\mu >> 1$ ($>10^3$)

Example 14 *How is the magnetic moment of a substance determined from molar magnetic susceptibility?*

Solution Molar magnetic susceptibility (χ_M) is related to magnetic moment according to the equation

$$\chi_M = \alpha_m \times \frac{\mu_m^2 N}{3kT}$$

A plot of χ_m vs. $1/T$ gives a straight line with slope $= \frac{\mu_m^2 N}{3k}$ from which μ_m can be

calculated.

Example 15 *How are magnetic moment and molar magnetic susceptibility calculated from the number of unpaired electrons?*

Solution

$$\mu_m = \sqrt{n(n+2)}\ \text{BM},\ \chi_M = \frac{\mu_m^2 N}{3kT}$$

$$-\frac{N}{3kT}[n(n+2)]$$

Example 16 *How is magnetic susceptibility (χ) related to magnetic permeability (μ)? Comment on its value for diamagnetic, paramagnetic and ferromagnetic substances.*

Solution $\chi - \dfrac{\mu - 1}{4\pi\rho}$ (ρ = density of the substance)

For diamagnetic substance, $\mu < 1$; therefore, χ is –ve.

For paramagnetic substance, $\mu > 1$; therefore, χ is +ve but small.

For ferromagnetic substances, $\mu >> 1$; χ is +ve and very large.

Example 17 *How do meso form and racemic mixture of tartaric acid differ from each other?*

Solution :Both are optically inactive but for different reasons. In case of meso form, it is due to ***internal compensation***, i.e. the molecule has a plane of symmetry so that rotation caused by one half of the molecule is compensated by the other half within the molecule. In case of racemic mixture, optical inactivity is due to ***external compensation.*** It is a mixture of *d*–and *l*–forms such that the rotation to the right by *d*–form is neutralised by equal rotation to the left by the *l*–form.

Example 18 *Write the expression for finding the specific rotation of a substance when it is taken in the form of solution. How is the specific rotation of a pure liquid or a solid determined?*

Solution Specific rotation, $[\alpha]_\lambda^t = \dfrac{v \times \alpha}{l \times m} = \dfrac{100 \times \alpha}{l \times c}$

where v is the volume of solution in cm^3 containing m grams of the substance dissolved in it, l is the length of the tube in dm and α is the angle of rotation Second equation may be used if the concentration of the solution is c g/100 cc.

For a pure liquid or a pure solid, m/v may be replaced by the density of the pure substance. Hence, for a pure liquid or solid, the equation takes the form,

$$[\alpha]_\lambda^t = \frac{\alpha}{l \times d}$$

Example 19 *How is the dipole moment calculated for a molecule AB_2 with bond angle θ?*

Solution In general, for triatomic molecule with bond moment μ_1 and μ_2, net dipole moment of μ of the molecule is given by,

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

For AB_2, $\mu_1 = \mu_2 = \mu_{AB}$ so that

$$\mu = 2\mu_{AB} \cos\frac{\theta}{2} \left\{ \because 1 + \cos\theta = 2\cos^2\frac{\theta}{2} \right\}$$

SUMMARY

1. *Physical properties* of a substance depend upon the structure of molecules and the intermolecular forces in the substance
2. An *additive property* is defined as the property, the aggregate value of which is the sum of the values of its constituents.
3. A *constitutive property* is defined as the property which depends upon the constitution or structure of the molecules
4. Light which has vibrations only in one plane is called *plane polarised* light.
5. *Specific rotation* of a substance may be defined as the angle of rotation produced when one gram of the substance is dissolved in one ml of the solution and the length of the solution through which light passes is 1 dm.
6. An *optically active* substance contains at least one asymmetric carbon atom. Optical activity is a property that is related to the asymmetry of the molecule
7. *Internal compensation* is caused when the rotation caused by one half of the molecule is compensated by the other half. External compensation is caused when equal amounts of *d*– and *l*–forms of a substance are mixed.
8. *Dipole moment* of a polar diatomic molecule is the product of the charge on each end of the molecule and the average distance between the centre of their nuclei
9. *Induced molar polarisation* is defined as the amount of polarisation produced in 1 mole of the substance when placed between the plates of an electric field of unit strength
10. Dipole moment of a substance can be measured by vapour-temperature, refraction and dilute solution methods
11. Dipole moment of a substance can be used (i) to determine percentage ionic character of a polar covalent bond, (ii) to compare relative properties of molecules, (iii) to predict the shapes of molecules, and (iv) to distinguish between *o*–, *m* – and *p*– isomers of a substance.
12. *Molar magnetic susceptibility* may be defined as the intensity of magnetisation induced per mole of the material by unit field strength. Magnetic susceptibility of a substance can be determined by Gouy's method
13. Diamagnetism is the property of a substance containing paired electrons only, while paramagnetism is the property of a substance containing a certain number of unpaired electrons. According to Longevin, diamagnetism results from the orbited motion of atoms and molecules
15. Magnetic susceptibility measurements can be used to (i) calculate the number of unpaired electrons, (ii) establish the formula of certain compounds, (iii) explain the existence of odd electron molecules, and (iv) study coordination compounds.

KEY RELATIONS

1. $[\alpha]_\lambda^t = \frac{v \times \alpha}{l \times m}$

2. $\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

3. $\mu_i = q \times d$

4. $\left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha$

5. $P_i = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\left[\frac{\mu^2}{3kT}\right]$

6. $F = \frac{1}{\mu}\frac{m_1 \times m_2}{r^2}$

7. $B = H + 4\pi I$

8. $\chi_m = \frac{M}{\rho} \cdot \frac{I}{H}$

9. $\Delta mg = \frac{1}{2}(\chi - \chi_a) AH^2$

10. $\chi_m^d = -\frac{Z Ne^2}{6\,mc^2}\sum r_i^2 = -2.832 \times 10^{10} r_i^2$

11. $\chi_m^P = \frac{N\mu_m^2}{3kT} = \frac{\text{constant}}{T}$

12. $\chi_m = \alpha_m - \frac{\mu_m^2 N}{3kT}$

13. $\mu_m = \sqrt{n(n+2)}$

14. $\chi_m = \frac{N}{3kT}[n(n+2)]$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. An equimolar mixture of (+) tartaric acid and (–) tartaric acid is called
   (a) enantiomer
   (b) optically active mixture
   (c) racemic mixture
   (d) asymmetric mixture
2. Dichlorobenzene exists in three isomers—*ortho, meta* and *para* isomers. Out of these three isomers, one with highest dipole moment will be

(a) *ortho*-isomer

(b) *meta*-isomer

(c) *para*-isomer

(d) all will have the same dipole moment.

3. A racemic mixture has

(a) zero optical rotation

(b) positive optical rotation

(c) negative optical rotation

(d) infinite optical rotation.

4. A net dipole moment of a molecule is

(a) sum of the all individual bond moments

(b) product of all individual bond moments

(c) vector resultant of all the individual bond moments

(d) none of the above

5. The substances which retain their magnetic field when removed from the magnetic field are called

(a) paramagnetic

(b) diamagnetic

(c) ferrimagnetic

(d) ferromagnetic

6. A diamagnetic substance is…..by/in the magnetic field.

(a) attracted

(b) repelled

(c) rotated

(d) revolved

7. The dipole moment of a polar substance is given by the formula, where q is the charge at one end and r is the distance between the opposite charges

(a) $\mu = q + r$

(b) $\mu = q - r$

(c) $\mu = q \times r$

(d) $\mu = q \div r$

8. A chiral molecule has

(a) no plane of symmetry

(b) one plane of symmetry

(c) infinite planes of symmetry

(d) none of these

9. The paramagnetism is due to the presence of

(a) paired electrons

(b) unpaired electrons

(c) both paired as well as unpaired electrons

(d) none of these

10. Optical activity is

(a) an additive property

(b) a constitutive property

(c) both an additive and constitutive property

(d) none of these

11. The magnetic moment, m, is given by a formula in which n is the number of unpaired electrons

(a) $\mu = n \times (n + 2)$

(b) $\mu = \sqrt{n \times (n + 1)}$

(c) $\mu \cdot \sqrt{n \times (n + 2)}$

(d) $\mu = n \times (n + 1)$

12. The molecules that are nonsuperimposible mirror images are called

(a) optical isomers

(b) racemic isomers

(c) enantiomers

(d) none of these

13. The necessary condition for a compound to be optically active is

(a) the presence of no chiral atom

(b) the presence of atleast one asymmetric atoms

(c) the presence of chirality in the molecule

(d) none of these

Answers

1. (c)
2. (a)
3. (a)
4. (c)
5. (d)
6. (b)
7. (c)
8. (b)
9. (b)
10. (b)
11. (c)

12. (c)
13. (c)

SHORT-ANSWER QUESTIONS

1. What information can dipole moment give about the structure of molecule? Give examples.
2. How can you justify the following?
   (a) O_2 has two unpaired electrons
   (b) $[Fe(CN)_6]^{3-}$ has less magnetic moment than $[FeF_6]^{3-}$, though both are octahedral.
   (c) Formula of hypophosphoric acid is $H_4P_2O_6$ and not H_2PO_3.
3. How can you differentiate between the following by dipole moment measurements?
   (a) *cis* and *trans* isomers of dichloroethane
   (b) o, *m* and *p*- isomers of dichlorobenzene.
4. What do you understand by additive and constitutive properties? Name some physical properties of molecules which are additive as well as constitutive.
5. Derive the relationship between
   (a) Magnetic moment of a substance and the number of unpaired electrons
   (b) Molar magnetic susceptibility and the number of unpaired electrons
6. What are the factors on which optical rotation depends? Derive an expression for specific rotation.
7. What is 'magnetic permeability'? Differentiate between diamagnetic, paramagnetic and ferromagnetic substances in terms of magnetic permeability.
8. Write an expression for total polarisation of a molecule. How does it help in determining the dipole moment of a substance?
9. What do you understand by internal compensation and external compensation in optical activity? Explain with suitable examples.
10. Briefly explain temperature method for measurement of dipole moment. How is the dielectric constant required determined?
11. What do you understand by magnetic induction, specific magnetic susceptibility and molar magnetic susceptibility?
12. How is dipole moment of a solid determined from molar polarisation studies?
13. How can molar magnetic susceptibility be used to find the magnetic moment of paramagnetic substance?
14. What is the cause of optical activity? How is measurement of optical rotation helpful in deciding chemical contribution of a substance?
15. Briefly explain the principle of refraction method for determining dipole moment of a substance.
16. How do you explain the action of magnetic field on diamagnetic and paramagnetic substances?
17. Write Clausius-Mosotti equation giving the relationship between distortion (or induced) polarisation and dielectric constant of the medium. What important result do you draw from it?

18. What is dipole moment? What are its units? How is dipole moment of a triatomic molecule calculated?

GENERAL QUESTIONS

1. Explain the effect of temperature on molar polarisation of molecules. How does it help in finding the dipole moment of a substance?
2. Define dipole moment. How is it determined by
   (a) Vapoure-Temperature method?
   (b) Refraction method?
3. What do you understand by 'optical rotation' and 'specific rotation'? How will you determine the specific rotation of a substance? Explain the principle of the instrument used.
4. Briefly describe at least five important applications of dipole moment in deciding chemical constitution.
5. Briefly explain the following terms:
   (a) Magnetic permeability
   (b) Magnetic induction
   (c) Specific magnetic susceptibility
6. Briefly explain the following terms:
   (a) Induced dipole moment
   (b) Induced or distortion polarisation
   (c) Orientation polarisation.
7. What is optical activity? What is the cause of optical activity? Briefly explain with suitable examples. How is measurement of optical rotation helpful in elucidating the chemical construction of a substance?
8. What do you understand by magnetic susceptibility? Briefly describe Gouy's method for its measurement. How does it help
   (a) in deciding the molecular structure of a substance?
   (b) in explaining the existence of odd electron molecules?
9. What do you understand by electrical polarisation of molecules? Derive Clausius-Mosotti equation.



Liquid-Liquid Mixtures

24

LEARNING OBJECTIVES

- Learn different modes of expressing concentration of a solution
- Classify liquid mixtures into different types
- Understand Raoult's law and its applications
- Define Henry'slaw in different ways
- Know different factors affecting the solubility of a gas in a liquid
- Appreciate different applications of Henry's law in real life situations
- Study limitations of Henry's law
- Derive Duhem-Margules equation
- Differentiate between ideal and non-ideal solutions
- Study vapour pressure-composition diagram for ideal and non-ideal solutions
- Derive Konowaloff's rule from Duhem-Margules equation
- Study the principle involved in the distillation of binary miscible solutions
- Define azeotropes and their different types
- Study the behaviour of immiscible liquids
- Understand the principle involved in steam distillation

24.1 INTRODUCTION

Most processes in chemistry and biochemistry are carried out in solution. These solutions could be solid in liquid, liquid in liquid or gas in liquid. In this chapter, we shall discuss the last two types in some detail. Solutions are generally two-component (binary) systems consisting of a solute and a solvent. The solubility of a liquid in another liquid is determined by the molecular structure of the solute and the solvent.

Mixtures of liquids can be classified into three types:

1. **Miscible Liquids** If both the components of a mixture are either polar or nonpolar, we get a liquid mixture of this type. Examples include methanol + water, benzene + toluene, *n*-hexane + *n*-heptane.
2. **Immiscible Liquids** If one of the liquids is polar and the other is nonpolar, we get this type of mixture. Examples are benzene + water, aniline + water, *n*-hexane + water, etc.
3. **Partially Miscible Liquids** If one of the liquids is slightly polar and the second is polar or nonpolar, we get this type of mixtures. Examples include phenol + water, triethylamine + water, nicotine + water.

There are several ways in which we can express the concentration of a solution. These are separately described as under:

1. Mass Percentage (w/w) Mass percentage of a component in a solution is defined as under:

$$\text{Mass \%} = \frac{\text{Mass of the component (solute or solvent)}}{\text{Total mass of the solution}} \times 100$$

2. Volume Percentage (v/v) It is expressed as under:

$$\text{Volume \%} = \frac{\text{Volume of the component (solute or solvent)}}{\text{Total volume of the solution}} \times 100$$

3. Mass by Volume Percentage (w/v) This unit is commonly used in medicine and pharmacy. It is expressed as under:

Mass by volume percentage = Mass of the solute dissolved in 100 mL of the solution

4. Part per Million This expression of concentration is used when the solute is present in traces. It is abbreviated as ppm

$$\text{Parts per million} = \frac{\text{Parts (mass or volume) of the solute}}{\text{Total parts (mass of volume) of the solution}} \times 10^6$$

The concentration of pollutants in water or atmosphere is often expressed in μg mL^{-1} or ppm

5. Mole Fraction It is another mode of expression of concentration. This mode is insulated from the volume change with variation of temperature.

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components in the solution}}$$

A commonly used symbol for mole fraction is *x*. For a solution containing two components *A* and *B*, if n_A and n_B are number of moles of *A* and *B* respectively in the solution, we have

$$x_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad x_B = \frac{n_B}{n_A + n_B}$$

It may be noted that sum of mole fraction of all the components of the solution is *unity*.

6. Molarity It is defined as number of moles of the solute dissolved in one litre of the solution. It is represented as **M**.

$$\text{Molarity} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in litre}}$$

For example, 0.2 M solution of NaOH means that 0.2 mole of NaOH has been dissolved in one litre of the solution.

7. Molality It is defined as the number of moles of the solute dissolved in 1000 g of the solvent. It is represented as *m*.

$$\text{Molality } (m) = \frac{\text{No. of moles of the solute}}{\text{Mass of the solvent in kg}}$$

Example 1 *Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.*

Solution: Mass of solution = Mass of the benzene + Mass of carbon tetrachloride
= 22 g + 122 g = 144 g

$$\text{Mass percentage of benzene} = \frac{\text{Mass of benzene}}{\text{Mass of the solution}} \times 100 = \frac{22\text{ g}}{144\text{ g}} \times 100 = 15.28$$

$$\text{Mass percentage of carbon tetrachloride} = \frac{\text{Mass of carbon tetrachloride}}{\text{Mass of the solution}} \times 100$$

$$= \frac{122\text{ g}}{144\text{ g}} \times 100 = 84.72\%$$

Example 2 *Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.*

Solution: Let the mass of the solution = 100 g

Then, mass of benzene = 30 g

Mass of carbon tetrachloride = (100 − 30) = 70 g

Molar mass of benzene (C_6H_6) = (6 × 12) + (6 × 1) = 78 g mol^{-1}

Molar mass of carbon tetrachloride (CCl_4) = (1 × 12) + (4 × 35.5) = 154 g mol^{-1}

Number of moles of benzene, $n_{C_6H_6} = \frac{30\text{ g}}{78\text{ g mol}^{-1}} = 0.385\text{ mol}$

Number of moles of carbon tetrachloride, $n_{CCl_4} = \frac{70\text{ g}}{154\text{ g mol}^{-1}} = 0.455\text{ mol}$

Mole fraction of benzene $x_{C_6H_6} = \frac{0.385}{0.385 + 0.455} = \frac{0.385}{0.84} = 0.458$

Mole fraction of carbon tetrachloride $x_{CCl_4} = 1 - 0.458 = 0.542$

Example 3 *Calculate the molarity of each of the following: (a) 30 g of Co $(NO_3)_2 \cdot 6H_2O$ in 4.3 L of solution (b) 30 mL of 0.5 MH_2SO_4 diluted to 500 mL.*

Solution

(a) Molar mass of Co $(NO_3)_2 \cdot 6H_2O$ = 58.7 + 2 (14 + 48) + (6 × 18) = 310.7 g mol^{-1}

Number of moles of Co $(NO_3)_2 \cdot 6H_2O = \frac{30\text{ g}}{310.7\text{ g mol}^{-1}} = 0.0966\text{ mol}$

Volume of the solution = 4.3 L

Molarity of solution = $\frac{0.0966}{4.3} = 0.022\text{ M}$

(b) 1000 mL of 0.5 M H_2SO_4 contain = 0.5 mol H_2SO_4

$$\therefore \quad 30\text{ mL of } 0.5\text{ M } H_2SO_4 \text{ contain} = \frac{0.5}{1000} \times 30\text{ mol } H_2SO_4 = 0.015\text{ mol}$$

Volume of the solution = 500 mL = 0.5 L

Molarity of the solution = $\frac{\text{Number of moles of the solution}}{\text{Volume of the solutiuon in L}}$

$$= \frac{0.015}{0.500} = 0.03 \text{ M}$$

Example 4 *Calculate the mass of urea (NH_2CONH_2) in making 2.5 kg of 0.25 molal aqueous solution.*

Solution: 0.25 molal aqueous solution of urea means 0.25 mole of urea is present in 1000 g of water

Molar mass of urea (NH_2 CO NH_2) = 60 g mol^{-1}

0.25 mole of urea = 0.25 × 60 g = 15 g of urea

Total mass of the solution = 1000 + 15 = 1015 g

Thus, 1.015 kg of solution contains 15 g urea

2.5 kg of solution will require $\frac{15}{1.015}$ × 2.5 = 37 g urea

Example 5 *Calculate (a) molality, (b) molarity, and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}.*

Solution: Let the mass of solution in water = 100 g

Mass of KI = 20 g

Mass of solvent = 100 − 20 = 80 g = 0.080 kg

(a) *Molality*

Molar mass of KI = 39 + 127 = 166 g mol^{-1}

Number of moles of KI = $\frac{20}{166}$ = 0.120

Molality of the solution = $\frac{\text{No. of moles of KI}}{\text{Mass of the solvent in kg}} = \frac{1.120}{0.080}$ = 1.5 m

(b) *Molarity*

Density of the solution = 1.202 g mol^{-1}

Volume of the solution = $\frac{100 \text{ g}}{1.202 \text{ g mL}^{-1}}$ = 83.2 mL = 0.0832 L $\left[\text{Volume} = \frac{\text{Mass}}{\text{Density}}\right]$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in } L} = \frac{0.120}{0.0832} = 1.44 \text{ M}$$

(c) *Mole fraction*

Number of moles of KI = 0.120

Number of moles of water = $\frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{80}{18}$ = 4.44

Mole fraction of KI = $\frac{0.120}{0.120 + 4.44} = \frac{0.120}{4.560}$ 0.0263

PROBLEMS FOR PRACTICE

1. Concentrated nitric acid used in the laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of solution is 1.504 g mL^{-1}? **[Ans.** 16.23 M]

2. A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole

fraction of each component in the solution? If the density of the solution is 1.2 g mL^{-1} then what shall be the molarity of the solution? **[Ans.** 0.67 M]

3. A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be carcinogen. The level of contamination was 15 ppm (by mass).

   (a) Express this in per cent by mass.

   (b) Determine the molality of chloroform in the water sample.

   [Ans. (a) 15×10^{-4} (b) 1.25×10^{-4} m]

4. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

   [Ans. Percentage of solute = 33.5, Percentage of solvent = 66.5]

5. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.

   [Ans. 4.575 g)]

6. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} then what shall be the molarity of the solution? **[Ans.** 9.11 M]

24.3 RAOULT'S LAW

Raoult's law states

"In a solution the vapour pressure of a component at a given temperature is equal to the mole traction of that component in the solution multiplied by the vapour pressure of that component in the pure state. Mathematically, it can be expressed as-

$$p_i = x_i \times p^\circ$$

In a ***binary*** solution,

Vapour pressure of the solvent in the solution = Mole fraction of the solvent in the solution × Vapour pressure of the pure solvent ... (24.1)

If the solute is nonvolatile, it will not contribute to the total vapour pressure of the solution. Thus, the vapour pressure of the solution will be the vapour pressure due to solvent in the solution only.

For such solutions, vapour pressure of the solution = Mole fraction of the solvent in solution × Vapour pressure of the pure solvent.



Fig. 24.1 *Francois Marie Raoult (1839-1901) French chemist. His work was mainly in solution properties.*

In terms of symbols, we can write

$$p_s = x_1 \times p^\circ \qquad \ldots(24.2)$$

This can be rewritten in the form,

$$\frac{p_s}{p^\circ} = x_1 \qquad \ldots(24.3)$$

We are using the subscript 1 for solvent and subscript 2 for the solute.

If the solution contains n_2 moles of the solute dissolved in n_1 moles of the solvent, we have

$$\text{Mole fraction of the solvent in the solution } (x_1) = \frac{n_1}{n_1 + n_2}$$

Substituting this value in Eq. (24.3), we get,

$$\frac{p_s}{p^\circ} = \frac{n_1}{n_1 + n_2}$$

Subtracting each side from 1, we get,

$$1 - \frac{p_s}{p^\circ} = 1 - \frac{n_1}{n_1 + n_2}$$

or

$$\boxed{\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1 + n_2}} \qquad \ldots(24.4)$$

In this expression, $p^\circ - p_s$ expresses the lowering of vapour pressure, $\frac{p^\circ - p_s}{p^\circ}$ is called relative lowering of vapour pressure, $\frac{n_2}{n_1 + n_2}$ represents the mole fraction of the solute in the solution. Mathematically, Eq. (24.4) may be stated as

The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

This is how we can define Raoult law in another way.

Example 6 *The vapour pressure of two pure liquids A and B are 15000 and 30000 Nm^{-2} at 298 K. Calculate the mole fraction of A and B in vapour phase when an equimolar solution of the liquids is made.*

Solution: $p_A^\circ = 15000 \text{ Nm}^{-2}$ and $p_B^\circ = 30000 \text{ Nm}^{-2}$

In equimolar solution, mole fractions of *A* and *B*, i.e. x_A and x_B, are equal. Let

$$x_A = x_B = 0.5. \quad x_A = 0.5, \quad x_B = 1 \quad 0.5 = 0.5$$

Applying Raoult's law of ideal solution

$$p_A = p_A^\circ x_A = 15000 \times 0.5 = 7500 \text{ Nm}^{-2}$$

and

$$p_B = p_B^\circ x_B = 30000 \times 0.5 = 15000 \text{ Nm}^{-2}$$

Total pressure

$$p = p_A + p_B = 7500 + 150000 = 225000 \text{ Nm}^{-2}$$

In the vapour phase,

$$\text{Mole fraction of } A = \frac{\text{Partial pressure of } A}{\text{Total pressure}} = \frac{7500}{22500} = 0.3333$$

Mole fraction of $B = 1 - 0.3333 = 0.6667$

Example 7 *The vapour pressures of pure components A and B are 120 mmHg and 96 mmHg. What will be the partial pressures of the components and the total pressure when the solution contains 1*

mole of the component A and 4 moles of the component B and the solution is ideal? What will be the composition in the vapour phase?

Solution: $p_A^\circ = 120$ mm, $p_B^\circ = 96$ mm

Here,

Mole fraction of A, $$x_A = \frac{\text{Number of moles of } A}{\text{Number of moles of } A + \text{No. of moles of } B}$$

$$= \frac{1}{1+4} = \frac{1}{5} = 0.2$$

Mole fraction of B, $x_B = 1 - 0.2 = 0.8$

Partial pressure of Component A, $p_A = p_A^\circ \times x_A = 120 \times 0.2 = 240$ mmHg

Partial pressure of B, $p_B = p_B^\circ \times x_B = 96 \times 0.8 = 76.8$ mm

Total pressure $= p_A + p_B = 24 + 76.8$ mm $= 100.8$ mm.

Mole fraction of A in vapour phase $= \frac{p_A}{\text{Total pressure}} = \frac{24}{100.8} = 0.238$

Mole fraction of B in vapour phase $= 1 - 0.238 = 0.762$

Example 8 *Liquid A (molecular mass 46) and liquid B (molecular mass 18) form an ideal solution. At 293 K, the vapour pressures of pure A and B are 44.5 and 17.5 mm Hg respectively. Calculate (a) the vapour pressure of solutions of A in B containing 0.2 mole fractions of A, and (b) the composition of the vapour phase.*

Solution:

(a) $p_A^\circ = 44.5$ mm. $x_A = 0.2$, $p_B^\circ = 17.5$ mm, $x_B = (1 - 0.2) = 0.8$

According to Raoult's law,

$$p_A = p_A^\circ \cdot x_A$$

Partial pressure of A, $p_A = p_A^\circ x_A = 44.5 \times 0.2 = 8.9$ mm.

Partial pressure of B, $p_B = p_B^\circ x_B = 175 \times 0.8 = 14.0$ mm.

Total pressure $p = p_A + p_B = 8.9 + 14 = 22.9$ mm.

(b) In vapour phase,

Mole fraction of $$A = \frac{\text{Partial pressure of } A}{\text{Total pressure}}$$

or $$x_A = \frac{P_A}{P_A + P_B} = \frac{8.9}{8.9 + 14} = \frac{8.9}{22.9} = 0.39$$

$$x_B = 1 - 0.39 = 0.61$$

Example 9 *Benzene (C_6H_6 b.p. 353.1 K) and toluene (C_7H_8, b.p. 383.6 K) are two hydrocarbons that form a very nearly ideal solution. At 313 K, the vapour pressure of pure liquids are 160 mm Hg and 60 mm Hg respectively. Assuming an ideal solution behaviour, calculate the partial pressures of benzene and toluene and the total pressure over the following solutions:*

(a) One made by combining equal number of toluene and benzene

(b) One made by combining 4 mol of toluene and 1 mol of benzene

(c) One made by combining equal masses of toluene and benzene

Solution:

(a) When the number of molecules of toluene and benzene are equal, it means the number of moles of the two liquids are also equal.

Thus, mole fraction of benzene $x_A = \frac{1}{1+1} = 0.5$

and mole fraction of toluene $x_B = 1 - 0.5 = 0.5$

According to Raoult's law, $p = p^\circ \cdot x$

Partial pressure of benzene, $p_A = p_A^\circ \cdot x_A = 160 \times 0.5 = 80$ mm

Partial pressure of toluene, $p_B = p_B^\circ x_B = 60 \times 0.5 = 30$ mm

Total vapour pressure $p_A + p_B = 80 + 30 = 110$ mm

(b) Mole fraction of benzene, $x_A = \frac{1}{1+4} = \frac{1}{5} = 0.2$

Mole fraction toluene, $x_B = 1 - 0.2 = 0.8$

Partial pressure of benzene, $p_A = p_A^\circ x_A = 160 \times 0.2 = 32$ mm

Partial pressure of toluene, $p_B = 60 \times 0.8 = 48$ mm

Total vapour pressure $p_A + p_B = 32 + 48 = 80$ mm

(c) Here, the masses of the two liquids are the same. Let the amount of each be mg.

Then mole fraction of benzene, $x_A = \frac{m/78}{m/78 + m/92} = 0.541$

Mole fraction of toluene, $x_B = 1 - 0.541 = 0.459$

Partial pressure of benzene, $p_A = p_A^\circ x_A = 160 \times 0.541 = 86.56$ mm of Hg

Partial pressure of toluene, $p_B = p_B^\circ x_B = 60 \times 0.459 = 27.54$ mmHg

Total vapour pressure = 86.56 + 27.54 = 114.1 mmHg

Example 10 *The vapour pressure of pure liquids A and B are 450 and 700 mmHg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mmHg. Also find the composition of the vapour phase.*

Solution:

$p_A^\circ = 450$ mm, $p_B^\circ = 700$ mm, $p_{total} = 600$ mm

Applying Raoult's law,

$$p_A = x_A \times p_A^\circ$$
$$p_B = x_B \times p_B^\circ = (1 - x_A) p_B^\circ$$
$$p_{total} = p_A + p_B = x_A p_A^\circ + (1 - x_A) p_B^\circ$$
$$= p_B^\circ + (p_A^\circ - p_B^\circ) x_A$$

Substituting the values in the above equation, we get

$$600 = 700 + (450 - 700) x_A \quad \text{or} \quad 250 x_A = 100 \quad \text{or} \quad x_A = \frac{100}{250} = 0.4$$

Thus, the composition of the liquid mixture will be

$$x_A = 0.4, \quad x_B = 1 - 0.4 = 0.6$$
$$p_A = x_A \times p_A^\circ = 0.40 \times 450 \text{ mm} = 180 \text{ mm}$$
$$p_B = x_B \times p_B^\circ = 0.60 \times 700 \text{ mm} = 420 \text{ mm}$$

Mole fraction of A in the vapour phase $= \dfrac{p_A}{p_A + p_B} = \dfrac{180}{180 + 120} = 0.3$

Mole fraction B in the vapour phase = 1 − 0.30 = 0.70

PROBLEMS FOR PRACTICE

1. Vapour pressure of pure water at 298 K is 23.8 mmHg. 50 g of urea (NH_2 CO NH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

[Ans. V.P. of water = 23.4 mm, Relative lowering = 0.017]

2. An aqueous solution of 2% nonvolatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute? **[Ans.** 41.35 g mol^{-1}]

3. The vapour pressure of water is 12.3 kPa at 300 K. Calculate the vapour pressure of 1 molal solution of a nonvolatile solute in it. **[Ans.** 12.08 kPa]

4. Calculate the mass of a nonvolatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce the vapour pressure to 80%. **[Ans.** 10 g]

5. A solution containing 30 g of nonvolatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate

   (a) Molar mass of the solute

   (b) Vapour pressure of water at 298 K.

[Ans. (a) 23 g mol^{-1} (b) 3.53 kPa]

6. 100 g of Liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of Liquid B (molar mass 180 g mol^{-1}). Vapour pressure of pure liquid B was found to be 500 torr. Calculate (a) the vapour pressure of pure liquid A, and (b) its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr.

[Ans. (a) 280.7 torr (b) 32 torr]

24.4 HENRY'S LAW

Henry's law states

"The mass of a gas dissolved in a given volume of a liquid at constant temperature is directly proportional to the pressure of the gas present in equilibrium with the liquid."

Mathematically, $m \propto p$

or $m = kp$ ...(24.5)

where m = Mass of the gas dissolved in a unit volume of solvent.

p = Pressure of the gas in equilibrium with the solvent, and

k = Constant called ***Henry's law constant.*** It is characteristic of the nature of the gas, the nature of the solvent and the temperature.

This is further illustrated with the help of Fig. 24.12.

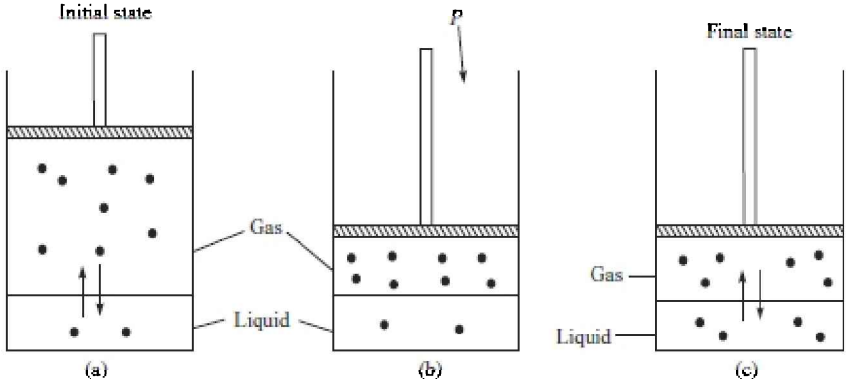


Fig. 24.2 *(a) Equilibrium exists between the gas molecules and those in solution. (b) When pressure is applied, gas volume decreases and concentration in gas phase increases. (c) More gas molecules pass into solution to re-establish equilibrium whereby the pressure above the gas is decreased.*

Figure 24.2 explains how the concentration of the gas in the solvent increases with rise of pressure. second statement of Henry's law is

"The ***volume of a gas dissolved in a liquid measured at the pressure used, is independent of the pressure."***

The second statement of Henry's law is just a corollary of the first. This can be proved as under:

Suppose volume of the liquid taken = Vml

Pressure of the gas = p mm

Mass of the gas dissolved = m grams

Obviously, volume of the gas dissolved = Vml

Now, suppose if the pressure is doubled = $2p$

$\therefore$ The mass of the gas dissolved will be = $2m$

But volume of m grams of the gas at pressure p = Vml

$\therefore$ volume of $2m$ grams of the gas at pressure p = 2 Vml

or volume of $2m$ grams of the gas at pressure $2p$ = Vml

(by Boyle's law, volume and pressure are inversely related)

Thus, the volume of the gas dissolved at pressure $2p$ is again the same, viz. V ml.

The quantitative relation between the pressure and solubility of a gas as put forwarded by Henry may be stated as:

"The solubility of a gas in a liquid is directly proportional to the pressure of the gas at a constant temperature". This is another statement of Henry's law.

If we use the mole fraction of the gas in the solution as a measure of its solubility then it can be said that

"The mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution". This is just another statement of the law.

The most commonly used from of Henry's law states that ***the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.*** Mathematically, the law may be expressed as

$$p = K_H x \quad \ldots(24.6)$$

K_H is Henry's law constant. Different gases have different K_H values at the same temperature meaning K_H is a function of the nature of the gas. Table 24.1 gives the values of K_H for different gases in water.

K_H values ofsome gases in water

Gas	Temperature *(K)*	K_H *(k*bar)
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	303	46.82
CO_2	298	1.67



Fig. 24.3 *William Henry (1775-1836) English chemist. His major contribution to science was his law governing solubility of gases in liquids.*

Equation (24.6) above shows that higher the value of K_H at a given pressure (p), lower is the solubility of gas in the liquid. Thus, CO_2 which has a very low value of K_H has very high solubility in water. Oxygen dissolves to a small extent in water (see Table 24.1). It is this oxygen which sustains aquatic life.

We find from Table 24.1 that K_H values for both N_2 and O_2 increase with increase of temperature indicating that solubility increases with decrease of temperature. It is due to this reason that aquatic animals feel more comfortable in cold water than in warm water due to greater concentration of O_2 in water. It is quite surprising that when the surface of a water body freezes due to extremely cold weather, the aquatic animals move comfortably beneath it.

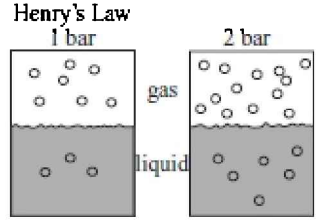


Fig. 24.4 *Representation Henry's law*

Extremely cold weather conditions convert the surface water of water bodies into ice. Ice, being lighter, floats over the surface of water (water at 4°C has the maximum density, it forms the lower layer). Aquatic animals survive in this water below the layer of ice. In fact, they are more comfortable due to greater availability of oxygen and nitrogen.

24.4.1 Applications of Henry's Law

1. Soft drinks give out fizz due to the pressure of CO_2 in them. Greater the concentration (solubility) of CO_2, greater will be the fizz and taste. To obtain the maximum fizz, cold-drink bottles are sealed under high pressure.
2. Scuba divers face problems under deep water while breathing air from the cylinders. Increased pressure downwater increases the solubility of atmospheric gases in the blood. When divers come to the surface, the pressure gradually decreases thus reducing solubility of atmospheric gases. This results in the release of dissolved gases which causes formation of bubbles of nitrogen in the blood. Remember N_2 is less soluble in blood compared to O_2 and hence is released in priority. This creates a medical condition called ***bends*** which are painful and dangerous to life. To guard against this problem, the cylinders used by scuba divers are filled with air containing 11.7% helium, 56.2% nitrogen and 32.1% oxygen to avoid problem arising out of high concentration of nitrogen.
3. A different problem is faced at high altitudes. Partial pressure of oxygen is less than that at the ground level. This causes low concentration of oxygen (as per Henry's law) in the blood and tissues of people living there, or the climbers. Low blood oxygen makes climbers weak and unable to think, a condition known as ***anoxia.***

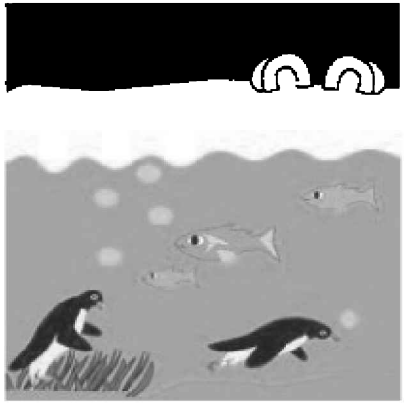


Fig. 24.5 *How do aquatic animals survive in icy water?*

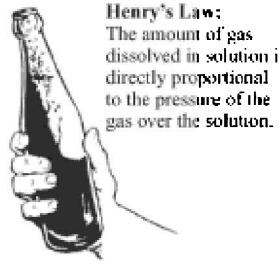


Fig. 24.6 *Sealing of carbonated drink bottles*

24.4.2 Factors Affecting Solubility of a Gas

The following factors affect the solubility of a gas in a liquid,

1. Nature of the Gas and the Solvent Gases like hydrogen, oxygen, nitrogen, etc., dissolve in water only to a small extent whereas gases like CO_2, HCl, NH_3, etc., are highly soluble. The greater solubility of the latter gases is due to their reaction with the solvent.

Again, oxygen, nitrogen and carbon dioxide are much more soluble in ethyl alcohol than in water at the same temperature and pressure while H_2S and NH_3 are more soluble in water than in ethyl alcohol. Evidently, the greater solubility of gas is again due to the chemical similarity between the gas and the solvent.

2. Effect of Pressure This is the most important factor influencing the solubility of a gas in a liquid at a particular temperature. It is governed by ***Henry's law*** according to which the solubility increases with the increase of pressure.

3. Effect of Temperature ***The solubility of a gas decreases with increase in temperature.*** This is expected because on heating the solution of a gas, some gas is usually expelled out of the solution. The same result also follows in an alternate manner:

The dissolution of a gas in a liquid is an exothermic process, i.e. it is accompanied by evolution of heat, i.e.

$$\text{Gas} + \text{Solvent} \rightleftharpoons \text{Solution} + \text{Heat}$$

Applying Le Chatelier's principle, it is evident that increase of temperature would shift the equilibrium in the backward direction, i.e. the solubility would decrease.

It may be pointed out though generally the solubility of a gas in a liquid decreases with increase of temperature, there are some exceptions. For example, the solubility of some sparingly soluble gases, such as hydrogen and inert gases, increases slightly with increase of temperature, especially in the non-aqueous solvents such as hydrocarbons, alcohols and acetone.

24.4.3 Limitations of Henry's Law

Henry's law is applicable only if the following conditions are satisfied:

1. ***The pressure should be low and the temperature should be high, i.e. the gas should behave like an ideal gas.***
2. ***The gas should not be involved in compound formation with the solvent. It should not undergo association in the solvent.***

Thus, the law is not applicable in case of dissolution of ammonia in water because it forms a compound and then there is dissociation.

$$NH_3(g) + H_2O \rightarrow NH_4OH(aq.)$$

$$NH_4OH(aq.) \rightleftharpoons NH_4^+(aq.) + OH^-(aq.)$$

Similarly, the law is not applicable in the dissolution of HCl gas in water because it undergoes

dissociation after dissolution.

$$HCl(g) + aq \rightarrow HCl(aq.)$$

$$HCl(aq.) \rightarrow H^{+}(aq.) + Cl^{-}(aq.)$$

Example 11 *The solubility of pure oxygen in water at 20°C and 1.00 atmosphere pressure is 1.38 × 10^{-3} mole/litre. Calculate the concentration of oxygen at 20°C and partial pressure of 0.20 atmosphere.*

Solution: *Calculation of k*

$$m = kp \qquad \text{Refer Eq. (24.5),}$$

or

$$k = \frac{m}{p}$$

Substituting the values for pure oxygen,

$$k = \frac{1.38 \times 10^{-3} \text{ mole/litre}}{1.00 \text{ atm}} = 1.38 \times 10^{-3} \frac{\text{mol/litre}}{\text{atm}}$$

Calculation of concentration of O_2 at given pressure

$$m = kp$$

Concentration of $O_2 = 1.38 \times 10^{-3} \frac{\text{mol/litre}}{\text{atm}} \times 0.20 \text{ atm} = 2.76 \times 10^{-4}$ mole/litre

Example 12 *H_2S, a toxic gas with rotten-egg-like smell, is used for qualitative analysis of cations. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry 's law constant.*

Solution: Solubility of H_2S gas = 0.195 m, i.e. 0.195 moles in 1 kg of solvent (water)

$$1 \text{ kg of solvent water} = 1000 \text{ g} = \frac{1000}{18} = 55.55 \text{ moles}$$

$$\therefore \text{ Mole fraction of } H_2S \text{ gas in the solution } (x) = \frac{0.195}{0.195 + 55.55} = 0.0035$$

Pressure at STP = 0.987 bar (1 atm = 0.987 bar)

Applying Henry's law,

$$p_{H_2S} = k_H \times x_{H_2S}$$

or

$$k_H = \frac{p_{H_2S}}{x_{H_2S}} = \frac{0.987 \text{ bar}}{0.0035} = 282 \text{ bar}$$

Example 13 *Henry 's law constant for CO_2 in water is 1.67 × 10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.*

Solution: $k_H = 1.67 \times 10^8$ Pa, $p_{CO_2} = 2.5$ atm $= 2.5 \times 101325$ Pa

Applying Henry's law,

$$p_{CO_2} = k_H \times x_{CO_2} \quad \text{or} \quad x_{CO_2} = \frac{p_{CO_2}}{k_H}$$

Substituting the values, we get

$$x_{CO_2} = \frac{2.5 \times 101325 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}} = 1.517 \times 10^{-3}$$

or $$\frac{n_{CO_2}}{n_{H_2O} + n_{CO_2}} \simeq \frac{n_{CO_2}}{n_{H_2O}} = 1.517 \times 10^{-3}$$

In 500 mL of soda water, number of moles of water $= \frac{500}{18} = 27.78$ moles

$\therefore$ $$\frac{n_{CO_2}}{27.78} = 1.517 \times 10^{-3}$$

or $$n_{CO_2} = 27.78 \times 1.517 \times 10^{-3} \text{ mole}$$
$$= 42.14 \times 10^{-3} \times 44 \text{ g}$$
$$= 1.854 \text{ g}$$

Example 14 *If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolved in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 k bar.*

Solution: Apply the relation

$$p_{N_2} = k_H \times x_{N_2}$$

where p_{N_2} and x_{N_2} represent partial pressure N_2 and mole fraction of N_2 in the solution respectively. Substituting the values, we get

$$0.987 \text{ bar} = 76480 \text{ bar} \times x_{N_2}$$

Mole fraction of $$N_2(x_{N_2}) = \frac{0.987 \text{ bar}}{76480 \text{ bar}} = 1.29 \times 10^{-5}$$

Let n be the number of moles of N_2 in one litre of solution.

Number of moles of water in 1 litre $= \frac{1000}{18} = 55.5$ (approx)

Mole fraction of $N_2(x_{N_2}) = \frac{n \text{ moles}}{n \text{ moles} + 55.5 \text{ moles}} \simeq \frac{n}{55.5}$ [Neglecting n compared to 55.5]

or $$1.29 \times 10^{-5} = \frac{n}{55.5}$$

or $$n = 1.29 \times 10^{-5} \times 55.5 = 7.16 \times 10^{-4} \text{ mol}$$
$$= 7.16 \times 10^{-4} \times 10^3 \text{ m mole}$$
$$= 0.716 \text{ m mole}$$

PROBLEMS FOR PRACTICE

1. The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{2} g of ethane then what shall be the partial pressure of the gas?

[Ans. 0.762 bar]

2. Henry's law constant for the solubility of methane in benzene at 298 K is 4.27×10^{5} mm Hg. Calculate the solubility of methane in benzene at 298 K.

[Ans. Mole fraction of methane in benzene = 1.78×10^{-3}]

24.5 DUHEM-MARGULES EQUATION

Let us consider a liquid mixture of two components in equilibrium with their vapour. ***At constant temperature and pressure,*** the condition for an infinitesimal change of composition is give by Gibbs-Duhem equation in the form

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad \ldots(24.7)$$

where n_1 and n_2 are the number of moles of constituents 1 and 2 respectively in the solution and μ_1 and μ_2 are their chemical potentials.

Dividing Eq. (24.7) by $n_1 + n_2$, we get

$$\frac{n_1}{n_1 + n_2} d\mu_1 + \frac{n_2}{n_1 + n_2} d\mu_2 = 0$$

or

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \qquad \ldots(24.8)$$

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

where x_1 and x_2 represent the mole fractions of the components 1 and 2 in the mixture (solution).

The chemical potential of any component in the mixture depends upon temperature, pressure and composition of the mixture. If the temperature and pressure are kept constant, the chemical potential depends only upon the composition. Then for any infinitesimal change of composition, we may write

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 \qquad \ldots(24.9)$$

and

$$d\mu_2 = \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} dx_2 \qquad \ldots(24.10)$$

Substituting these values in Eq. (24.8), we get

$$x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} dx_2 = 0 \qquad \ldots(24.11)$$

We know that the sum of the mole fractions of components in a mixture is unity.

or

$$x_1 + x_2 = 0$$

Hence,

$$dx_1 + dx_2 = 0$$

or

$$dx_1 = -dx_2 \qquad \ldots(24.12)$$

Substituting this value in Eq. (24.11) and cancelling the common factor dx_2, we get

$$x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} - x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} = 0$$

or
$$x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} \quad \ldots(24.13)$$

The chemical potential of any constituent of liquid mixture is given by,

$$\mu = \mu_0 + RT \ln p \quad \ldots(24.14)$$

where p is the partial pressure of that constituent.

Differentiating Eq. (24.14) w.r.t. x at constant temperature, we get

$$\frac{\partial \mu}{\partial x} = RT \frac{d \ln p}{dx}$$

For the constituents 1 and 2, we can write two separate equations given below:

$$\frac{\partial \mu_1}{\partial x_1} = RT \frac{d \ln p_1}{dx_1} \quad \ldots(24.15)$$

$$\frac{\partial \mu_2}{\partial x_2} = RT \frac{d \ln p_2}{dx_2} \quad \ldots(24.16)$$

Substituting these values in Eq. (24.13) and simplifying, we get

$$x_1 \frac{d \ln p_1}{dx_1} = x_2 \frac{d \ln p_2}{dx_2} \quad \ldots(24.17)$$

It can also be written in the form,

$$\frac{d \ln p_1}{d \ln x_1} = \frac{d \ln p_2}{d \ln x_2} \quad \ldots(24.18)$$

Equations (24.17) and (24.18) are two different forms of Duhem-Margules equation.

These equations are used in the derivation of Konowaloff's rule which is useful in the binary liquid mixtures by distillation.

24.6 COMPLETELY SOLUBLE LIQUIDS

1. Ideal Solutions ***A solution of two components is said to be ideal if each component of the solution obeys Raoult's law at all temperatures and concentrations. That is, vapour pressure of each component in the solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state at the same temperature.*** Thus, if two liquids A and B are mixed together, the solution formed by them will be ideal if the following relations hold.

$$p_A = x_1 \times p_A^\circ$$
$$p_B = x_B \times p_B^\circ$$

and

where, p_A = Vapour pressure of component A in the solution

x_A = Mole fraction of the component A in the solution

p_A° = Vapour pressure of the liquid A in the pure state

p_B, x_B and p_B° are the corresponding terms for the component B.

It is observed that the ***solution formed by two liquids A and B is ideal if the interactions (i.e. the intermolecular forces of attraction) among the molecules of A and B in the solution are just the same as among the molecules of pure A or B.***

It is observed that ***the solution formed on mixing the two liquids is ideal if***

(a) ***there is no volume change on mixing,*** i.e. $\Delta V_{mix} = 0$

(b) ***there is no enthalpy change on mixing,*** i.e. $\Delta H_{mix} = 0$

For example, if 50 ml *n*-hexane is mixed with 50 ml of *n*-heptane, the total volume of the solution is found to be 100 ml and the temperature of the solution is found to be the same as that of pure *n*-hexane and *n*-heptane before mixing. It shows that no heat is evolved or absorbed on mixing. Such a solution is an ideal solution.

2. Non-ideal Solution A solution formed by mixing two liquids is said to be non-ideal if it does not obey Raoult's law or the interactions of *A* and *B* molecules in the solution are not similar to those of pure *A* and pure *B*

or $$\Delta V_{mix.} \neq 0 \quad \text{and} \quad \Delta H_{mix.} \neq 0$$

24.7 | VAPOUR PRESSURE COMPOSITION DIAGRAM FOR IDEAL SOLUTIONS

In case of ideal solutions, the partial pressure of each component can be calculated using Raoult's law, i.e.

$$p_A = x_A \times p_A^\circ$$

and $$p_B = x_B \times p_B^\circ$$

where, p_A, p_A°, p_B and p_B° are measured at the same temperature.

Thus, $$p_{sol} = x_A p_A^\circ + x_B p_B^\circ$$

At any particular temperature, we can determine the values of $P_{sol.}$ experimentally for different mole fractions. The values P_A° and P_B° for the pure liquids can be measured at the same temperature and hence, P_A and P_B can be calculated for any particular mole fraction. For an ideal solution, the straight-line plots are obtained for vapour pressure vs. composition as shown in Fig. 24.7. The dotted lines represent the plots of the partial pressure and the solid line that of the solution.

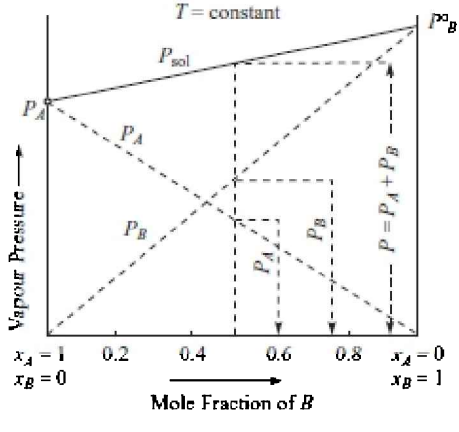


Fig. 24.7 *Vapour-pressure composition diagram for an ideal solution*

In these plots, for any mole fraction, the total vapour pressure of the solution is the sum of the partial pressures of its components *A* and *B*.

24.8 | VAPOUR PRESSURE COMPOSITION CURVES FOR NON-IDEAL SOLUTIONS (DERIVATION FROM IDEAL BEHAVIOUR)

In case of non-ideal solutions, the plots of vapour pressure vs. composition (mole fraction) are curved lines. Non-ideal solutions are divided into the following three types:

Type I *Those which show small positive deviation from Raoult law.* The vapour-pressure composition graphs of these solutions are slightly upward as shown in Fig. 24.8. The dotted straight plots are for ideal solutions calculated by using Raoult's law.

Examples of solutions of this type are benzene + toluene, water + methyl alcohol, carbon tetrachloride + cyclohexane, etc.

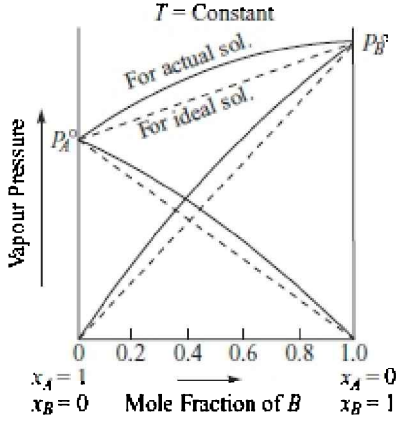


Fig. 24.8 *Vapour-pressure composition plots for non-ideal solution showing small positive deviation.*

Type II *Those which show large positive deviation from Raoult's law.* The vapour-pressure composition plots of these solutions curve upwards considerably as shown in Fig. 24.9. The dotted straight line plots, included in the figure are for ideal solution (calculated by using Raoult's law).

We can see from Figs. 24.8 and 24.9 that for any mole fraction, the total vapour pressure of the solution is more than that for ideal solution. This means that the tendency for molecules to escape from solution is more than from the pure liquids. In such solutions, the intermolecular forces of attraction between the molecules of the solution (*A*-*B* attractions) are weaker than those of either of the pure components (*A*-*A* attractions or *B*-*B* attractions). Such a behaviour is associated with an increase in volume and absorption of heat on mixing.

Some examples of liquid pairs showing large positive deviation include water + ethanol, ethanol + chloroform.

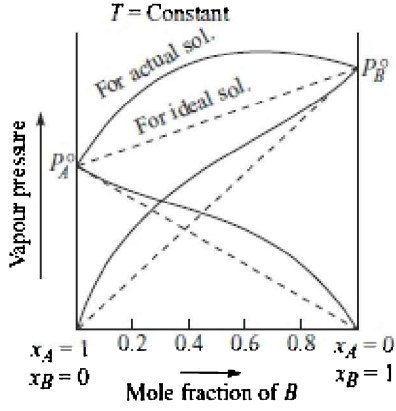


Fig. 24.9 *Vapour-pressure composition plots for non-ideal solution showing large positive deviation*

Type III ***Those which show negative deviation from Raoult's law.*** The vapour-pressure composition plots of these solutions curve downwards as shown in Fig. 24.10. The dotted straight-line plots are for the ideal solution calculated on the basis of Raoult's law and are included in the figure. We can see from the figure that for any mole fraction, the total vapour pressure of the solution is less than that of ideal solution. This means that the tendency for the molecules to escape from the solution is less than that from the pure liquid. In such solutions, the intermolecular forces of attraction between the molecules of the solution (*A*-*B* attractions) are stronger than those of either of the pure components (*A*-*A* attractions or *B*-*B* attractions). It causes contraction in volume and evolution of heat in making the solution.

Some examples of the liquid pairs showing negative deviation are water + nitric acid, water + sulphuric acid, acetone + chloroform, etc.

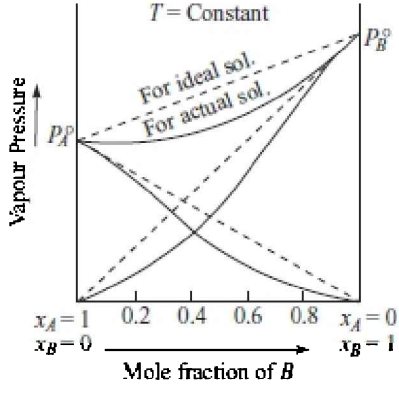


Fig. 24.10 *Vapour-pressure composition plots for non-ideal solution showing negative positive deviation*

24.9 PRINCIPLE OF DISTILLATION OF BINARY MISCIBLE LIQUIDS

1. Konowaloff's Rule Konowaloff's rule states that ***in case of ideal solutions or solutions showing small positive or negative deviations, at any fixed temperature, the vapour phase is always richer in the more volatile component as compared to the solution phase. In other words, the mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.***

The rule is very useful in the separation of binary liquid solutions by distribution.

Deviation of Konowaloff's Rule from the Duhem-Margules Equation

According of Duhem-Margules equation,

$$x_1 \frac{d \ln p_1}{dx_1} = x_2 \frac{d \ln p_2}{dx_2} \qquad \ldots(24.19)$$

It works out to

$$\frac{x_1}{dx_1} \frac{dp_1}{p_1} = \frac{x_2}{dx_2} \frac{dp_2}{p_2} \qquad \ldots\left(\because d \ln p = \frac{dp}{p}\right)$$

or

$$\frac{x_1}{p_1} \frac{dp_1}{dx_1} = \frac{x_2}{p_2} \frac{dp_2}{dx_2} \qquad \ldots(24.20)$$

But $x_1 + x_2 = 1$ (sum of mole fractions = 1)

$\therefore$ $dx_1 + dx_2 = 0$ or $dx_1 = -dx_2$

$\therefore$Eq. (24.20) takes the form,

$$\frac{x_1}{p_1} \frac{dp_1}{dx_1} = -\frac{x_2}{p_2} \frac{dp_2}{dx_1} \qquad \ldots(24.21a)$$

or

$$\frac{dp_1}{dx_1} = -\frac{x_2}{x_1} \frac{p_1}{p_2} \frac{dp_2}{dx_1} \qquad \ldots(24.21b)$$

The total vapour pressure p is the sum of partial pressures or the components.

$$p = p_1 + p_2 \quad \text{or} \quad dp = dp_1 + dp_2$$

or

$$\frac{dp}{dx_1} = \frac{dp_1}{dx_1} + \frac{dp_2}{dx_1} \qquad \ldots(24.22)$$

Substituting the value of dP_1/dx_1 from Eq. (24.21b) in Eq. (24.22) we get

$$\frac{dp}{dx_1} = -\frac{x_2 p_1}{x_1 p_2} \frac{dp_2}{dx_1} + \frac{dp_2}{dx_1}$$

$$= \frac{dp_2}{dx_1}\left(1 - \frac{x_2 p_1}{x_1 p_2}\right) \qquad \ldots(24.23)$$

Also, we have

$$dx_1 = -dx_2 \quad \therefore \quad \frac{dp_2}{dx_1} = -\frac{dp_2}{dx_2}$$

Thus, $\frac{dp_2}{dx_1}$ is a negative quantity. Hence, according to Eq. (24.23), $\frac{dp}{dx_1}$ can be positive only when

$$\frac{x_2 p_1}{x_1 p_2} > 1 \quad \text{or} \quad \frac{p_1}{p_2} > \frac{x_1}{x_2}$$

This means that the vapour is richer in component 1 (or A) than in the liquid from which it vaporises. This is what is implied by konowaloff's rule

2. Vapour Pressure-Liquid Composition and Vapour Pressure-Vapour Composition Curves for Liquid Mixtures At any particular temperature, the composition of the vapour phase is not the same as that of the liquid phase. Hence, we have different ***vapour pressure-vapour composition curves.*** At any particular temperature, these can be obtained by measuring the vapour pressure as well as the composition of the vapour phase corresponding to each composition of the liquid mixture.

For the real solutions, there are three types of vapour pressure-composition diagrams:

Type I ***Those in which total vapour pressure is intermediate between those of the pure components and do not show any maximum and minimum.***

Type II ***Those which show a maximum in the total vapour pressure curve.***

Type III ***Those which show a minimum in the total vapour pressure curve.***

The vapour pressure-liquid composition curves as well as the vapour pressure-vapour composition curves of all the three types are shown in Fig. 24.11 in which Liquid *B* is more volatile than Liquid *A*.

It may be observed that in all the three types, the vapour composition curve lies below the liquid composition curve. This is explained for each type as under:

(a) In Type I, as *B* is more volatile than *A*, corresponding to the composition *a* of the liquid phase, vapour pressure will be richer in *B*, i.e. corresponding to the composition *a*′.

(b) In Type II, up to the point *C*, behaviour is the same as in Type I, at *C*, the liquid phase and the vapour phase have the same composition and after point *C*, the vapour phase is richer in *A* (or less rich in B) as seen from points *c* and *c*′.

(c) In Type III, up to the point *D*, the vapour phase is richer in *A* (or less rich in *B*) than the liquid phase. At the point *D*, both have the same composition and after the point *D*, the behaviour is similar to Type I. This can be seen from points *d*, *d*′, *e* and *e*′.

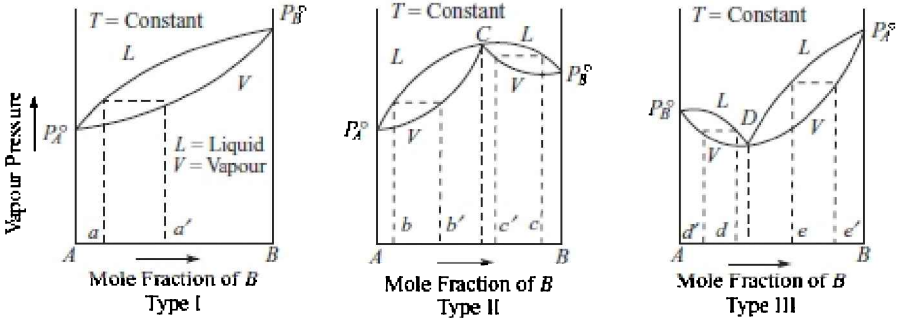


Fig. 24.11 *Vapour-pressure composition diagrams ofbinarymiscible realsolution atconstant temperature.*

3. Boiling Point Composition Diagrams for Liquid Mixtures

Boiling point is defined as the temperature at which the total vapour pressure becomes equal to the atmospheric pressure. Thus, a liquid or a solution having low vapour pressure will have a higher boiling point because it has to be heated more to make the vapour pressure equal to the atmospheric pressure. Thus, pure liquid *A* which has less vapour pressure will have a higher boiling point, and the pure liquid *B* which has higher vapour pressure will have lower boiling point. Similarly, a solution of any composition having lower vapour pressure will have higher boiling point. These facts help us construct the boiling-point composition diagrams from the vapour-pressure composition diagrams as shown in Fig. 24.12.

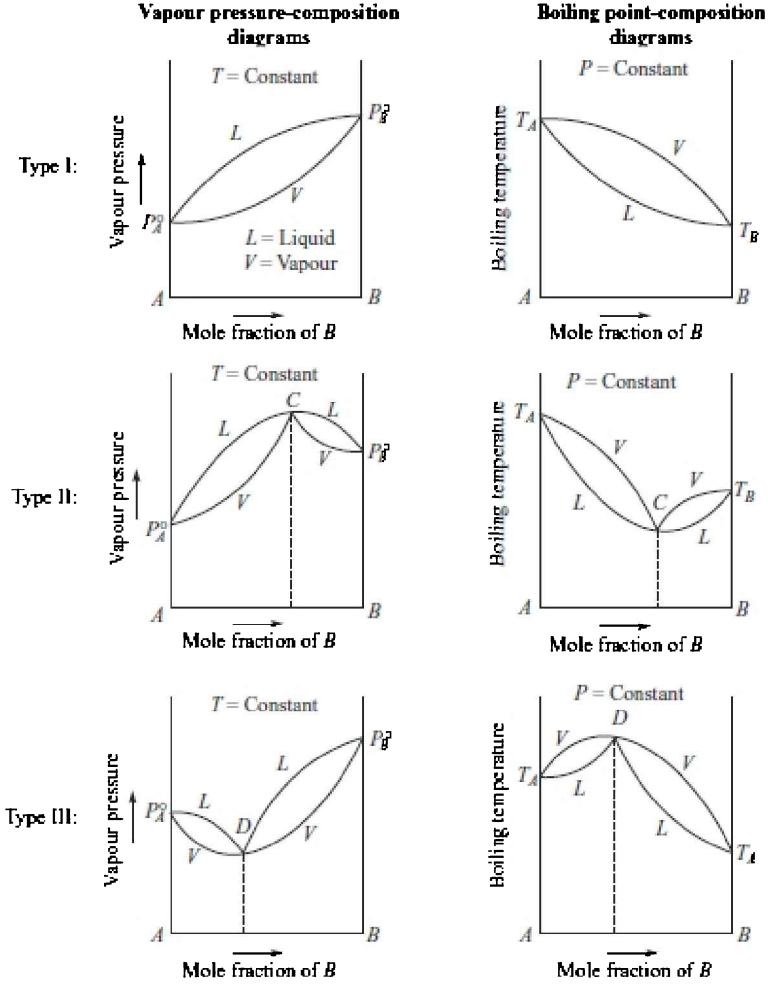


Fig. 24.12 *Boiling-point composition diagrams constructed from the vapour-pressure composition diagrams of binary miscible solutions.*

The point C in Type II, which corresponds to maximum vapour pressure, represents the lowest boiling point. Similarly, the point D in Type III, which represents the lowest vapour pressure, corresponds to the highest boiling point. The liquid mixtures having compositions corresponding to points C and D having constant boiling points are called ***azeotropes.***

24.10 | ISTILLATION OF BINARY MISCIBLE SOLUTIONS

Distillation of Solutions of Type I (Fractional Distillation).

The boiling-temperature composition diagram for such a solution involving the liquids A and B in which 'B' is more volatile than 'A' is explained with the help of Fig. 24.13.

Suppose we have a solution corresponding to the composition '*a*'. No boiling will start until temperature T_a is reached. The composition of the vapour phase at this stage will be *a'*, i.e. it is richer in the component *B*. The residue, therefore, must become richer in *A*, i.e. the composition of the residue shifts towards *A*, say it becomes equal to *b*. Now, if this liquid mixture is heated, it will boil only when the temperature becomes equal to T_b. The vapour will have composition corresponding to *b*', i.e. again it is richer in *B* and consequently, the composition of the residue will be further enriched in *A*. If the process of heating the residue is continued, the boiling point of the solution moves from the initial point T_a towards the boiling point T_A of the pure liquid *A*. Every time the residue becomes richer in *A* than the original solution. This means that if the process is continued for a sufficiently long time, a final residue of pure *A* can be obtained.

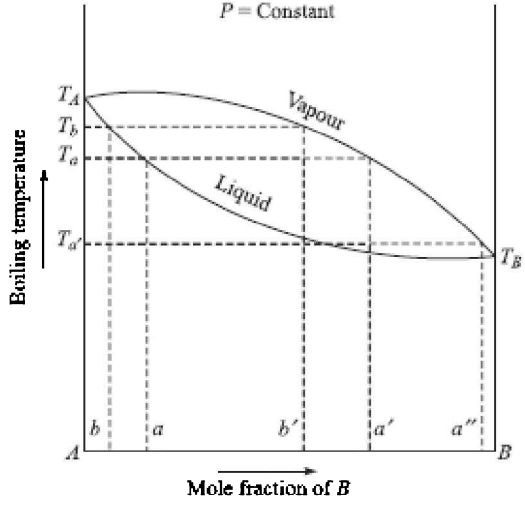


Fig. 24.13 *Distillation behaviour of solutions of Type I*

If the vapours obtained in the first stage are condensed, we shall get a liquid mixture corresponding to composition *a'* as shown in Fig. 24.13. Now if this liquid mixture is distilled, it will boil when the temperature becomes T_a'. The composition of the vapours coming off will correspond to the point *a''* i.e. the vapours have become richer in *B* than the original solution. This means that the process of condensing the vapour and redistilling the liquid mixture is continued, ultimately a distillate of pure *B* will be obtained.

Hence, we conclude that in case of solutions of Type I, a complete separation of the components is possible by distillation, the less volatile component being left as the residue and the more volatile component being obtained as a distillate.

Distillation of Solutions of Type II The boiling temperature-composition diagram for the solutions of this type is reproduced as in Fig. 24.14.

An example of this type is the water (*A*)-ethyl alcohol *(B)* system. If a solution of composition between *A* and *C*, such as *a*, is distilled, the vapour coming off will have composition *a'* and will be richer in *B* and the residue will, therefore, become richer in *A*, i.e. the composition of the residue shifts towards *A* till ultimately the ***residue of pure A*** is obtained. The liquid obtained on condensing the vapours (corresponding to composition *a*'), if distilled, will give a vapour richer in *B*. If the condensation of vapours and the distillation of the liquid is continued, ultimately the vapours of composition *C* will be obtained. If these vapours are condensed and the solution distilled, the distillate obtained will have the same composition as the solution. Hence, no further separation is possible by distillation.

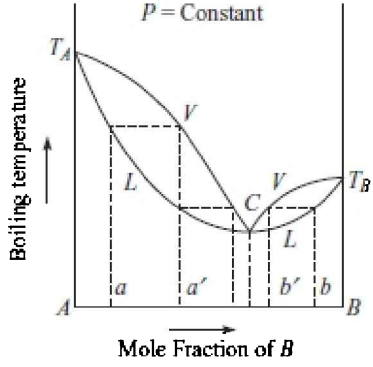


Fig. 24.14 *Distillation behaviour of solutions of Type II*

Thus, *"**in case of solutions of Type II, a solution of composition between** A **and** C **on fractional distillation gives residue of pure** A **and the final distillate of composition** C. **No pure** B **can be recovered"***

Now, consider the distillation of a solution having composition between *C* and *B*, say corresponding to the point *b*. The vapour coming off will be richer in *A* and so the residue will be richer in *B*. Hence, on repeated distillations, ultimately a residue of pure *B* and the final distillate of composition *C* will be obtained. Thus,

"For a solution of composition between C and B, on fractional distillation, a residue of pure B and a final distillate of composition C is obtained. No pure 'A' can be recovered"

Distillation of Solutions of Type III The boiling temperature-composition diagram for solutions of this type is explained with the help of Fig. 24.15.

The behaviour of solutions of Type III on distillation is analogous to that of solutions of Type II with the exception that the residue tends towards the constant boiling mixture corresponding to the composition *D*, whereas distillates tend towards the pure constituents. Also, from Fig. 24.15, it is clear that for a mixture having composition between *A* and *D* (say corresponding to *a*), the vapour coming off are richer in *A* and hence, the residue is richer in *B*. In other words, the composition of the residue shifts towards *D* and ultimately becomes equal to that of *D*. The composition of the vapours shifts towards *A* and finally a distillate of pure *A* is obtained. Thus, for a mixture having composition between *A* and *D*, distillate of pure *A* is obtained and the residue has a composition corresponding to the point *D* (i.e. a constant boiling mixture with maximum boiling point). In a similar manner, it can be seen for a mixture having composition between *D* and *B*, ***ultimately distillate of pure* B *and residue of composition corresponding to* D *is obtained.***

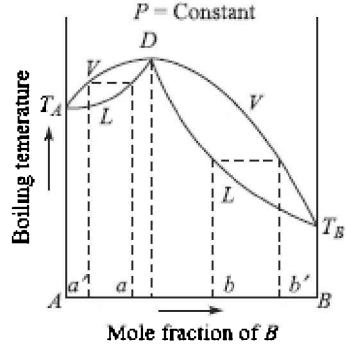


Fig. 24.15 *Distillation behaviour of solutions of Type III*

24.11 AZEOTROPES

Mixtures of liquids which boil at constant temperature like a pure liquid such that the distillate has the same composition as that of the liquid mixture, are called constant boiling mixtures or azeotropic mixtures, or simply azeotropes. Obviously, the components of an azeotrope cannot be separated by fractional distillation. These azeotropes are of two types.

1. Minimum Boiling (Point) Azeotropes These azeotropes are formed by liquid pairs which show positive deviations from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the highest and hence the boiling point is the lowest. Such azeotropes have boiling points lower than either of the pure components. Ethyl alcohol-water is an example of this type of azetrope.

2. Maximum Boiling (Point) Azeotropes These azeotropes are formed by those liquid pairs which show negative deviation from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is minimum and hence, the boiling point is maximum. Such azeotropes have boiling points higher than either of the pure components. Water-HCI is an example of this type of azeotrope.

24.12 IMMISCIBLE LIQUIDS

Immiscible liquids mean those liquids which do not mix with each other at all. Thus, if such a mixture of two liquids is heated, each will behave as if the other were not present. Hence, the total vapour pressure above the mixture will be same as the sum of the vapour pressures of the two pure constituents, i.e.

$$p = p_A^\circ + p_B^\circ$$

where p is the total vapour pressure and p_A°, p_B° stand for the vapour pressures of the two pure liquids A and B at the same temperature.

Normal boiling point is the temperature at which the total vapour pressure becomes equal to the atmospheric pressure. In an immisible liquid pair, since each liquid exerts vapour pressure, the total vapour pressure will become equal to atmospheric pressure at the temperature lower than the boiling point of either of the two liquids. As soon as one of the liquids is boiled away, the boiling temperature will rise from that of the mixture to either T_A or T_B depending upon which liquid has already boiled off.

At the boiling point of the mixture, the vapour pressure exerted by each liquid is proportional to its number of molecules and hence, to the number of moles present in the vapour phase.

Therefore, we can write,

$$\frac{p_A^\circ}{p_B^\circ} = \frac{n_A}{n_B}$$

where, n_A and n_B are the number of moles of A and B respectively present in vapour phase at the boiling point of the mixture.

Changing moles into weights, we have

$$n_A = \frac{W_A}{M_A}, n_B = \frac{W_B}{M_B}$$

where, W_A is the weight of the vapours of A, M_A is the molecular weight of A

W_B is the weight of vapours of B, M_B is the molecular weight of B.

Thus,

$$\frac{p_A^\circ}{p_B^\circ} = \frac{W_A/M_A}{W_B/M_B} = \frac{W_A \cdot M_B}{W_B \cdot M_A}$$

or

$$\boxed{\frac{W_A}{W_B} = \frac{p_A^\circ \times M_A}{p_B^\circ \times M_B}}$$

If the vapours are condensed to give a distillate, the ratio of the weights of *A* and *B* in the distillate will be given by the above expression.

24.13 STEAM DISTILLATION

This method of distillation is based upon the principle of boiling of two immiscible liquids and is used in the laboratory or in the industry for puri?cation of organic liquids.

1. Applicability The process is generally carried out if

(a) The organic liquid to be purified is immiscible with water

(b) It has high molecular mass

(c) It has vapour pressure at about 100°C

(d) Impurities present are nonvolatile.

2. Experimental Details The apparatus used is shown in Fig. 24.16. The steam is produced in the steam generator and is passed into the flask containing the impure liquid and kept in a slanting position. This flask is heated from below to prevent the excessive condensation of steam into it. Thus, in the space above the liquid in the flask, water vapours as well as vapours of the liquid are present. The liquid-water mixture present in the flask will, therefore, boil at a temperature lower than the boiling point of either of the two. The vapours on passing through the condenser will give a distillate containing the liquid and the water in the ratio calculated using the formula given below:

$$\frac{W_l}{W_w} = \frac{p_l^\circ \cdot M_l}{p_w^\circ \cdot M_w}$$

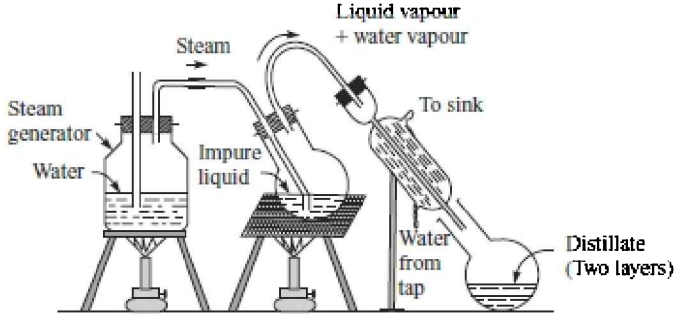


Fig. 24.16 *Experimental set-up forsteam distillation*

The subscripts *l* and *w* stand for liquid and water respectively.

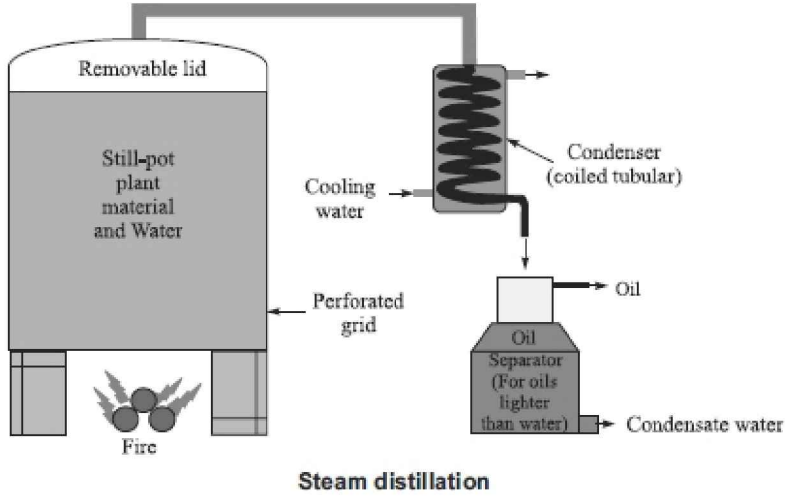


Fig. 24.17 *Steam distillation is one of the processes to extract essential oils from plants. The still pot contains the plant material and water*

Example 15 *An organic liquid was subjected to steam distillation. The liquid in the flask was boiled at 90°C. The external pressure (atmospheric pressure) was found to be 734.4 mm. The vapour pressure of water at 90°C is 526.0 mm. The ratio of the weights of liquid to water in the distillate was found to be 2.47. Calculate the molecular weight of the liquid.*

Solution: Here, external pressure = 734.4 mm, Boiling point of the mixture = 90°C

Vapour pressure of water at 90°, p_w = 526.0 mm.

$\therefore$ vapour pressure of liquid at 90°, p_l° = 734.4 − 526.0 = 208.4 mm.

Ratio of the weights

$$W_l/W_w = 2.47$$

Molecular weight of water = M_w = 18

Substituting the value in the formula,

$$\frac{W_l}{W_w} = \frac{p_l^\circ \times M_l}{p_w^\circ \times M_w}$$

We get,

$$2.47 = \frac{208.4 \times M_l}{526.0 \times 18} \quad \text{or} \quad M_l = \frac{2.47 \times 526.0 \times 17}{208.4} = 112.2$$

Example 16 *A mixture of water and aniline boil at a temperature of 98.5°C at a pressure of 760 mm. The vapour pressure of water at this temperature is 717 mm. Find the composition of the distillate.*

Solution: Here, $p_w^\circ = 717$ mm, $p_l^\circ = 760 - 717 = 43$ mm

Further $M_w = 18, M_l = 93$

$$\frac{W_l}{W_w} = \frac{p_l^\circ \cdot M_l}{p_w^\circ \cdot M_w} = \frac{43 \times 93}{717 \times 18} = 0.31$$

i.e., in the distillate, weight of aniline: weight of water = 0.31 : 1

$$\text{Percentage by weight of aniline} = \frac{0.31}{1 + 0.31} \times 100 = \frac{0.31}{1.31} \times 100 = 23.66$$

Percentage by weight of water = 100 – 23.66 = 76.34

24.14 PARTIALLY MISCIBLE LIQUIDS

Between the two extremes of completely miscible and completely immiscible liquid pairs, there is a category of liquids called partially miscible liquids. If a little phenol is added to water at ordinary temperature, we get a clear solution. On continued addition of phenol into water, a stage is reached when no more phenol can be dissolved in water. We get two layers. One of these layers forms a saturated solution of water in phenol and the other layer is a saturated solution of phenol in water. The two solutions (layers) which are in equilibrium are called ***conjugate solutions.***

Critical Solution Temperature The temperature at which two liquids which are otherwise partially miscible at ordinary temperature, become completely miscible is called ***Critical Solution Temperature (CST).*** There can be three types of partially miscible systems. Each type is briefly discussed below by taking one example.

Type I *System with an Upper Critical Solution Temperature (Upper Consolute Temperature): Phenol-water System* If phenol and water are mixed in equal proportions, two layers are produced, one is a solution of phenol in water and the other is a solution of water in phenol. At any given temperature, the composition of these layers is fixed and can be determined by analytical methods. If the system is warmed, the amount of water in the phenol layer increases as well as the amount of phenol in the water layer increases.

Ultimately, a temperature is reached where the composition of both the layers becomes the same and thus the two become completely miscible. Experiments have shown that the minimum temperature at which phenol and water become completely miscible is 66°C and the composition is 34% of phenol by weight. Thus, phenol water system has an upper critical solution temperature of 66°C. The results on being plotted give a parabolic curve as shown in Fig. 24.18.

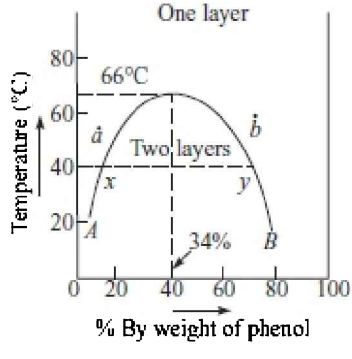


Fig. 24.18 *Phenol-water system*

Alternatively, the same curve is obtained if solutions of phenol of different suitable compositions are prepared and the temperature at which the two liquids become completely miscible is determined in each case from the disappearance of the turbidity and then plotted against the composition.

We observe that at a temperature above 66°C, phenol and water are completely miscible, irrespective of composition. For a temperature below 66°C, the composition lying within the parabola, there are two layers in equilibrium. The points *x* and *y* give the composition of two layers.

The line *xy* is called ***tie-line.*** For a temperature below 66°C, but composition lying outside the curve, there is unsaturated Q solution of phenol in water on LHS (say point *a*) while there is unsaturated solution of water in phenol outside the curve on RHS (say point *b*).

Type II *System with a Lower Critical Solution Temperature (Lower Consolute Temperature): Triethylamine-water system* In this system, it is observed that the mutual solubility of the two liquids increases not with increase of temperature but with decrease of temperature. Thus, on cooling such a system, ultimately a stage is reached when the two liquids become completely miscible. This temperature is called the ***lower consolute temperature*** and is 18.5°C for the triethylamine-water system. Thus, below 18.5°C, triethylamine and water are completely miscible in all proportions. The curve obtained by plotting the temperatures against composition is just an inverted form of Type I and is shown in Fig. 24.19.

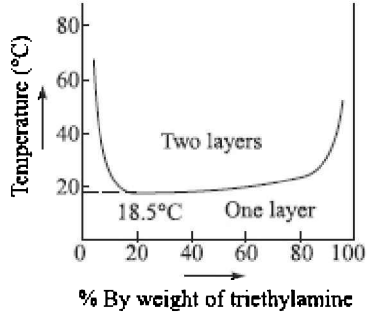


Fig. 24.19 *Triethylamine-watersystem*

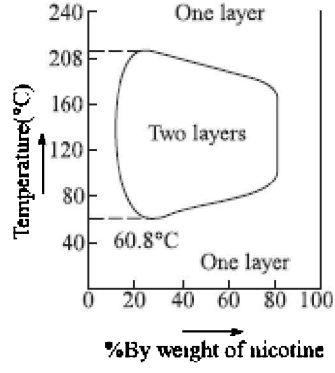


Fig. 24.20 *Nicotine-watersystem.*

Type III *System with an Upper as well as Lower Critical Solution Temperature: Nicotine-Water System*This is the system in which the mutual solubility of the two liquids increases with increase of temperature as well as with decrease of temperature. In such systems, the two liquids become completely miscible above a particular temperature. Thus, such systems have an upper critical

solution temperature as well as lower critical solution temperature which are 208°C and 60.8°C respectively for the nicotine-water system. The plot obtained between the temperature and composition in such cases is a closed curve as shown in Fig. 24.20. As before, for the temperature and composition corresponding to any point within the closed curve there are two layers while outside it, there is one layer only.

24.15 | EFFECT OF IMPURITIES ON CONSOLUTE TEMPERATURE (CRITICAL SOLUTION TEMPERATURE)

Presence of an impurity alters the consolute temperature of a system of two liquid components, just as a presence of an impurity in a compound alters its melting and boiling points. The impurity causes a change in mutual solubility of the two liquids. We come across different situations as given below:

Case 1 In the case of phenol-water system, if we add some hydrocarbon, which is soluble in phenol only, we find that the consolute temperature is raised from 66°C to 68.4°C. Similarly, if we add KCI to the same system, again we observe that the consolute temperature is raised. KCI is soluble in water only. We can, therefore, generalise that if the ***impurity is soluble in one of the two liquids,*** it results into rise of consolute temperature. The magnitude of change is proportional to the relative amount of the impurity.

Case 2 Addition of succinic acid has considerable solubility in both components of phenol-water system—this property is used in the preparation of commercial disinfectant solutions. Thus, if the impurity is soluble in both the liquids, the consolute temperature of the liquid mixture is lowered.

Case 3 Addition of salts, which are soluble in water but insoluble in the organic component, raises the consolute temperature as mentioned in Case 1. However, addition of lithium iodide to aniline-water depresses the consolute temperature. This is because lithium iodide is partially ionic and partially co-valent. In small amounts, it dissolves both in aniline and water.

Example 17 *Why does the mixture of two immiscible liquids boil at a lower temperature? Which will distill over in a large amount and why?*

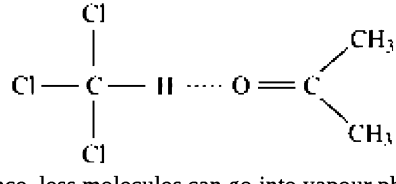
Solution: At any temperature, each liquid exerts vapour pressure equal to that of the pure liquid independent of the presence of the other liquid. Hence, total vapour pressure will be sum of the vapour pressures of the pure constituents, i.e. $p_{\text{total}} = p_A^\circ + p_B^\circ$. As total vapour pressure becomes equal to the atmospheric pressure at a lower temperature, the mixture boils at a lower temperature than either of the pure liquids. Further

$$\frac{p_A^\circ}{p_B^\circ} = \frac{W_A/M_A}{W_B/M_B} \quad \text{or} \quad \frac{W_A}{W_B} = \frac{p_A^\circ \times M_A}{p_B^\circ \times M_B}$$

Thus, liquid which has higher vapour pressure and higher molecular mass will distil over in larger amount as evidenced by the above equation.

Example 18 *When chloroform and acetone are mixed, the vapour pressure is less than that expected from Raoult's law? Why?*

Solution: Strong dipole-dipole attraction takes place between chloroform and acetone as follows:



Hence, less molecules can go into vapour phase.

Example 19 *When ethanol and cyclohexane are mixed, the vapour pressure is more than expected from Raoult's law. Why?*

Solution: Ethanol exhibits hydrogen boiling. On adding cyclohexane, its molecules get in between the molecules of ethanol, thereby decreasing the hydrogen bonding, i.e. ethanol-ethanol attractions are weakened. Hence, more molecules can go into the vapour phase.

Example 20 *Why does a vapour pressure of a solvent decrease when a nonvolatile solute is added of it?*

Solutionr Some of the molecules on the surface of the solvent are replaced by solute molecules. Thus, the percentage of solvent molecules on the surface is decreased which results in the decrease of vapour pressure.

Example 21 *Comment on the signs of ΔV_{mixing} and ΔH_{mixing} for solutions showing (a) positive deviations and, (b) negative deviations.*

Solution: For non-ideal solutions showing positive deviations, ΔV_{mixing} and ΔH_{mixing} are both positive, i.e. volume increases on mixing and heat is absorbed. For those showing negative deviations, both ΔV_{mixing} and ΔH_{mixing} are negative, i.e. volume decreases and heat is evolved.

Example 22 *Define Henry's law in terms of mole fractions of the solute dissolved in the solution. How does Raoult's law follow from it?*

Solution: According to Henry's law, solubility of a gas expressed in mole fraction in a particular solvent at a particular temperature is directly proportional to the pressure of the gas, i.e.

$$x_2 \propto p_2 \quad \text{or} \quad x_2 = kp_2 \qquad \ldots(i)$$

(k = Henry's constant)

Raoult's law follows Henry's law: This can be proved as under:

When $x_1 = 1$, p_2 becomes vapour pressure of pure solute, i.e. $p_2 = p_2^\circ$.

Substituting the values in Eq. (i), we get

$$1 = kp_2^\circ \quad \text{or} \quad k = \frac{1}{p_2^\circ}$$

SUMMARY

1. *Raoult*s law: In a solution, the vapour pressure of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state
2. The relative lowering of vapour pressure of a solution containing a nonvolatile solute is equal to the mole fraction of the solute in the solution.
3. *Henry's law:* The mass of a gas dissolved in a given volume of a liquid at constant temperature is directly proportional to the pressure of the gas present in equilibrium with the liquid.
4. *An alternative statement of Henry's law* : The mole fraction of a gas in the solution is proportional to partial pressure of the gas over the solution.
5. Volume of a gas dissolved in a liquid, measured at the pressure used, is independent of the pressure.
6. Factors that affect solubility of a gas in a liquid are nature of the gas and the solvent, pressure and temperature.
7. A solution of two components is said to be *ideal* if each component of the solution obeys Raoult's law at all temperatures and pressures. It is non-ideal if the components do not obey Raoult's law.
8. *Konowaloff rule:* In case of ideal solutions or solutions showing small deviation at any fixed temperature, the vapour phase is always richer in the more volatile component as compared to the solution phase.
9. Mixtures of liquids which boil at constant temperature like a pure liquid such that the distillate has the same composition as that of the liquid mixture are called constant boiling mixtures or

azeotropes.

KEY RELATIONS

$$p_i = x_i \times p^\circ \quad \text{Raoult's law}$$

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1 + n_2}$$

$$m = kp \quad \text{Henry's law}$$

$$p = k_H x \quad \text{Henry's law}$$

$$x_1 \frac{d \ln p_1}{dx_1} = x_2 \frac{d \ln p_2}{dx_2} \quad \text{Duhem–Margules equation}$$

$$\frac{d \ln p_1}{d \ln x_1} = \frac{d \ln p_2}{dx_2} \quad \text{–do–}$$

$$\frac{w_A}{w_B} = \frac{p_A^\circ \times M_A}{p_B^\circ \times M_B}$$

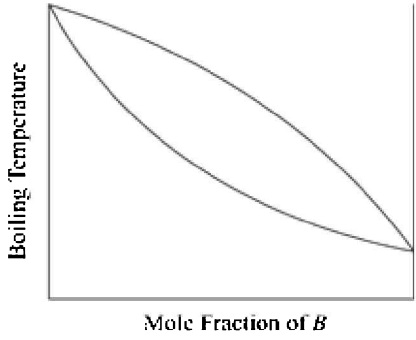
EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. Relative lowering of vapour pressure of a solution containing a nonvolatile solute is equal to the mole fraction of
   (a) solute
   (b) solvent
   (c) solvent minus solute
   (d) solvent plus solute
2. A solution formed on mixing of two liquids is ideal if
   (a) $\Delta V_{mix} = 0$, $\Delta H_{mix} \neq 0$
   (b) $\Delta V_{mix} \neq 0$, $\Delta H_{mix} = 0$
   (c) $\Delta V_{mix} = 0$, $\Delta H_{mix} = 0$
   (d) $\Delta V_{mix} = 0$, $\Delta H_{mix} \neq 0$
3. The vapour phase is relatively richer in the component whose addition to the liquid mixture results in an increase of total vapour pressure. This is the statement of
   (a) Duhem-Margules law
   (b) Raoult's law
   (c) Konowaloff's rule
   (d) none of the above

4. In a solution, the vapour pressure of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state. This is the statement of
   (a) Henry's law
   (b) Raoult's law
   (c) Konowaloff's law
   (d) none of the above
5. Mathematical form of Henry's law is
   (a) $m = k_p$
   (b) $p = k_m$
   (c) $p = \frac{k}{m}$
   (d) $m = \frac{1}{k} p$
6. Benzene + Toluene mixture shows
   (a) negative deviation
   (b) no deviation
   (c) large positive deviation
   (d) small positive deviation
7. Triethylamine-water system is an example of
   (a) upper CST
   (b) lower CST
   (c) upper as well as lower CST
   (d) none of the above
8. Addition of KCI to phenol-water system
   (a) raises the CST
   (b) lower the CST
   (c) has no effect on CST
   (d) none of the above
9. Look at the figure below.
   This figure illustrates the distillation behaviour of solutions of
   (a) Type I
   (b) Type II
   (c) Type III
   (d) Both Type I and III
10. Which of the following is not true about the applicability of steam distillation?
   (a) The organic liquid to be purified should be immiscible with water.
   (b) It should have high molecular weight.
   (c) It should have high vapour pressure.
   (d) The impurities present should be volatile.



Answers

1. (a)
2. (c)
3. (c)
4. (b)
5. (a)
6. (d)
7. (b)
8. (a)
9. (a)
10. (d)

SHORT-ANSWER QUESTIONS

1. State and explain Raoult's law for volatile solutes as well as for nonvolatile solutes.
2. Using boiling point-composition diagram, explain how the distillation of binary miscible solution showing positive deviation takes place.
3. Using boiling point-composition diagram, explain how the distillation of a binary miscible solution showing negative deviation takes place.
4. Differentiate between ideal and non-ideal solutions.
5. Describe Konowaloff's rule. Bring out its importance in the study of boiling point-composition curves of completely miscible ideal binary solutions.
6. Briefly explain the effect of impurities on consolute temperature.
7. State 'Henry's law'. What are the conditions under which it holds good? Show that the volume of a gas that dissolves in a fixed volume of a liquid at a given temperature is independent of pressure.
8. Explain the principle (or theory) underlying the process of steam distillation.
9. Derive the expression for the total vapour pressure in terms of mole fractions of the components in the vapour phase for a binary miscible liquid mixture.
10. Explain the vapour pressure-composition diagrams of ideal solutions.
11. State Henry's law in as many forms as you can. Give its limitations.

12. What are 'conjugate solution' and 'critical solution' temperatures? Explain a system which has both upper CST as well as lower CST. What is the effect of pressure on such a system?
13. Prove that Raoult's law is a special case of Henry's law.
14. Write a short note on 'azeotropes'.
15. What do you understand by critical solution temperature?

GENERAL QUESTIONS

1. Derive Duhem-Margules equation.
2. Discuss vapour pressure-composition curves of a system containing binary mixtures of liquids miscible in all proportions. From these, construct boiling point-composition diagrams and describe briefly how their distillation will take place.
3. Derive the equation $\frac{d\ln p_1}{d\ln x_1} = \frac{d\ln p_2}{d\ln x_2}$
4. Using boiling point-composition diagram, explain the principle of fractional distillation.
5. Briefly explain giving one example each of the following types:
   (a) System with upper CST
   (b) System with lower CST
   (c) System with upper and lower CST.
6. Briefly explain the principle (or theory) and the method of steam distillation. When is the method used?
7. Explain the two main types of non-ideal solutions. How do they lead to the concept of azeotropic mixtures? Explain briefly the types of azeotropic mixtures.
8. Briefly explain the following:
   (a) Effect of impurities on consolute temperature
   (b) Effect of pressure on critical solution temperature
   (c) Isotropic effect on critical solution temperature
9. State and explain Raoult's law and Henry's law. Prove that Raoult's law follows as a special case of Henry's law.
10. What are ideal and non-ideal solutions? How does the vapour pressure of the component and the total vapour pressure vary with mole fraction of any one of the components in case of an ideal solution?
11. How are non-ideal solutions classified into different types? Briefly explain the behaviour of each type graphically giving reason with a suitable example in each case.
12. Derive the following relationships:
   (a) Total vapour pressure in terms of mole fractions of the components in the vapour phase
   (b) Between mole fractions of the components in the liquids phase and in the vapour phase:



Dilute Solutions and Colligative Properties

25

LEARNING OBJECTIVES

- Know the different colligative properties
- Learn to determine the vapour pressure and lowering of vapour pressure
- Derive a relation between relative lowering of vapour pressure and the molecular mass of the solute (Raoult's law)
- Learn the phenomenon of osmosis and derive a relation between the osmotic pressure and molecular mass of the solute
- Derive a relation between lowering of vapour pressure and osmotic pressure
- Grasp Van't Hoff theory of dilute solutions taking the example of osmosis
- Learn the methods for the determination of osmotic pressure
- Understand isotonic solutions and their biological importance
- Learn different theories of osmosis
- Learn reverse osmosis and its applications
- Learn elevation in boiling point and its determination
- Derive thermodynamically a relation between elevation in boiling point and molecular mass of the solute
- Derive a relation between boiling-point elevation and relative lowering of vapour pressure
- Derive a relation between boiling-point elevation and osmotic pressure
- Derive a relation between depression in freezing point and molecular mass of the solute
- Learn the cause of abnormal molecular masses of solutes using colligative properties
- Learn Van't Hoff factor

25.1 INTRODUCTION

It has been observed that certain properties of dilute solutions are not dependent on the nature of the solute (nonvolatile) present in the solution. These properties depend upon the number of particles (or concentration) of the solute in the solution. Such properties are known as ***colligative properties*** and are listed below:

1. Lowering of vapour pressure of the solvent
2. Osmotic pressure of the solution
3. Elevation in boiling point of the solvent
4. Depression in freezing point of the solvent

It has been observed that the validity of the above behaviour is limited to dilute solutions when they behave nearly as ideal solutions. As these properties are observed with nonvolatile solutes, it can be visualised that the escaping tendency of the solvent is reduced in the presence of such solutes and consequently, the vapour pressure of the solvent is lowered. With the lowering of vapour pressure of

the solvent, we can explain the elevation in boiling point and depression in freezing point. An important application of the study of colligative properties is to determine the molecular masses of the unknown substances and in the study of their molecular state in solution. In the following sections, we shall take up a detailed study of each of the colligative properties.

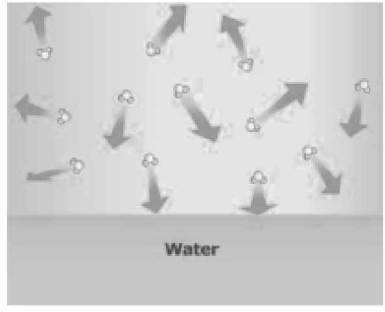


Fig. 25.1 Water-vapour equilibrium *Molecules of higher energy leave the liquid phase and move to the vapour phase. At the same time, some molecules from the vapour phase condense and move to the liquid phase. This is a continuous process.*

25.2 | DETERMINATION OF VAPOUR PRESSURE OF A LIQUID BY MANOMETRIC METHOD

The vapour pressure of a liquid of solution can be measured with the help of a manometer (Fig. 25.2). The tube *B* is filled with the liquid or solution. The air in the connecting tube is then removed with a vacuum pump. When the stopcock is closed, the pressure inside is due only to the vapour exaporating from the solution or liquid. This method is generally used for aqueous solutions. The manometric liquid is usually mercury which has low volatility.

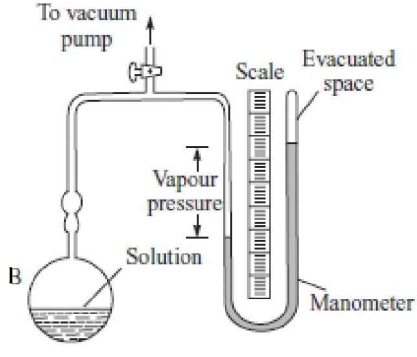


Fig. 25.2 *Measurement of vapour pressure of aqueous solutions with a manometer*

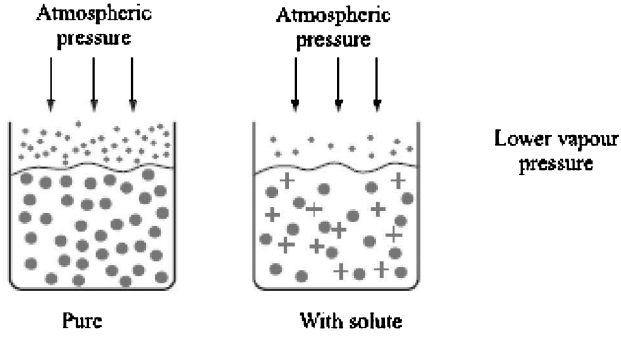


Fig. 25.3 *Lowering of vapour pressure Vapour pressure of a liquid is lowered on addition of a solute*

25.3 | DETERMINATION OF LOWERING OF VAPOUR PRESSURE OF THE SOLVENT

Ostwald and Walker's Dynamic Method (Gas Saturation Method)

In this method, the relative lowering of vapour pressure can be determined straightaway. The measurement of individual vapour pressures of a solution and solvent is thus eliminated.

1. Procedure The apparatus used by Ostwald and Walker is shown in Fig. 25.4.

It consists of two sets of bulbs:

(a) Set *A* containing the solution

(b) Set *B* containing the solvent

Each set is weighed separately. A slow stream of dry air is then drawn by a suction pump through the two sets of bulbs. At the end of the operation, these sets are reweighed. From the loss of weight in each of the two sets, the lowering of vapour pressure is calculated. The temperature of the air in the solution and the solvent must be kept constant throughout.

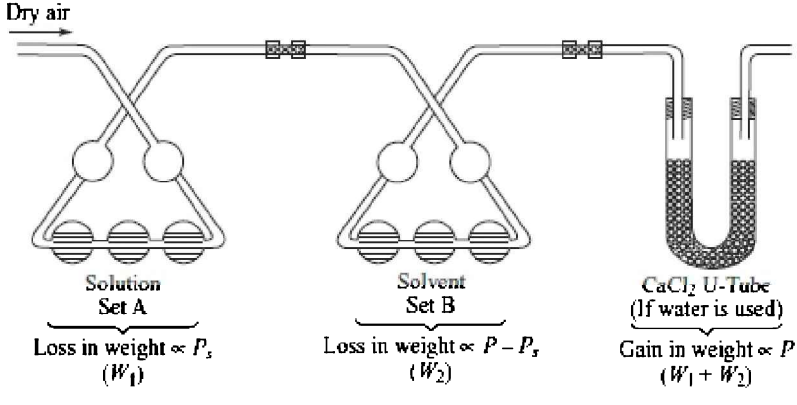


Fig. 25.4 *Ostwald-Walker method of measuring the relative lowering of vapour pressure*

2. Calculations As the air bubbles through Set *A* it is saturated upto the vapour pressure p_s, of the solution and then up to the vapour pressure p of the solvent in Set *B*. Thus, the amount of solvent taken up in Set *A* is proportional to p_s and the amount taken up in Set *B* is proportional to $(p\text{-}p_s)$.

$$w_1 \propto p_s \quad \ldots(25.1a)$$

$$w_2 \propto p - p_s \quad \ldots(25.1b)$$

Adding (25.1a) and (25.1b), we have

$$w_1 + w_2 \propto p_s - p \quad p_s$$

$$\propto p \quad \ldots(25.2)$$

Dividing (25.1b) and (25.2), we can write

$$\frac{p - p_s}{p} = \frac{w_2}{w_1 + w_2} \quad \ldots(25.3)$$

Knowing the loss of mass in Set *B* (w_2) and the total loss of mass in the two sets ($w_1 + w_2$), we can find the relative lowering of vapour pressure from Eq. (25.3).

If water is the solvent used, a set of calcium chloride tubes is attached to the end of the apparatus to catch the escaping water vapour. Thus, the gain in mass of the $CaCl_2$ tubes is equal to ($w_1 + w_2$), the total loss of mass in sets *A* and *B*.

Example 1 *A stream of dry air was passed through a bulb containing a solution of 7.50 g of an aromatic compound in 75.0 g of water and through another bulb containing pure water. The loss in mass in the first bulb was 2.810 g and in the second bulb, it was 0.054 g. Calculate the molecular mass of the aromatic compound (Mo. mass of water = 18)*

Solution According to the theory of Ostwald-Walker method,

$$\frac{p - p_s}{p} = \frac{w_2}{w_1 + w_2}$$

In the present case,

w_1, loss in mass of solution = 2.810 g

w_2, loss in mass of solvent (water) = 0.054 g

Substituting the values in the above equation,

$$\frac{p - p_s}{p} = \frac{0.054}{2.810 + 0.054} = \frac{0.054}{2.864} = 0.0188$$

According to Raoult's law,

$$\frac{p - p_s}{p} = \frac{w/m}{w/m + W/M}$$

Substituting the values, we have

$$0.0188 = \frac{7.50/m}{7.50/m + 75.0/18} \text{ or } m = 93.6$$

25.4 | RELATION BETWEEN THE RELATIVE LOWERING OF VAPOUR PRESSURE AND THE MOLECULAR MASS OF THE SOLUTE (RAOULT'S LAW)

Suppose vapour pressure of the pure solvent $A = p_A^\circ$

Let the solute be *B*.

Let the vapour pressure of the solvent in the solution = p_A

Since $p_A^\circ > p_A$,

$\therefore$ lowering of vapour pressure = $p_A^\circ - p_A$

Relative lowering of vapour pressure = $\frac{p_A^\circ - p_A}{p_A^\circ}$

According to Raoult's law, ***relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.***

Let mole fraction of the solute $B = X_B$

$$\therefore \quad \frac{p_A^\circ - p_A}{p_A^\circ} = X_B \qquad \ldots(25.4)$$

$$\text{Mole fraction of the solute} = \frac{n_2}{n_1 + n_2}$$

where n_2 = No. of moles of the solute

n_1 = No. of moles of the solvent

$$\therefore \quad X_B = \frac{n_2}{n_1 + n_2}$$

Thus, the relation (25.4) becomes

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_2}{n_1 + n_2} \qquad \ldots(25.5)$$

It is evident from (25.5) that the relative lowering of vapour pressure depends only upon mole fraction or molar concentration of the solute. Therefore, relative lowering of vapour pressure is a colligative property.

Molecular Mass of the Non-Volatile Solute Now, number of moles of the solute $n_2 = \frac{w}{m}$

where w = Mass of the solute

m = Molecular mass of the solute

And number of moles of the solvent $n_1 = \frac{W}{M}$

where W = Mass of the solvent

M = Molecular mass of the solvent

The expression (25.5) becomes

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}} \qquad \ldots(25.6)$$

In a dilute solution, n_2 is negligible as compared to n_1. Therefore, neglecting n_2 (or w/m) in the denominator, we get from expression (25.6),

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{w/m}{W/M} = \frac{w}{m} \times \frac{M}{W}$$

or

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{wM}{mW} \qquad \ldots(25.7)$$

Thus, by measuring the lowering of vapour pressure of a solution, the molecular mass m of a solute in a given solution of a known concentration can be determined, if other quantities are known.

Example 2 *The vapour pressure of water at 293 K is 17.51 mm and lowering of vapour pressure of sugar solution is 0.0614 mm.*

Calculate

(a) Relative lowering of vapour pressure

(b) Vapour pressure of the solution

(c) Mole fraction of water

Solution Vapour pressure of solvent (water) = 17.51

Let vapour pressure of the solution = p (to be calculated)

$\therefore$ Lowering of vapour pressure = $p^\circ - p = 0.0614$ mm

(a) Relative lowering of vapour pressure = $\dfrac{p^\circ - p}{p^\circ} = \dfrac{0.0614}{17.51} = 0.00351$

(b) Vapour pressure of the solution

$$p = p^\circ - (p^\circ - p)$$
$$= 17.51 - (0.0614) = 17.4486 \text{ mm}$$

Now according to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \text{mole fraction of the solute}$$

$$\frac{p^\circ - p}{p^\circ} = \frac{n_1}{n_1 + n_2} = x_2$$

$\therefore$ Mole fraction of the solute = $= \dfrac{p^\circ - p}{p^\circ} = \dfrac{0.0614}{17.51} = 0.00351$

(c) Hence, mole fraction of the solvent = (1 – 0.00351) = 0.99649

Mole fraction of water = 0.99649

Example 3 *At 298 K, the vapour pressure of water is 23.75 mm of Hg. Calculate the vapour pressure at the same temperature over 5% aqueous solution of urea (NH_2CONH_2).*

Solution This solution may be considered a dilute solution and the approximate relation given below may be used,

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{wM}{mW}$$

In the present case, $p_A^\circ = 23.75$ and $w = 5$ g

Therefore, $W = 100 - 5 = 95$ g

$M = 18$ $m = 60$ (mol. wt. of urea)

Substituting these values in the equation above,

$$= \frac{23.75 - p_A}{23.75} = \frac{5 \times 18}{60 \times 95} \quad \text{or} \quad p_A = 23.375 \text{ mm}$$

Example 4 *Solution containing 6.0 grams of benzoic acid in 50 g of ether ($C_2H_5OC_2H_5$) has a vapour pressure equal to 5.466 × $10^4 Nm^{-2}$ at 300 K. Given that the vapour pressure of ether at the same temperature is 5.893 × 10^4 NM^{-2}, calculate the molecular mass of benzoic acid.*

Solution Vapour pressure of ether (solvent) = $p^\circ = 5.893 \times 10^4$ Nm^{-2}

Vapour pressure of ether solution = $p = 5.466 \times 10^4$ Nm^{-2}

Molecular mass of solvent (C_2H_5-O-C_2H_5)(M) = 74
Mass of solute (benzoic acid) w = 6 grams
Mass of solvent (ether) W = 50 grams
Let the molecular mass of solute (benzoic acid) = m
Substituting the values in the relation,

$$\frac{p^\circ - p}{p^\circ} = \frac{w}{m} \times \frac{M}{W}$$

$$\frac{5.893 \times 10^4 - 5.466 \times 10^4}{5.893 \times 10^4} = \frac{6 \times 74}{m \times 50}$$

$$\frac{0.427 \times 10^4}{5.893 \times 10^4} = \frac{6 \times 74}{m \times 50} \quad \text{or} \quad \frac{0.427}{5.893} = \frac{6 \times 74}{m \times 50}$$

or $$m = \frac{6 \times 74 \times 5.893}{50 \times 0.427}$$

$$m = 122.55$$

i.e. the molecular mass of solute (benzoic acid) = 122.55 amu

Example 5 *The vapour pressure of a 5% aqueous solution of nonvolatile organic substance at 373 K is 745 mm. Calculate the molecular mass of the solute.*

Solution Weight of nonvolatile organic solute, w = 5 g
Weight of solvent (water), W = 95 g
Molecular mass of solvent (water) M = 18
Molecular mass of nonvolatile solute m = ?
$p°$, the vapour pressure of pure solvent (water) at 373 K = 760 mm
Vapour pressure of the solution P = 745 mm
Substituting the values in the relation,

$$\frac{p^\circ - p}{p^\circ} = \frac{w}{m} \times \frac{M}{W} \quad \text{or} \quad \frac{760 - 745}{760} = \frac{5 \times 18}{m \times 95}$$

or $$m = \frac{5 \times 18 \times 760}{15 \times 95} = 48$$

PROBLEMS FOR PRACTICE

1. Dry air was passed through a solution containing 40 g of solute in 90 g of water and then through water. The loss in weight of water was 0.05 g. The wet air was then passed through sulphuric acid, whose weight increased by 2.0 g. What is the molecular mass of the dissolved substance? **[Ans.** 320]

2. The vapour pressure of 2.1% of an aqueous solution of non-electrolyte at 100°C is 755 mm. Calculate the molecular mass of the solute. **[Ans.** 58.68]

3. A current of dry air was passed through a series of bulbs containing a solution of 3.458 g of a substance in 100 g of ethyl alcohol and then through pure ethyl alcohol. The loss in weight of the former was 0.9675 g and in the latter, 0.055 g. Calculate the molecular mass of the solute. **[Ans.** 29.6]

4. A solution containing 6 g of benzoic acid in 50 g of ether ($C_2H_5OC_2H_5$) has a vapour pressure of 410 mm of mercury at 20°C. Given that the vapour pressure of ether at the same temperature is 442

mm of mercury. Calculate the molecular mass of benzoic acid. **[Ans.** 122.56)]

5. The vapour pressure of an aqueous solution of cane sugar (mol. wt. 342) is 756 mm at 100°C. How many grams of sugar are present in 1000 g of water? **[Ans.** 100.4 g]

6. A current of dry air was passed through a bulb containing 26.66 g of an organic substance in 200 g of water, then through a bulb at the same temperature containing pure water and finally through a tube containing fused calcium chloride. The loss in weight of the water bulb was 0.0870 g and the gain in the weight of $CaCl_2$ tube was 2.036 g. Calculate the molecular mass of the organic substance in the solution. **[Ans.** 53.8]

7. The vapour pressure of water is 92 mm at 50°C. 18.1 g of urea are dissolved in 100 g of water. The vapour pressure is reduced by 5 mm. Calculate the molecular mass of urea.

   [Hint. The solution is not dilute. Apply the relation $\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1 + n_2}$]

8. The vapour pressure of water of 20°C is 17 mm. Calculate the vapour pressure of a solution containing 2 g of urea (mol. mass = 60) in 50 g of water. Assume that the solution is not dilute. **[Ans.** 16.706 mm]

9. Calculate the vapour at 22°C of a 0.1 M solution of urea. The density of the solution may be taken as 1 g/ml. The vapour pressure of pure water at 22° is 20 mm. **[Ans.** 19.96 mm]

25.5 | OSMOSIS PHENOMENON

Before coming to the phenomenon of osmosis, let us understand clearly about semipermeable membrane.

The membrane which allows the flow of solvent molecules through it but not the solute molecules is called a semipermeable membrane. Examples are parchment, collodion, animal membrane, etc. In nature, the plant cells are protected by a semipermeable membrane. Chemically, we can prepare a semipermeable membrane of cupric fer-rocyanide within the walls of a porous pot.

Osmosis and Osmotic Pressure A solute tends to dissolve in a solvent as the most predominant randomness factor favours such a tendency. But when a pure solvent is separated from its solution by a semipermeable membrane, the molecules of the solvent diffuse through the semipermeable membrane into the solution. This is called ***osmosis.*** As a result of this transference of the solvent to solution, the level of solvent decreases while that of solution increases. It may be demonstrated by taking the solvent and solution in two compartments of a box separated by semipermeable membrane as shown in Fig. 25.6.

As more and more of the solvent molecules pass through the membrane into the solution, the concentration of the solution falls gradually. After some time, the hydrostatic pressure exerted by the solution column prevents the flow of more of solvent molecules and ***osmosis*** stops, i.e. there is no further rise in the level of solution in the column. Hence, osmotic pressure is defined as follows:

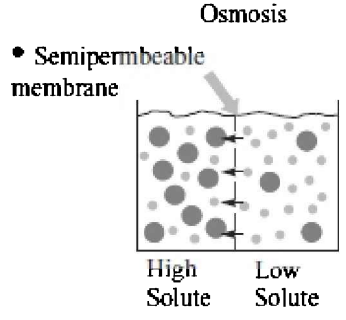


Fig. 25.5 *Osmosis phenomenon*

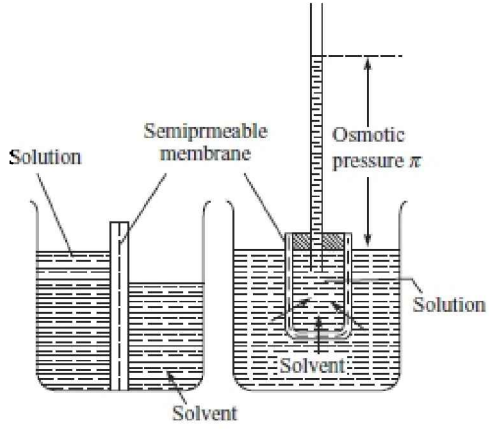


Fig. 25.6 *Osmosis and osmotic pressure*

(a) Osmotic Pressure ***is the equilibrium hydrostatic pressure exerted by the solution column which just prevents the flow of solvent molecules into the solution through a semipermeable membrane.***
(b) Osmosis ***is a phenomenon by which the pure solvent molecules tend to diffuse through a semipermeable membrane into the solution.***

25.6 | VAN'T HOFF RELATION BETWEEN THE OSMOTIC PRESSURE OF A SOLUTION AND MOLECULAR MASS OF THE SOLUTE

In dilute solutions, the behaviour of solute molecules is similar to that of molecules of a gas. Osmotic pressure (π) of a solution is found to be directly proportional to the molar concentration C of the solution and its absolute temperature T. Thus,

$$\pi \propto C$$

and $$\pi \propto T$$

or $$\pi \propto C.T$$

or $$\pi = R.C.T$$

where R is a constant and its value is found to be same as that of the gas constant.

If a solution is prepared by dissolving n moles of the solute in V litres of the solution, the molar concentration

$$C = \frac{n}{V} \text{ moles per litre}$$

$\therefore$ $$\pi = \frac{n}{V}RT \quad \text{or} \quad \pi V = nRT$$

The above equation is known as ***van't Hoff equation of dilute solutions*** and shows that osmotic pressure π is proportional to the molar concentration of the solute in the solution. Hence, it is a colligative property.

1. Determination of Molecular Mass from Osmotic Pressure If w grams of the solute are dissolved in V litres of the solution and m is the molecular mass of the solute then

$$n = w/m$$

Substituting this value in the equation $\pi V = nRT$, we get

$$\pi V = \frac{w}{m} \times R.T \quad \text{or} \quad m = \frac{wR.T}{\pi V}$$

Then molecular mass m of the solute can be calculate from this equation if the osmotic pressure π of the solution is known. The value of the constant R is taken as 0.0821 litre atmosphere per degree per mole when π is expressed in atmosphere and T in degree kelvin.

2. Relation Between Lowering of Vapour Pressure and Osmotic Pressure of a Solution The relation between lowering of vapour pressure and mole fraction of the solute is

$$\frac{p^\circ - p}{p^\circ} = \frac{w}{m} \times \frac{M}{W} \text{ (for a dilute solution)} \qquad \ldots(25.8a)$$

or
$$\frac{p^\circ - p}{p^\circ} = n \times \frac{M}{W} \qquad \ldots(25.8b)$$

where n is the number of moles of the solute.

The relation between the osmotic pressure and the number of moles of the solute is given by

$$\pi = \frac{nRT}{V} \qquad \ldots(25.9)$$

From Eq. (25.8b), $$n = \frac{p^\circ - p}{p^\circ} \times \frac{W}{M} \qquad \ldots(25.10)$$

From Eq. (25.9), $$n = \frac{\pi V}{RT} \qquad \ldots(25.11)$$

Equating RHS of equations (25.10) and (25.11)

$$\frac{p^\circ - p}{p^\circ} \frac{W}{M} = \frac{\pi V}{RT}$$

or
$$\frac{p^\circ - p}{p^\circ} = \frac{M}{W} \frac{\pi V}{RT}$$

or
$$\frac{p^\circ - p}{p^\circ} = \frac{M\pi}{(W/V) \cdot RT}$$

or
$$\frac{p^\circ - p}{p^\circ} = \frac{M\pi}{\rho \cdot RT}$$

where, M = Mol. mass of the solvent
ρ = Density of the solution
R = Solution (gas) constant
T = Temperature

3. Interesting Experiments to Demonstrate the Phenomenon of Osmosis Two interesting experiments to demonstrate the phenomenon of osmosis are described here.

(a) Silica Garden Crystals of many salts, e.g. ferrous sulphate, nickel chloride, cobalt nitrate and ferric chloride are placed in a solution of water glass (sodium silicate). The layers of metallic silicates formed on the surface of crystals by double decomposition are semipermeable. The water from outside enters through these membranes which burst and form what we call a silica garden. It makes an interesting sight.

(b) The Egg Experiment The outer hard shell of two eggs of the same size is removed by dissolving in dilute hydrochloric acid. One of these is placed in distilled water and the other in saturated salt solution. After a few hours, it will be noticed that the egg placed in the water swells and the one in salt solution shrinks. In the first case, water diffuses through the skin (a semipermeable membrane) into the egg which swells. In the second case, the concentration of the salt solution being higher than the material, some water leaves the egg and goes into salt solution and the egg shrinks (Fig. 25.7).

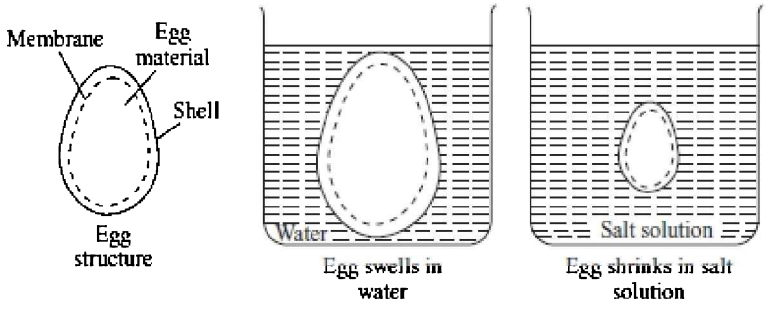


Fig. 25.7 *Demonstration ofosmosis by the egg experiment*

25.7 | VAN'T HOFF THEORY OF DILUTE SOLUTION TAKING THE EXAMPLE OF OSMOSIS

van't Hoff noted the striking resemblance between the behaviour of dilute solutions and gases. Dilute solutions obeyed laws analogous to the gas laws. To explain it, van't Hoff visualised that gases consist of molecules moving in vacant space (or vacuum), while in the solutions the solute particles are moving in the solvent. The exact analogy between solutions and gases is illustrated with Fig. 25.8.

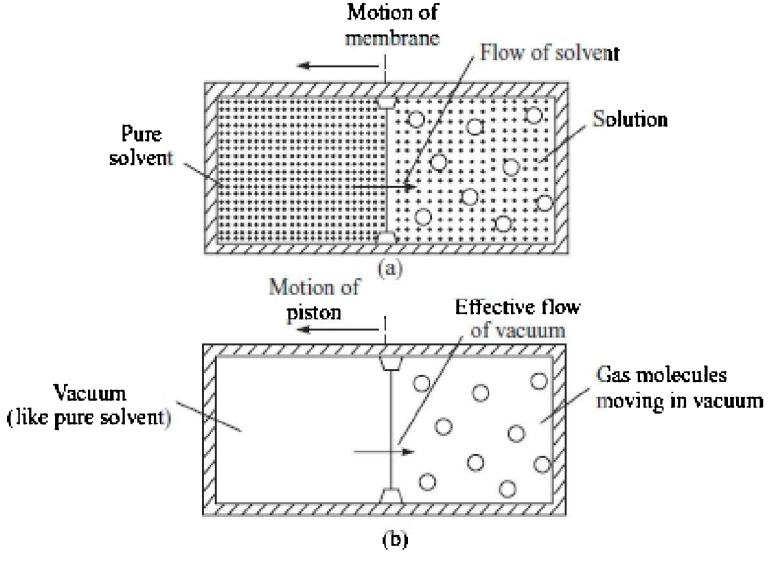


Fig. 25.8 *Analogy between osmotic pressure and gas pressure*

As shown in Fig. 25.8 (a), the pure solvent flows into the solution by osmosis across the semipermeable membrane. The solute molecules striking the membrane cause osmotic pressure and the sliding membrane is moved towards the solvent chamber. In case of a gas [Fig. 25.8 (b)], the gas molecules strike the piston and produce pressure that pushes it towards the empty chamber. Here it is the vacuum which moves into the gas. This demonstrates clearly that there is close similarity between a gas and a dilute solution.

Thinking on these lines, van't Hoff propounded his theory of dilute solution. The ***van't Hoff theory of Dilute solutions*** states:

A substance in solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature occupying the same volume as the solution.

According to van't Hoff theory of dilute solutions, all laws or relationships obeyed by gases would be applicable to dilute solutions.

From the van't Hoff theory, it follows that just as 1 mole of a gas occupying 22.4 litres at 0°C exerts 1 atmosphere pressure, so 1 mole of any solute dissolved in 22.4 litres would exert 1 atmosphere osmotic pressure.

25.8 DETERMINATION OF OSMOTIC PRESSURE

Prominent methods for the determination of osmotic pressure are described as under:

1. Pfeffer's Method The apparatus used by Pfeffer consists of a semipermeable membrane of copper ferrocyanide, supported on the walls of a porous pot. A T-shaped wide tube is fitted into the porous pot as shown in Fig. 25.9. The side tube *S* of the T-tube is connected to a closed manometer containing mercury and nitrogen. A simple tube *R* is fitted at the top of *T*-tube, through which the experimental solution is added into the porous pot till the porous pot and space above the mercury in the left limb of the manometer are completely filled. After filling, the tube *R* is sealed off. The pot is then placed in the pure solvent maintained at constant temperature. As a result of osmosis, the solvent passes into the solution. The highest pressure developed is recorded on the manometer.

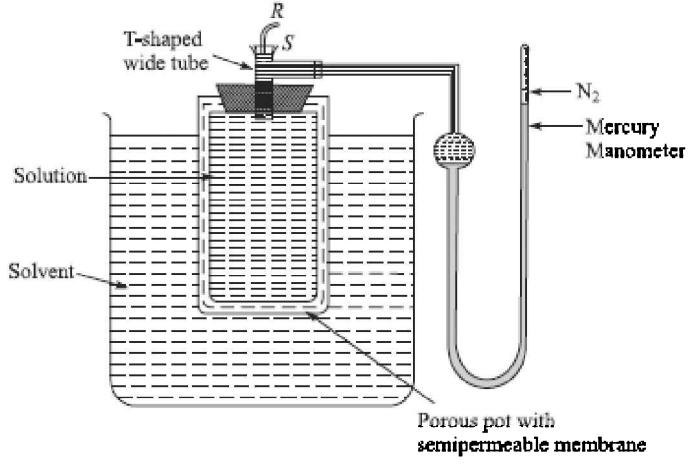


Fig. 25.9 *Pfeffer's apparatus*

2. Morse and Frazer's Method In this method, the solvent is taken in a porous pot (having semipermeable membrane in its walls) and the solution is kept outside the porous pot in the vessel made of bronze and connected to a manometer at the top. *A* tube *T* open at both the ends is fixed to the porous pot, as shown in Fig. 25.10 to keep the porous pot filled with the solvent. Morse and Frazer prepared a semipermeable membrane of better quality by electrolytic method to measure osmotic pressure up to 300 atmospheres.

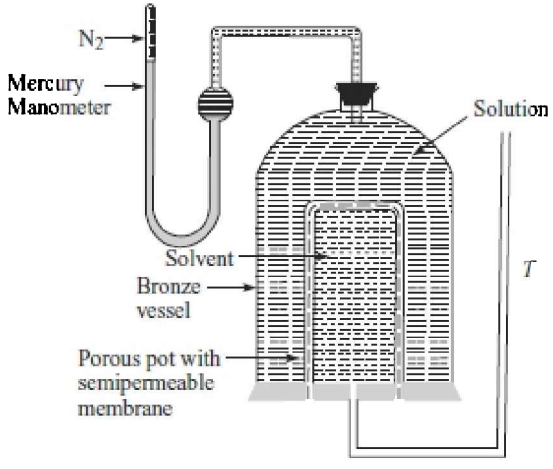


Fig. 25.10 *Morse and Frazer's apparatus*

3. Barkeley and Hartley Method The apparatus used for the determination of osmotic pressure by this method is shown in Fig. 25.11.

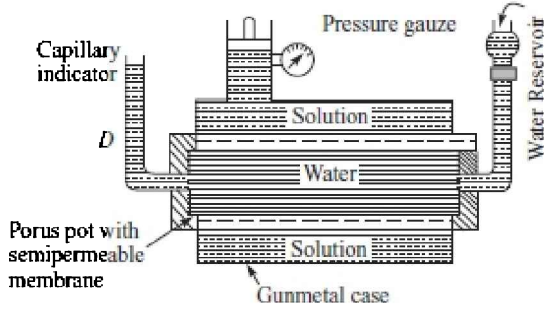


Fig. 25.11 *Barkeley and Hartley method for osmotic-pressure determination.*

It consists of a porous pot containing potassium ferrocyanide deposited on its walls and fitted into a metallic cylinder. A piston and a pressure gauge is attached to the metallic cylinder which is filled with the solution whose osmotic pressure is to be determined. The porous pot is filled with a capillary tube and water reservoir on the opposite sides. Water from the porous pot moves towards the solution in the cylinder through the semipermeable membrane. As a result, the level of water tends to fall down. External pressure is applied on the piston to such an extent that the water level in the capillary tube does not change. The magnitude of pressure applied can be read from the pressure gauge. This pressure is equal to the osmotic pressure.

25.8.1 IsotonicSolutions

Solutions of equimolecular concentrations at the same absolute temperature have the same osmotic pressure. ***Such solutions which have the same osmotic pressure at the same temperature are called isotonic solutions***.

25.8.2 Biological Importance of Osmosis

Osmosis plays a very important role in plants and animals i.e. living organisms, as described below:

1. Animal and vegetable cells contain solutions of sugars and salts enclosed in their semipermeable membranes (cell sap). On placing such a cell in water or in a solution, the osmotic pressure of water which is less than that of the cell sap within water enters the cell. However, on placing, the cells in a solution of higher osmotic pressure, water passes out of the cell and the cell shrinks. This shrinkage of the cell is called ***plasmolysis*** which can be illustrated by taking two hen eggs of the same size. Their outer shells are dissolved by placing them in dilute HCl. One egg is then placed in distilled water and the other in a saturated solution of NaCl (i.e. of higher osmotic pressure). In the first case, water ***enters into the egg*** through the membrane, while in the second case, ***water comes out of the egg*** through the membrane, i.e. the egg ***swells in the first case and shrinks in the second case***.

   Using solutions of varying concentrations and placing plants and animal cells in them, it is possible to find out the concentration when plasmolysis just stops. Such a solution is then said to be ***isotonic*** (i.e. having same osmotic pressure) with the cell solution. This process is thus helpful in measuring osmotic pressure of cell saps.

   It is found that red blood corpuscles and a 0.91% sol. of NaCl are isotonic.

2. Plant cells at their roots contain root hair, which are in contact with the soil. Since the osmotic pressure inside the cell is higher, water from the soil flows into the cell by osmosis.
3. Damage done to plants by use of excess of fertilizer is due to higher osmotic pressure of the fertilizer solution than that of the cell.
4. Plant movements such as opening and closing of flowers, opening and closing of leaves, etc., are also regulated by osmosis.

Applying Chemistry to Life

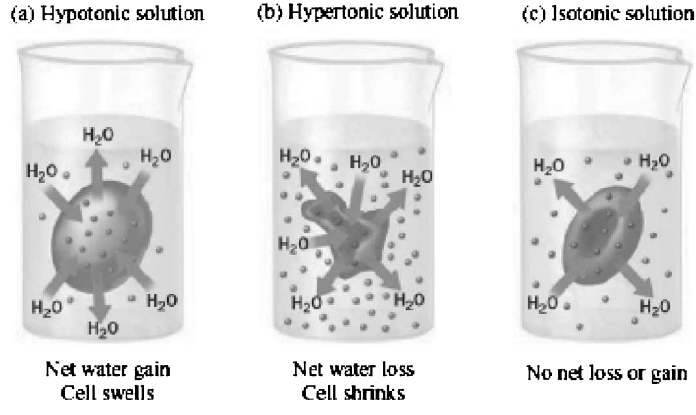


Fig. 25.12 *Hypotonic, hypertonic and isotonic solutions*

Human blood consists of blood cells suspended in plasma which is an aqueous solution containing salts and proteins. Each blood cell is surrounded by a protective semipermeable membrane. Inside the membrane, the concentration of solutes is about 0.3 M. Similarly, the plasma is also 0.3 M in concentration. If the concentration inside and outside the blood cell is the same, no movement of water into or out of the cell through the membrane takes places. The solution outside (plasma) is thus isotonic (same osmotic pressure) with the solution inside the blood cell. To maintain the balance of osmotic pressure, fluids that are given intravenously must be isotonic to plasma. Five percent dextrose (sugar) and normal saline which is 0.9% sodium chloride are two of the most commonly used isotonic intravenous fluids

Example 6 *A solution of sucrose (molecular mass 342) is prepared by dissolving 68.4 g of it per litre of the solution. What is its osmotic pressure at 300 K? R = 0.082 litre atm K^{-1} mol^{-1}.*

Solution: We know,

$$\pi = \frac{n}{V} \times RT$$

Given, molecular mass of the solute = 342
Mass of the solute = 68.4 g
Volume *V* of the solution = 1 litre

$$T = 300 \text{ K}$$

Osmotic pressure π = ?

$$R = 0.082 \text{ litre atm } K^{-1} \text{ mol}^{-1}$$

$$n, \text{ number of moles of solute} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}} \quad \text{or} \quad n = \frac{68.4}{342}$$

Substituting the values in the equation,

$$\pi = \frac{n}{V}RT \quad \text{or} \quad \pi = \frac{68.4}{342} \times \frac{0.082 \times 300}{1}$$

$$= 4.22 \text{ atm}$$

$\therefore$ Osmotic pressure = 4.22 atm

Example 7 *At 298 K, 100 cm^3 ofa solution, containing 3.002 g of an unidentified solute, exhibits an osmotic pressure of 2.55 atmospheres. What would be the molecular mass of the solute?*

Solution $\pi V = nRT$ where *n* is the number of moles of the solute

Also, $nV = \frac{w}{M}RT$ where *w* is the mass and *M* is the molecular mass of the solute.

or

$$M = \frac{wRT}{\pi V}$$

Substituting the values,

$$M = \frac{3.002 \times 0.0821 \times 298}{2.55 \times 0.1} \quad (V = 100 \text{ cm}^3 = 0.1 \text{ litre}) \quad \text{or} \quad M = 288 \text{ a.m.u.}$$

Example 8 *Osmotic pressure of solution containing 7 grams of dissolved protein per 100 cm^3 of a solution is 25 mm of Hg at body temperature (310 K). Calculate the molar mass of the protein (R = 0.08205 litre atm deg $^{-1}$ mot $^{-1}$).*

Solution: We know,

$$\pi = \frac{n}{V} \times RT$$

$$\pi = 25 \text{ mm} = \frac{25}{760} \text{ atmosphere } (\because 760 = 1 \text{ atm})$$

$$R = 0.08205 \text{ L atmosphere K}^{-1}\text{mol}^{-1}$$

$$T = 310 \text{ K}$$

$$V = 100 \text{ cm}^3 = \frac{100}{1000} = \frac{1}{10} \text{ litre}$$

$\therefore$ n, number of moles of solute $= \dfrac{\pi \times V}{RT}$ ...(i)

Also, $n = \dfrac{\text{Mass of solute}}{\text{Molecular mass of solute}}$ ...(ii)

From (i) and (ii),

$$\frac{\text{Mass of solute}}{\text{Molecular mass of solute}} = \frac{\pi \times V}{RT}$$

$$\text{Molecular mass of solute} = \frac{\text{Mass of solute} \times R \times T}{\pi \times V}$$

Substituting the values, we have

$$\text{Molecular mass of the solute} = \frac{7 \times 0.08205 \times 310}{\frac{25}{760} \times \frac{1}{10}}$$

or $$\text{Molecular mass of solute} = \frac{7 \times 0.08205 \times 310 \times 760 \times 10}{25} = 54126.7$$

Example 9 *Calculate the osmotic pressure of 95% solution of cane sugar at 288 K. R = 0.082 litre atm K^{-1} mol^{-1}.*

Solution: Molecular mass of cane sugar ($C_{12}H_{22}O_{11}$) = 342

$\therefore$ the solution is 5%

$\therefore$ Weight of sugar per litre = 50 g

$\therefore$ n, number of moles $= \dfrac{\text{Weight of solute}}{\text{Molecular mass of solute}} = \dfrac{50}{342}$, $V = 1$ litre, $T = 288$ K

Substituting the values in the relation

$$\pi = \frac{n}{V} \cdot RT$$

we have, $$\pi = \frac{50}{342} \times \frac{0.082 \times 288}{1} = 3.45 \text{ atm}$$

Example 10 *The vapour pressure of a solution containing 2.47 g ethyl benzoate in 100 g of benzene (mol. wt. 78 and density 0.8149 g/ml) was found to be 742.6 mm of Hg at 80°C while that ofpure benzene at the same temperature, it is 751.86 mm of Hg. Calculate the osmotic pressure of the solution.*

Solution It is given that,

$$p_s = 742.6 \text{ mm}, p^\circ = 751.86 \text{ mm}. M = 78$$

$$\text{Density } (\rho) = 0.8149 \text{ g/ml} = 814.9 \text{ g/litre}$$

$$T = 80 + 273 = 353 \text{ K}$$

π (osmotic pressure) to be determined

Taking R = 0.0821 litre atmosphere per degree per mole and substituting these values in the formula,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{M\pi}{\rho RT} \quad \text{(Refer to section 25.6)}$$

$$\frac{751.86 - 742.60}{751.86} = \frac{76 \times \pi}{814.9 \times 0.0821 \times 353}$$

or
$$\pi = \frac{9.26}{751.86} \times \frac{814.9 \times 0.0821 \times 353}{78}$$

$$= 3.73 \text{ atm}$$

PROBLEMS FOR PRACTICE

1. Calculate the osmotic pressure at 25°C of a solution containing one gram of glucose ($C_6H_{12}O_6$) and 1 gram of sucrose ($C_{12}O_{22}O_{11}$) in 100 g of water. If it were not known that the solute was a mixture of glucose and sucrose, what would be the molecular mass of the solute corresponding to the calculated osmotic pressure?

[Ans. 0.2074 atm, 235.8]

2. Calculate osmotic pressure of a solution containing 5 grams of glucose in 100 ml of its solution at 17°C (R = 0.0821 litre atm/mol/degree). **[Ans.** 6.61 atm]

3. Calculate the osmotic pressure of solution obtained by mixing one litre of 7.5% solution of a substance *A* (mol. mass = 75) and two litres of 3% solution of a substance *B* (mol. mass = 60) at 18°C. **[Ans.** 7.954 atm]

4. Calculate the concentration of solution of glucose which is isotonic at the same temperature with a solution of urea containing 6.2 g/litre. **[Ans.** 18.6 g/litre]

5. Calculate the value of the constant R in litre atmosphere from the observation that solution containing 34.2 g of cane sugar in one litre of water has an osmotic pressure of 2.405 atm at 0°C. **[Ans.** 0.0821]

6. A solution of glucose containing 18 g/litre had an osmotic pressure of 2.40 atm at 27°C. Calculate the molecular mass of glucose (R = 0.082 litre atm.) **[Ans.** 183.5]

7. A 6% solution of sucrose ($C_{12}H_{22}O_{11}$) is isotonic with a 3% solution of an unknown organic substance. Calculate the molecular mass of the unknown substance. **[Ans.** 171]

8. A 4% solution of cane sugar gave an osmotic pressure of 208.0 cm of Hg at 15°C. Find its molecular mass.

[Ans. 345.2]

9. The vapour pressure of a solution of urea is 736.2 nm at 100°C. What is the osmotic pressure of this solution at 15°C? **[Ans.** 41.1 atm]

25.9 THEORIES OF OSMOSIS

1. Membrane Solution Theory Membrane proteins bearing functional groups such as –COOH, –OH, $–NH_2$, etc., dissolve water molecules by hydrogen bonding or chemical interaction. Thus, membrane dissolves water from the pure water (solvent) forming what may be called 'membrane solution'. The dissolved water flows into the solution across the membrane to equalise concentrations. In this way, water molecules pass through the membrane, while solute molecules being insoluble in the membrane

do not.

2. Membrane Bombardment Theory This theory suggests that osmosis results from an unequal bombardment pressure caused by solvent molecules on the two sides of the semipermeable membrane. On one side we have only solvent molecules, while on the other side there are solute molecules occupying some of the surface area. Thus, there are fewer bombardments per unit area of surface on the solution side than on the solvent side. Hence, the solvent molecules will diffuse more slowly through the membrane on the solution side than on the solvent side. The net result causes a flow of the solvent from the pure solvent to the solution across the membrane.

3. Molecular Sieves Theory According to this theory, the membrane contains lots of fine pores and acts as a sort of molecular sieve. ***Smaller solvent molecules can pass through the pores but the larger solute molecules cannot.*** Solvent molecules flow from a region of higher solute concentration to one of lower concentration across such a membrane (Fig. 25.13). But we observe that some membranes can act as sieves even when the solute molecules are smaller than the solvent molecules. This theory does not provide a satisfactory answer to this.

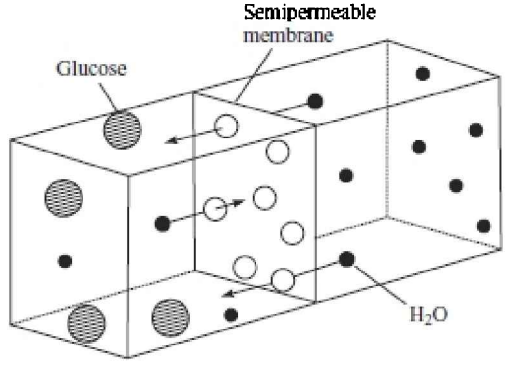


Fig. 25.13 *A semipermeable membrane can separate particles on the basis of size. It allows the passage of small water molecules in both directions. But it prevents of passage the glucose molecules which are larger than water molecules.*

Recently, it has been shown that the pores or capillaries between the protein molecules constituting an animal membrane are lined with polar groups ($-COO^-$, $-NH_3^+$, $-S^{2-}$, etc.). Therefore, the membrane acts not simply as a sieve but also regulates the passage of solute molecules by electrostatic or 'chemical interactions'. In this way, even solute molecules smaller than solvent molecules can be held back by the membrane.

4. Vapour Pressure Theory It suggests that a semipermeable membrane has many fine holes or capillaries. The walls of these capillaries are not wetted by water (solvent) or solution.

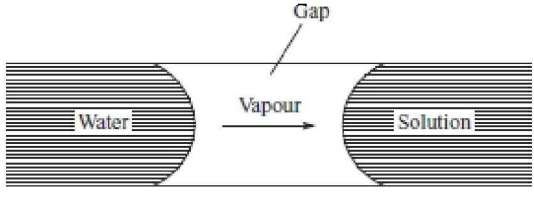


Fig. 25.14 *Water vapours diffuse into solution across the gap in a capillary ofthe membrane.*

Thus, neither solution nor water can enter the capillaries. Therefore, each capillary will have in it solution at one end and water at the other, separated by a small gap (Fig. 25.14). Since the vapour pressure of the solution is lower than that of the pure solvent, the diffusion of vapour will occur across the gap from water side to solution side. This results in the transfer of water into the solution.

Reverse Osmosis and its Applications

When a solution is separated from pure water by a semipermeable membrane, osmosis of water occurs from water to solution. This osmosis can be stopped by applying pressure equal to or more than osmotic pressure, on the solution (Fig. 25.15). If pressure greater than osmotic pressure is applied, osmosis is made to proceed in the reverse direction to ordinary osmosis, i.e. from solution to water.

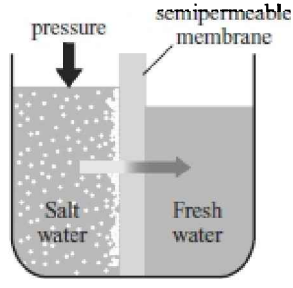


Fig. 25.15 *Principle ofreverse osmosis*

The osmosis taking place from solution to pure water by application of pressure greater than osmotic pressure on the solution is termed reverse osmosis.

The technology is used in the commercial production of water purifiers these days (RO water purifiers).

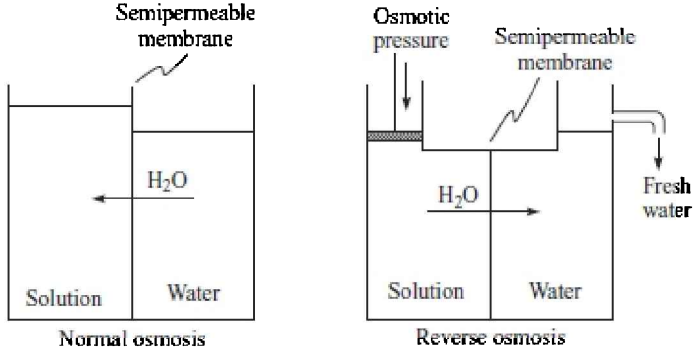


Fig. 25.16 *Reverse osmosis versus ordinary osmosis*

Desalination of Sea Water by Hollow-fibre Reverse Osmosis Reverse osmosis is used for the desalination of sea water for getting fresh drinking water. This is done with the help of hollow fibres (nylon or cellulose acetate) whose wall acts as semipermeable membrane. A hollow-fibre reverse osmosis unit is shown in Fig. 25.17.

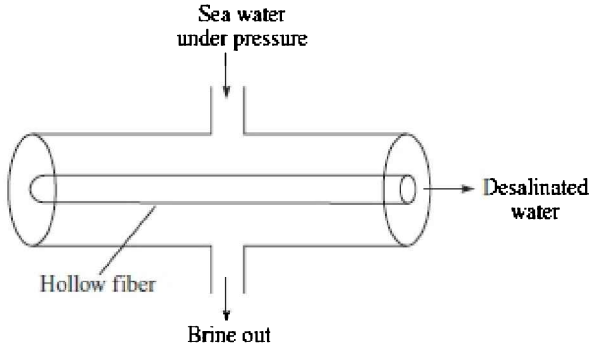


Fig. 25.17 *Desalination ofsea waterbyreverse osmosis in a hollowfibre unit*

Water is introduced under pressure around the hollow fibres. The fresh water is obtained from the inside of the fibre. In actual practice, each unit contains more than three million fibres bundled together. Each fibre is of about the diameter of a human hair.

25.10 | ELEVATION IN BOILING POINT

Determination of Elevation in Boiling Point

Two methods that are generally employed to measure boiling-point elevation are described below:

1. Cottrell's Method It consists of (i) a graduated boiling tube containing a solvent or solution; (ii) a reflux condenser which returns the vapourised solvent to the boiling tube; (iii) a thermometer reading to 0.01 K, enclosed in a glass hood; and (iv) a small inverted funnel with a narrow stem which branches into three jets projecting at the thermometer bulb. Figure 25.18 (a) shows all the four components.

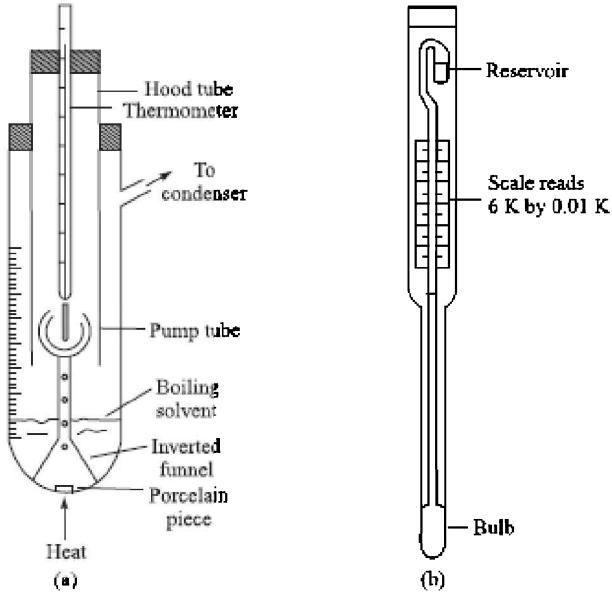


Fig. 25.18 *(a) Cottrell's apparatus (b) Beckmann thermometerreading to 0.01 K*

2. Beckmann Thermometer [Fig. 25.18 (b)]. It is a ***differential thermometer.*** It is designed to measure small changes in temperature and not the temperature itself. It has a large bulb at the bottom of a fine capillary tube. The scale is caliberated from 0 to 6 K. and subdivided into 0.01 K. The unique feature of this thermometer is the small reservoir of mercury at the top. The amount of mercury in this reservoir can be decreased or increased by tapping the thermometer gently. In this way, the thermometer is adjusted so that the level of the mercury thread will show up at the middle of the scale when the instrument is placed in the boiling (or freezing) solvent.

Procedure The apparatus is set up as shown in [Fig. 25.18 (a)]. The solvent is placed in the boiling tube with a porcelain piece lying in it. It is heated on a small flame. As the solvent starts boiling, solvent vapour arising from the porcelain piece pumps the boiling liquid into the narrow stem. Thus, a mixture of solvent vapour and boiling liquid is continuously sprayed around the thermometer bulb. The temperature soon becomes constant and the boiling point of the pure solvent is recorded.

Now a weighed amount of the solute is added to the solvent and the boiling point of the solution in the boiling tube is noted. The difference of the boiling temperatures of the solvent and solute gives the elevation of boiling point. While calculating the molecular mass of the solute, the volume of the solution is converted into mass by multiplying with density of the solvent at its boiling point.

3. Landberger-Walker Method

(a) Apparatus The apparatus used in this method is shown in Fig. 25.19 and consists of (i) an ***inner tube*** with a hole in its side and graduated in ml; (ii) a boiling flask which sends solvent vapour into the graduated tube through a bulb with several holes (rose bulb); (iii) an **outer tube** which receives hot solvent vapour issuing from the side-hole of the inner tube; and (iv) a thermometer reading to 0.1 K, dipping in solvent or solution in the inner tube.

(b) Procedure Pure solvent is placed in the graduated tube and vapour of the same solvent boiling in a separate flask is passed into it. The vapour causes the solvent in the tube to boil by its latent heat of condensation. When the solvent starts boiling and temperature becomes constant, its boiling point is recorded.

Now the supply of vapour is temporarily cut off and a weighed pellet of the solute is dropped into the solvent in the inner tube. The solvent vapour is again passed through until the boiling point of the solution is reached and this is recorded. The solvent vapour is then cut off, the thermometer and rose head raised out of the solution, and the volume of the solution read.

From the difference in boiling points of solvent and solution, we can find the molecular mass of the solute by using the expression,

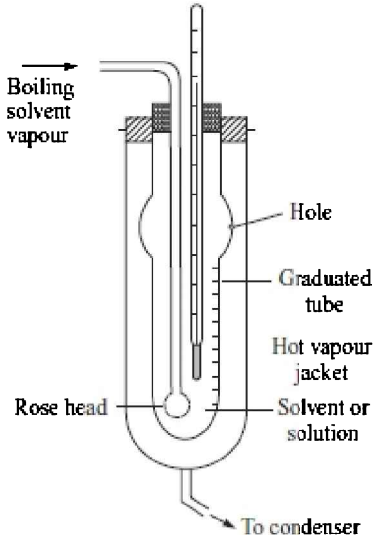


Fig. 25.19 *Landsberger-Walker apparatus.*

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

where w = weight of solute taken and W = weight of solvent which is given by the volume of solvent (or solution) measured in ml multiplied by the density of the solvent at its boiling point.

25.11 | RELATION BETWEEN ELEVATION IN BOILING POINT OF SOLUTION AND MOLECULAR MASS OF SOLUTE

The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. Since, at any temperature, the vapour pressure of the solution of a nonvolatile solute is always lower than that of the pure solvent, the boiling point of a solution is always higher than that of the pure solvent.

The fact can be illustrated in Fig. 25.20. The upper curve represents the pressure-temperature relationship of the dilute solution of a known concentration. It is evident that the vapour pressure of the solution is less than that of the pure solvent of each temperature. From Fig. 25.20, it is clear that for the pure solvent, the vapour pressure becomes equal to the atmospheric pressure at temperature $T_b°$. Similarly, the vapour pressure of the solution is equal to the atmospheric pressure T_b, which is obviously higher than $T_b°$. Therefore, $T_b - T_b°$ gives the elevation in the boiling point which is represented as ΔT_b.

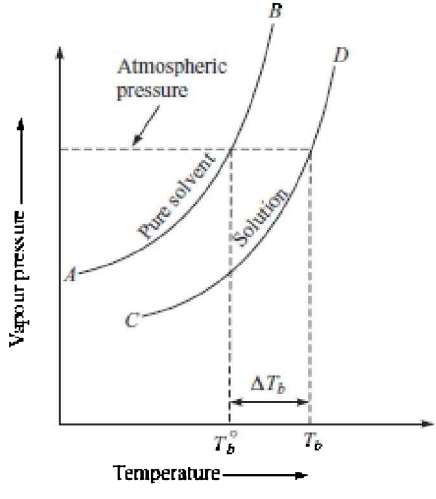


Fig. 25.20 *Vapour pressure of pure solvent or solution.*

or $$T_b - T_b^\circ = \Delta T_b$$

The elevation in boiling point depends upon concentration of the solute in the solution. In other words, ΔT_b is directly proportional to the molality (m) of the solution, i.e.

$$\Delta T_b \propto \text{Molality}$$

or $$\Delta T_b = K_b \times \text{Molality} \qquad \ldots(25.12)$$

where K_b is called ***molal elevation (ebullioscopic) constant.***

If molality = 1, $\Delta T_b = K_b$

Thus, ***molal elevation constant*** *may be defined as the elevation in boiling point of a solution containing 1 gram mole of a solute per 1000 grams of the solvent.*

1. Molecular Mass of Nonvolatile Solute By definition,

$$\text{Molality} = \frac{1000 \times w}{W \times m}$$

∴ Eq. (25.12) becomes,

$$\Delta T_b = \frac{1000 \times K_b \times w}{W \times m}$$

or

$$m = \frac{1000 \times K_b \times w}{W \times \Delta T_b}$$

where, ΔT_b = Elevation in boiling point

K_b = Molal elevation (Ebullioscopic) constant of the solvent

m = Molecular mass of the solute

w = Weight of the solute in grams

n = Weight of the pure solvent

W = Weight of the solvent in grams.

2. Thermodynamic Derivation of a Relationship between Elevation in Boiling Point and Molecular Weight of a Nonvolatile Solute Figure 25.21 gives the vapour pressure-temperature curves for the solvent and solution. The horizontal dotted line drawn corresponding the external pressure cuts the solvent and solution curves at the points E and F which correspond to temperatures T_o and T_s respectively. Then by deinition, T_o is the boiling point of the pure solvent and T_s that of the solution. Obviously, $T_s > T_o$. The increase $(T_s - T_o)$ is called the elevation in boiling point and is usually represented by ΔT_b. Thus,

$$\Delta T_b = T_s - T_o \qquad \ldots(25.13)$$

The relationship between the elevation in boiling point and the concentration of the solution can be obtained by applying Clausius-Clapeyron equation and Raoult's law to the different conditions shown in Fig. 25.21.

The Clausius-Clapeyron equation, which is applicable to a phase equilibrium, in the integrated form is given by

$$\ln \frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where p_1 is the vapour pressure at temperature T_1,p_2 is the vapour pressure at temperature T_2, and ΔH is the molar latent heat of transition.

Referring to Fig. 25.21, points G and F lie on the same solution curve. Suppose the vapour pressure of the pure solvent and the solution at temperature T_o are p_o and p_s respectively. Then from Fig. 25.21, we have

(a) Corresponding to the point G, temperature = T_o, vapour pressure = p_s

(b) Corresponding to the point F, temperature = T_s, vapour pressure = $p°$

Hence, for the equilibrium, solution $\rightleftharpoons$ vapour, according to Clausius-Clapeyron equation, we have (for the points G and F),

$$\ln \frac{p°}{p_s} = \frac{\Delta H_v}{R}\left(\frac{1}{T_o} - \frac{1}{T_s}\right) \qquad \ldots(25.14)$$

where, ΔH_v is the latent heat of vaporisation of one mole of the solvent from the solution. When the solution is dilute, ΔH_v is nearly equal to the latent heat of evaporation of the pure solvent.

Equation (25.14) can be written as

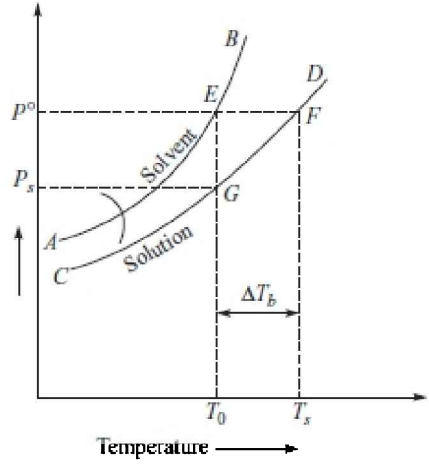


Fig. 25.21 *Relationship between elevation in boiling point and lowering of vapour pressure.*

$$\ln \frac{p^\circ}{p_s} = \frac{\Delta H_v}{R}\left(\frac{T_s - T_0}{T_s T_0}\right)$$

or
$$\ln \frac{p^\circ}{p_s} = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_b}{T_s T_0} \quad [\because T_s - T_0 = \Delta T_b] \qquad \ldots(25.15)$$

Further, when the solution is dilute, T_S is nearly equal to T_O. Hence, Eq. (25.15) can be written as

$$\ln \frac{p^\circ}{p_s} = \frac{\Delta H_v}{R} \frac{\Delta T_b}{T_0^2} \qquad \ldots(25.16)$$

According to Raoult's law, we have

$$\frac{p^\circ - p_s}{p^\circ} = x_2 \qquad \ldots(25.17)$$

where x_2 is the mole fraction of the solute in the solution.

Equation (25.17) can be written as

$$1 - \frac{p_s}{p_0} = x_2 \quad \text{or} \quad \frac{p_s}{p_0} = 1 - x_2$$

$$\therefore \quad \ln \frac{p_s}{p_0} = \ln(1 - x_2)$$

or
$$\ln \frac{p_s}{p_0} = -\ln(1 - x_2) \qquad \ldots(25.18)$$

or since x_2 is very small (less than 1), the expansion of $\ln (1 - x_2)$ as infinite series is given by

$$\ln(1 - x_2) = -x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3 \ldots$$

Neglecting x_2^2, x_2^2, etc. (as x_2 is much smaller than 1), we have

$$\ln(1 - x_2) \simeq -x_2 \qquad \ldots(25.19)$$

or $$-\ln(1 - x_2) \simeq x_2$$

From Eqs.(25.18) and (25.19),

$$\ln\frac{p_s}{p_0} = x_2 \qquad \ldots(25.20)$$

Substituting this values in Eq. (25.16),

$$x_2 = \frac{\Delta H_v}{R}\frac{\Delta T_b}{T_0^2} \qquad \ldots(25.21a)$$

or $$\Delta T_b = \frac{RT_0^2 x_2}{\Delta H_v} \qquad \ldots(25.21b)$$

However, the common practice in the studies on elevation in boiling point is not to express the concentrations in terms of mole fractions but in terms of ***moles of the solute per 1000 g of the solvent,*** i.e. in terms of molality, m. Hence, Eq. (25.21b) is further modified as follows:

If n_2 moles of the solute are dissolved in n_1 moles of the solvent, the mole fraction of the solute (x_2) in the solution will be given by

$$x_2 = \frac{n_2}{n_1 + n_2}$$

As the solution is supposed to be dilute, $n_2 << n_1$ so that in the denominator, n_2 can be neglected in comparison to n_1. Hence, for the dilute solution, the above equation can be written as

$$x_2 = \frac{n_2}{n_1}$$

Further, if $w_2 g$ of the solute is dissolved in $w_1 g$ of the solvent and M_2 and M_1 are the molecular masses of the solute and solvent respectively then

$$n_2 = \frac{w_2}{M_1} \text{ and } n_1 = \frac{w_1}{M_1}$$

Hence, $$x_2 = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 \times M_1}{w_1 \times M_2}$$

Putting this value of x_2 in Eq. (25.21b), we get,

$$\Delta T_b = \frac{RT_0^2}{\Delta H_v}\frac{w_2 M_1}{w_1 M_2}$$

$$= \frac{RT_0^2}{\Delta H_v/M_1}\frac{w_2}{w_1 M_2} \qquad (25.22)$$

Putting $\frac{\Delta H_v}{M_2} = l_v$ latent heat of vaporisation per gram of the solvent, Eq. (25.22) becomes

$$\Delta T_b = \frac{RT_0^2}{l_v}\frac{w_2}{w_1 M_2} \qquad \ldots(25.23)$$

Let us say molality of the solution is m. Thus, m moles of the solute are dissolved in 1000 g of the

solvent. We can write

$$\frac{w_2}{M_2} = m \quad \text{and} \quad w_1 = 1000$$

Putting these values in Eq. (25.23), we get

$$\Delta T_b = \frac{RT_o^2}{l_v}\frac{m}{1000} \qquad \ldots(25.24)$$

or

$$\Delta T_b = \frac{RT_o^2}{1000 l_v} m \qquad \ldots(25.25)$$

For a given solvent, the quantity $\frac{RT_o^2}{1000 l_v}$ is a constant quantity because l_v, T_o and R are constant. It is represented by K_b and is called ***molal elevation constant*** or ***ebullioscopic constant.***

i.e.

$$\boxed{K_b = \frac{RT_o^2}{1000 l_v}} \qquad \ldots(25.26)$$

Hence, Eq. (25.25) can be written as

$$\Delta T_b = K_b \cdot m \qquad \ldots(25.26)$$

Thus, molal elevation constant may be defined as the elevation in boiling point when the molality of the solution is unity.

Example 11 *A solution prepared from 0.3 g of an unknown nonvolatile solute in 30.0 g of CCl_4 boils at 350.392 K. Calculate the molecular mass of the solute. The boiling point of CCl_4 and its K_b values are 350.0 K and 5.03 respectively.*

Solution From the given data,

Weight of the solute, w = 0.3 g

Weight of the solvent, W = 30.0 g

Elevation of boiling point = ΔT_b = 350.392 – 350.0 = 0.392 K

Elevation constant K_b = 5.03 K kg mol^{-1}

Calculation of molality

30 g of CCl_4 contain 0.3 g of solute

$$\therefore \quad 1000 \text{ g of } CCl_4 \text{ contain } = \frac{1000 \times 0.3}{30} \text{ g} = \frac{1000 \times 0.3}{30 \times m} \text{ moles}$$

$$\therefore \quad \text{Molality (no. of moles in 1000 g of } CCl_4) = \frac{1000 \times 0.3}{30 \times m}$$

Substituting the values in the relation,

$$\Delta T_b = K_b \times \text{Molality}$$

$$0.92 = 5.03 \times \frac{1000 \times 0.3}{30 \times m} \quad \text{or} \quad m = \frac{5.03 \times 1000 \times 0.3}{30 \times 0.392} = 128.3$$

$\therefore$ molecular mass = 128.3

Example 12 *10 g of a nonvolatile solute when dissolved in 100 g of benzene raises its b.p. by 1°.*

What is the molecular mass of the solute (K_b for benzene = 2.53 K mol^{-1})?

Solution In this problem,

Mass of the solute (w) = 10 g

Mass of the solvent (W) = 100 g

Elevation in b.p. (ΔT_b) = 1°, K_b = 2.53

Substituting the values in the equation,

$$m = \frac{1000 \times K_b \times w}{W \times \Delta T_b} = \frac{1000 \times 2.53 \times 10}{1000 \times 1} = 253$$

Example 13 *A solution of 12.5 g of urea in 170 g of water gave boiling-point elevation of 0.63 K. Calculate the molar mass of urea. K_b = 0.52 K kg mol^{-1}.*

Solution From the given data

Wight of the solute, w = 12.5 g

Wight of the solvent, W = 170 g

Elevation of boiling point ΔT_b = 0.63 K

Elevation constant K_b = 0.52 K kg mol^{-1}

Let the molecular mass of solute (urea) = m

Calculation of molality

170 grams of water contain urea 12.5 gram

$\therefore$ 1000 grams of water contain urea $= \frac{1000 \times 12.5}{170}$ g or $= \frac{1000 \times 12.5}{170 \times m}$ mole

$\therefore$ Molality (no. of moles in 1000 g of solvent) $= \frac{1000 \times 12.5}{170 \times m}$

We know, $\Delta T_b = K_b \times$ molality

Substituting the value in above relation,

We have, $0.63 = 0.52 \times \left(\frac{1000 \times 12.5}{170 \times m} \right)$ or $m = \frac{0.52 \times 1000 \times 12.5}{170 \times 0.63}$

m 60.69 a.m.u.

Example 14 *A solution containing 0.5126 g of naphthalene (mol. mass 128) in 50 g of carbon tetrachloride yields a b.p. elevation of0.402°C, while a solution of 0.6216 g of an unknown solute in the same weight of the solvent gives a b.p. elevation of 0.647°C. Find the molecular mass of the unknown solute.*

Solution

1. *Determination of K_b from the first data*

w – 0.5126 g m –128 W – 50 g

$$K_b = \frac{m \times W \times T_b}{1000 \times w} = \frac{128 \times 50 \times 0.402}{1000 \times 0.5126} = 5.02$$

2. *Molecular mass of the unknown solute*

w – 0.6216 g W – 50 g ΔT_b – 0.647 K_b – 5.02

The value of K_b remains the same because the solvent is the same. Substituting the values in the equation,

$$m = \frac{1000 \times K_b \times w}{W \times \Delta T_b} = \frac{1000 \times 5.02 \times 0.6216}{50 \times 0.647} = 96.46$$

Example 15 *Find the b.p. of a solution containing 0.36 g of glucose ($C_6H_{12}O_6$) dissolved in 100 g of water (K_b = 0.52 K/m).*

Solution Mass of glucose *(w)* = 0.36 g
Mass of water *(W)* = 100 g
Molecular mass of glucose *(M)* = 180
Molar elevation constant for water (K_b) = 0.52
Substituting the values in the relation,

$$\Delta T_b = \frac{1000 \times K_b \times w}{W \times m} \quad \text{or} \quad \Delta T_b = \frac{1000 \times 0.52 \times 0.36}{100 \times 180}$$

Elevation in b.p. = 0.0104, b.p. of pure water = 373 K
Hence, b.p. of the solution = 373 + 0.0104 = 373.0104 K

PROBLEMS FOR PRACTICE

1. A solution containing 36 g of solute dissolved in 1 litre of water gave an osmotic pressure of 6.75 atmosphere at 27°C. The molal elevation constant of water is 0.52 K kg mol^{-1}. Calculate the boiling point of the solution.

[Ans. 100.1425°C]

2. A solution of 3.795 g sulphur in 100 g carbon disulphide (boiling point 46.30°C, ΔH_v = 6400 cal/mol) boils at 46.66°C. What is the formula of sulphur molecule in the solution?

[Ans. S_8]

[*Hint.* ΔH_v = 6400 cal/mol, $\therefore l_v = \frac{6400}{76}$ cal/g because mol mass of CS_2 = 76.
First, calculate K_b and then M_2.
We get M_2 = 255.2. Hence, atomicity of molecule $= \frac{255.2}{32} = 8$]

3. What elevation in the boiling point of alcohol is to be expected when 5 g of urea (mol. wt. = 60) are dissolved in 75 g of it? The molal elevation constant for alcohol is 1.15°C per molality.

[Ans. 1.28°C]

4. What is the molecular mass of a nonvolatile organic compound if the addition of 1.0 g of it in 50.0 g of benzene raises the boiling point of benzene by 0.30°C? K_b for benzene is 2.53°C per 1000 g of benzene.

[Ans. 170]

5. Calculate the molal boiling point constant for chloroform (M = 119.4) from the fact that its boiling point is 61.2°C and its latent heat of vaporisation is 59.0 cal/g.

[Ans. 3.79°C]

6. When 1.80 g of a nonvolatile compound are dissolved in 25.0 g of acetone, the solution boils at 56.86°C while pure acetone boils at 56.38°C under the same atmospheric pressure. Calculate the molecular mass of the compound. The molal elevation constant for acetone is 1.72°K kg mol^{-1}

[Ans. 258]

3. Relationship between Elevation in Boiling Point and Relative Lowering of Vapour Pressure
We have the following relation between elevation in boiling point and molecular mass:

$$\Delta T_b = \frac{1000 \times K_b w_2}{w_1 M_2} \quad \ldots(25.28)$$

Also, $$\frac{w_2}{M_2} = n_2 \quad \ldots(25.29)$$

and $$\frac{w_1}{M_1} = n_1 \quad \ldots(25.30)$$

Substituting the values of w_2 and w_1 from Eqs (25.29) and (25.30) in (25.28), we get

$$\Delta T_b = \frac{1000 \times K_b n_2}{n_1 M_1} = \frac{1000 \times K_b}{M_1} \frac{n_2}{n_1} \quad \ldots(25.31)$$

By Raoult's law, for dilute solutions, we have

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1} \quad \ldots(25.32)$$

where $\Delta p = p^\circ - p_s$ is the lowering of vapour pressure.

From Eqs (25.31) and (25.32), we get

$$\Delta T_b = \frac{1000 K_b w_2}{w_1 M_2} \quad \ldots(25.34a)$$

or $$\Delta T_b = \frac{1000 K_b w_2 / M_2}{w_1}$$

4. Relationship between Elevation in Boiling Point and Osmotic Pressure The equation for the osmotic pressure for n_2 moles of the solute dissolved in V litres of solution is

$$\pi V = n_2 RT$$

or $$n_2 = \frac{\pi V}{RT} \quad \ldots(25.33)$$

The equation for the elevation in boiling point is

$$\Delta T_b = \frac{1000 K_b w_2}{w_1 M_2} \quad \ldots(25.34a)$$

or $$\Delta T_b = \frac{1000 K_b w_2 / M_2}{w_1}$$

or $$\Delta T_b = \frac{1000 K_b \cdot n_2}{w_1} \quad \ldots(25.34b)$$

Substituting the value of n_2 from Eq (25.33) in Eq. (25.34b)

$$\Delta T_b = \frac{1000 K_b}{w_1} \times \frac{\pi V}{RT} = \frac{1000 K_b \cdot \pi}{(w_1 / V) \cdot RT} \quad \ldots(25.35)$$

As the solution is dilute,

Volume of the solution (V) $\simeq$ Volume of the solvent

$\therefore$ if d is the density of the solvent,

$$\frac{w_1}{V} = d$$

Substituting this value in the equation, we get

$$\Delta T_b = \frac{1000 K_b \pi}{dRT}$$

25.12 DEPRESSION IN FREEZING POINT

Methods for the determination of depression in freezing point are described here:

25.12.1 Beckmann's Method

1. Apparatus It consists of (i) a **freezing tube** with a side-arm to contain the solvent or solution, while the solute can be introduced through the side arm A; (ii) an outer tube into which is fixed the freezing tube, the space in between providing an air jacket which ensures a slower and more uniform rate of cooling, and (iii) a **large jar** containing a freezing mixture e.g. ice and salt with a stirrer (Fig. 25.22).

2. Procedure About 20 g of solvent is taken in the freezing-point tube and the apparatus set up as shown in Fig. 25.22 so that the bulb of the thermometer is completely immersed in the solvent. Determine the freezing point of the solvent by directly cooling the freezing-point tube in the cooling bath.

The freezing point of the solvent having been accurately determined, the solvent is remelted by removing the tube from the bath, and a weighed amount (0.1 –0.2 g) of the solute is introduced through the side tube. Now the freezing point of the solution is determined in the same way as that of the solvent. A further quantity of solute may then be added and another reading taken. Knowing the depression of the freezing point, the molecular mass of the solute can be determined by using the expression

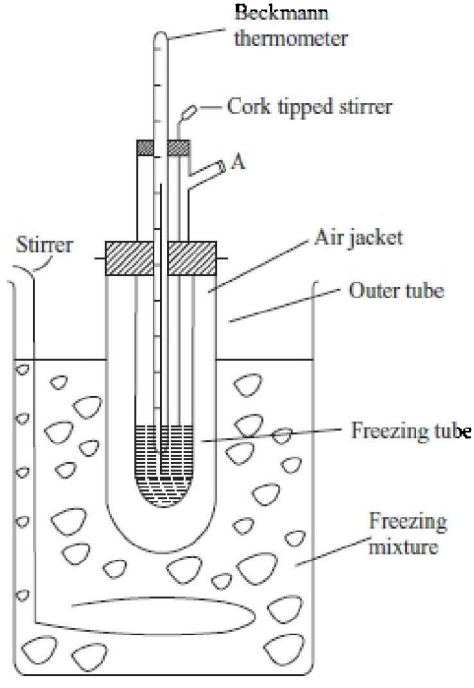


Fig. 25.22 *Beckmann's freezing-point apparatus*

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

25.12.2 Rast's Camphor Method (Cryoscopic Method)

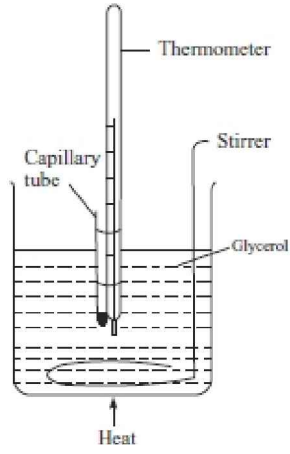


Fig. 25.23 *Determination of depression of melting point by capillary method*

This method is used for the determination of molecular weights of solutes which are soluble in molten camphor. The freezing-point depressions are so large that an ordinary thermometer can also be used.

Pure camphor is powered and introduced into a capillary tube which is sealed at the upper end. This is tied along the thermometer and heated in a glycerol bath (Fig. 25.23). The melting point of camphor is recorded. Then a weighed amount of solute and camphor (about 10 times as much) are melted in a test tube. The solution of solute in camphor is cooled in air. After solidification, the mixture is powdered and introduced into a capillary tube which is sealed. Its melting point is recorded and described before. The difference of the melting point of pure camphor and the mixture, gives the depression of freezing point. In modern practice, an electrical heating apparatus (Fig. 25.24) is used for a quick determination of melting points of camphor as also of the mixture.

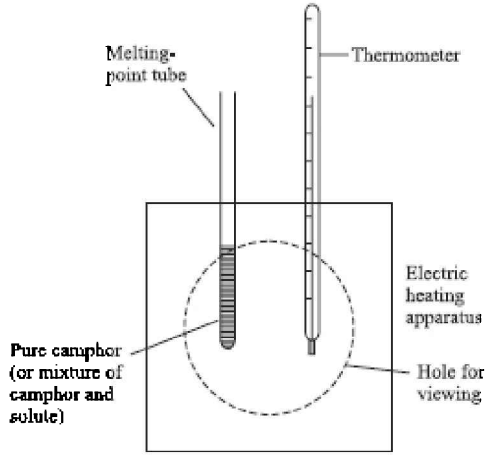


Fig. 25.24 *Determination of depression of melting point by electrical apparatus*

25.13 | RELATION BETWEEN DEPRESSION IN FREEZING POINT AND MOLECULAR MASS OF THE SOLUTE

Freezing point of a substance is the temperature at which solid and liquid states co-exists, i.e. the two states have the same vapour pressure. The presence of a nonvolatile solute lowers the vapour pressure of the solution. Thus, liquid and solid states will have equal vapour pressure at a much lower temperature. Hence, there is depression in the freezing point. In other words, the freezing point of a solution is lower than that of the pure solvent as is clear from Fig. 25.25. The curve *AB* represents the vapour pressure curve of the pure solvent. At the point *A*, the solvent co-exists with the liquid state. The temperature corresponding to the point *A* gives the freezing point of the solvent. Similarly, the curve *CD* represents the vapour pressure curve of the solution in which the point *D* corresponds to two states of the solvent existing simultaneously in the solution. Thus, temperature corresponding to the point *D* is the freezing point of the solution which is clearly lower than the freezing point of the pure solvent. Hence, there is a depression in the freezing point given by ΔT_f.

$$\Delta T_f = T_f^\circ - T_f$$

It has been found that depression in the freezing point is proportional to molal concentration of the solute in the solution i.e. molality is given below.

$$\Delta T_f = K_f \times \text{Molality}$$

where, K_f is constant known as ***molal depression constant*** or ***cryoscopic constant of the solvent***.

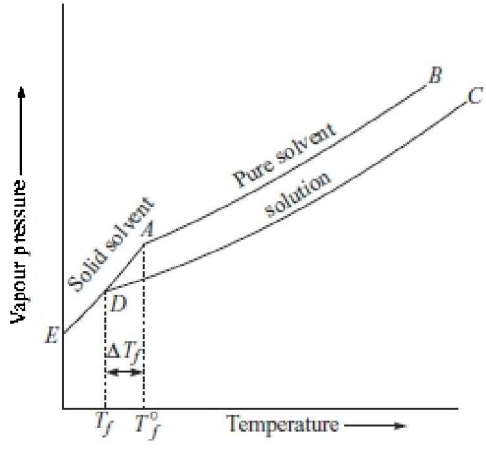


Fig. 25.25 *Plot of VP versus temperature*

If $\text{molality} = 1$, then $\Delta T_f = K_f$

Hence, ***molal depression constant may be defined as the depression in freezing point when 1 mole of the solute is dissolved in 1000 g of the solvent***.

1. Molecular Mass of Nonvolatile Solute

Since $$\text{molality} = \frac{1000 \times w}{W \times m}$$

$$\therefore \quad \Delta T_f = \frac{K_f \times 1000 \times w}{W \times m} \quad \text{or} \quad m = \frac{1000 \times K_f \times w}{W \times \Delta T_f}$$

Here, ΔT_f = Depression in freezing point

K_f = Molal depression constant or cryoscopic constant

w = Mass of solute in grams

m = Molecular mass of the solute

W = Mass of the solvent in grams.

2. Thermodynamic Derivation ofa Relationship between Freezing Point and Molecular Weight of a Nonvolatile Solute

The depression in freezing point of a solution can be explained on the basis of lowering of vapour pressure of the solution. If vapour pressure is plotted against temperature, the curve *AB* is obtained for the liquid solvent as shown in Fig. 25.26. At the point *B*, the liquid solvent starts solidifying and hence, the liquid solvent and the solid solvent are in equilibrium with each other. The temperature corresponding to the point *B* is thus, the freezing point of pure solvent (T_o). When whole of the liquid solvent has been solidified, there is a sharp change in the vapour pressure-temperature curve beyond the point *B*, as shown by the curve *BC* for the solid solvent. Vapour pressure temperature curve for the solution lies below the vapour pressure curve of the liquid solvent, as represented by the curve *DE* in Fig. 25.26. As the cooling of the solution is continued, at the point *E*, the separation of the solid solvent starts. Thus, the point *E* represents the freezing point of the solution (T_s). From Fig. 25.26, it is evident that $T_s < T_o$. The decrease ($T_o - T_s$) is called the depression in freezing point and is usually represented by ΔT_f. Thus,

$$\Delta T_f = T_o - T_s \qquad \ldots(25.36)$$

The relationship between the depression in freezing point and the concentration of the solution can be derived by applying Clausius-Clapeyron equation and Raoult's law to the curves shown in Fig. 25.26.

Suppose the vapour pressures corresponding to points *B*, *E* and *F* are $p°$, p and p_s respectively.

The equilibrium exists along the curve *BC* is

$$\text{Solid} \rightleftharpoons \text{Vapour}$$

The curve *BC* is, therefore, the sublimation curve of the solid solvent. For the points *B* and *E* lying on the curve, we have

(a) corresponding to the point *B*, temperature = T_o, vapour pressure = $p°$

(b) corresponding to the point *E*, Temperature = T_s, vapour pressure = p

Applying the Clausius-Clapeyron equation corresponding to points *B* and *E*, we have

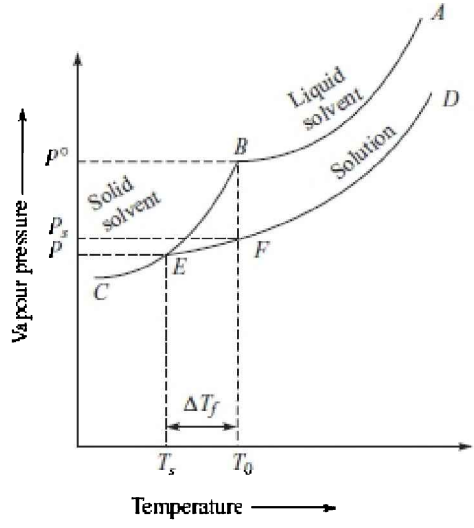


Fig. 25.26 *Relationship between depression in freezing point and lowering of vapour pressure.*

$$\ln \frac{p^\circ}{p} = \frac{\Delta H_s}{R}\left(\frac{1}{T_s} - \frac{1}{T_o}\right) \qquad (25.37)$$

where ΔH_s is the molar latent heat of sublimation of the solid solvent.

Equation (25.37) can be written as

$$\ln \frac{p^\circ}{p} = \frac{\Delta H_s}{R}\frac{T_o - T_s}{T_o T_s}$$

$$= \frac{\Delta H_s}{R} \cdot \frac{\Delta T_f}{T_o T_s} \qquad \ldots(25.38)$$

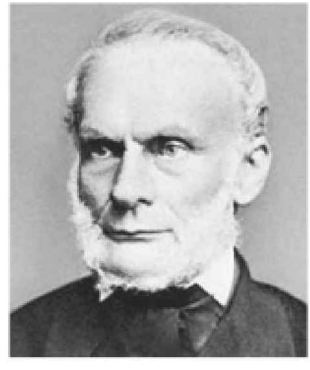


Fig. 25.27 *Rudolf Clausius was a German physicist and mathematician, considered as one of the central founders of thermodynamics.*

As the solution is dilute, $T_s \simeq T_o$ and, therefore, Eq. (25.38) becomes

$$\ln \frac{p_o}{p} = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_f}{T_o^2} \qquad \ldots(25.39)$$

The equilibrium existing along the curve *DE* is

$$\text{Solod} \rightleftharpoons \text{Vapour}$$

The curve *DE* is, thus, the vaporisation curve of the solution.

For the points *E* and *F* lying on this curve, we have

(a) corresponding to the point *E*, temperature = T_s, vapour pressure = $p°$

(b) corresponding to the point *F*, temperature = T_o, vapour pressure = p_s

Applying the Clausius-Clayperon equation to these conditions, we have

$$\ln \frac{p_s}{p} = \frac{\Delta H_v}{R}\left(\frac{1}{T_s} - \frac{1}{T_o}\right) = \frac{\Delta H_v}{R} \cdot \frac{T_o - T_s}{T_s \cdot T_o}$$

$$= \frac{\Delta H_v}{R} \frac{\Delta T_f}{T_o^2} \text{ (taking } T_s \simeq T_o) \qquad \ldots(25.40)$$

where ΔH_v is the latent heat of vaporisation of one mole of the solvent from the solution and is nearly equal to the molar latent of vaporisation of pure solvent for a dilute solution.

In order to get a relationship for the equilibrium,

$$\text{solid} \rightleftharpoons \text{Vapour}$$

Subtracting Eq. (25.40) from Eq. (25.39), we get

$$\ln \frac{p°}{p} - \ln \frac{p_s}{p} = \frac{\Delta H_s}{R} \frac{\Delta T_f}{T_o^2} - \frac{\Delta H_v}{R} \frac{\Delta T_f}{T_o^2}$$

or $$(\ln p° - \ln p) \quad (\ln p_s - \ln p) = \frac{\Delta T_f}{RT_o^2}(\Delta H_s \quad \Delta H_v)$$

$$\ln p° - \ln p_s = \frac{\Delta T_f}{RT_o^2} \Delta H_f$$

$$\ln \frac{p°}{p_s} = \frac{\Delta T_f}{RT_o^2} \Delta H_f \qquad \ldots(25.41)$$

where $\Delta H_s - \Delta H_v = \Delta H_f$ is molar latent heat of fusion of the solid solvent.

The left-hand term of Eq. (25.41) can be expressed in terms of mole fraction by applying Raoult's law,

$$\frac{p° - p_s}{p°} = x_2 \qquad \ldots(25.42)$$

where x_2 is the mole fraction of the solute in the solution.

Equation (25.42) can be written as

$$1 - \frac{p_s}{p°} = x_2 \text{ or } \frac{p_s}{p°} = 1 - x_2 \text{ or } \ln \frac{p_s}{p_o} = \ln(1 - x_2)$$

or $$\ln \frac{p°}{p_s} = -\ln(1 - x_2) \qquad \ldots(25.43)$$

The expansion of $\ln (1 - x_2)$ as an infinite series is given by

$$\ln(1 - x_2) = -x_2 - \frac{1}{2}x_2^2 - \frac{1}{3}x_2^3 \ldots$$

Neglecting x_2^2, x_2^3, etc. (because x_2 is very small, higher powers will be still smaller), we have

$$\ln(1 - x_2) = -x_2$$

Hence, Eq. (25.43) becomes,

$$\ln\frac{p^\circ}{p_s} = x_2$$

Substituting this value in Eq. (25.41), we get

$$x_2 = \frac{\Delta T_f}{RT_o^2} \cdot \Delta H_f$$

or
$$\Delta T_f = \frac{RT_o^2}{\Delta H_f} \cdot x_2 \qquad \ldots(25.44)$$

This equation gives the relationship between depression in freezing point and the mole fraction x_2 of the solute in the solution.

To obtain the equation in terms of molality instead of mole fraction x_2, we have

$$x_2 = \frac{n_2}{n_1 + n_2}$$

where n_2 = Number of moles of the solute in the solution

n_1 = Number of moles of the solvent in the solution.

For dilute solution $n_2 << n_1$, so that on neglecting n_2 in comparison to n_1, we have

$$x_2 = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 M_1}{w_1 M_2} \qquad \ldots(25.45)$$

where w_2 = Weight of the solute dissolved

M_2 = Molecular weight of the solute

w_1 = Weight of the solvent

M_1 = Molecular weight of the solvent

Putting the value of x_2 from Eq. (25.45) in Eq. (25.44), we get

$$\Delta T_f = \frac{RT_o^2}{\Delta H_f} \cdot \frac{w_2 M_1}{w_1 M_2} \qquad \ldots(25.46)$$

$$= \frac{RT_o^2}{\Delta H_f / M_1} \cdot \frac{w_2}{w_1 M_2} \qquad \ldots(25.47)$$

$$= \frac{RT_o^2}{l_f} \cdot \frac{w_2}{w_1 M_2}$$

where $l_f = \dfrac{\Delta H_f}{M_1}$ is the latent heat of fusion ***per gram*** for the solid solvent.

It m is the molality of the solution, i.e. m moles of the solute are dissolved in 1000 g of the solvent,

then $\dfrac{w_2}{M_2} = m$ and $w_1 = 1000$ g

Putting these values in Eq. (25.47), we get

$$\Delta T_f = \frac{RT_o^2}{l_f} \cdot \frac{m}{1000}$$

or
$$\Delta T_f = \frac{RT_o^2}{l_f} \cdot m \qquad \ldots(25.48)$$

Since T_o and l_f for a given solvent are constant, the quantity $\frac{RT_o^2}{1000 l_f}$ in Eq. (25.48) must be a constant quantity. It is usually represented by K_f and is called ***molal depression constant*** or ***cryoscopic constant.***

Thus,

$$K_f = \frac{RT_o^2}{1000 l_f} \qquad \ldots(25.49)$$

Substituting this value in Eq. (25.48), we get

$$\Delta T_f = K_f \cdot m \qquad \ldots(25.50)$$

If
$$m = 1, \Delta T_f = K_f$$

Thus, ***molal depression constant may be defined as the depression in freezing point which takes place when the molality of the solution is unity***.

Applying Chemistry to Life

Heavy snowfall is pleasant to gaze at but it becomes a potent hazard in the movement of traffic by road. Workers spray common salt on the snow and then use cleaning machines. The principle involved is that the freezing point of water is lowered on the addition of a solute. The frozen snow, therefore, melts into liquid state and removal of snow is facilitated.

In cold places, water in the radiators of automobiles gets frozen. This hinders the starting of engines. Also, it may cause damage to the radiator. This problem is overcome by adding a coolant (mostly glycol) to the radiator. Freezing point of a solvent is lowered by the addition of solutes. This prevents freezing of water in the radiator. In fact, glycol offers a double advantage. When the engine has worked for a long time, water has a tendency to evaporate. After some time, no water is left in the radiator. Addition of glycol raises the boiling point of water and reduces the evaporation of water.



Fig. 25.28 *Snow cleaning machine*



Fig. 25.29 *Radiatorcooling*

Example 16 *What is molal depression constant? How is it related to latent heat of fusion?*

Solution: For definition of molal depression constant molal, depression constant K_f is also given by the relation

$$K_f = \frac{RT_f^2}{1000 L_f} \text{ where}$$

T_f = Freezing point of solvent
L_f = Molal latent heat of fusion
R = Gas constant
For water, $T_f = 273$ K, $L_f = 336$ J g^{-1}

Example 17 *Find (a) the boiling point, and (b) the freezing point of a solution containing 0.52 g glucose ($C_6H_{12}O_6$) dissolved in 30.2 g of water. For water K_b = 0.52 K kg mol^{-1}, K_f = 1.86 K kg mol^{-1}.*

Solution: Given

Molecular mass of glucose $m = 180$
Weight of solute $w = 0.52$ g
Weight of solvent $W = 80.2$ g
Calculation of molality
80.2 g of the solvent contain = 0.52 g of solute

1000 g of the solvent contains $= \frac{1000 \times 0.52}{80.2}$ g $\quad \therefore$ Molality $= \frac{1000 \times 0.52}{80.2 \times 180}$

We know, $\Delta T_b = K_b \times \text{molality} = 0.52 \times \frac{1000 \times 1.52}{80 \times 180}$ g $= 0.018$ K

$\therefore$ Boiling point = 373 + 0.018 = 373.018 K
$\therefore$ Boiling point of water = 373 K
$\therefore$ Boiling point of solution = 373.018 K

For freezing point, $\Delta T_f = K_f \times \text{Molality} = 1.86 \times \frac{1000 \times 0.52}{80.2 \times 180} = 0.067$
Freezing point of water = 273 K
$\therefore$ Freezing point of solution = 273 – 0.067 = 272.933 K

Example 18 *A sample of camphor used in the Rast method of determination of molecular masses had*

a melting point of 176.5°C. The melting point of a solution containing 0.522 g camphor and 0.0386 g of an unknown substance was 158.5°C. Find the molecular mass of the substance. K_f of camphor per kg is 37.7.

Solution Applying the expression

$$m = \frac{1000 \times K_f \times w}{\Delta T \times W}$$

to the present case, we have

$\Delta T = 176.5 - 158.5 = 18$, or $K_f = 37.7$, $w = 0.0386$ g, $W = 0.522$ g

Substituting these values $m = \dfrac{1000 \times 37.7 \times 0.0386}{18 \times 0.522} = 154.8$

Example 19 *The normal freezing point of nitrobenzene $C_6H_5NO_2$ is 278.82 K. A 0.25 molal solution of a certain solute in nitrobenzene causes a freezing-point depression of 2 degrees. Calculate the value of K_f for nitrobenzene.*

Solution:

$\Delta T_f = K_f \cdot m$, $\Delta T_f = 2$, $m = 0.25$

Substituting the values in the first equation,

$$2 = K_f \times 0.25 \quad \text{or} \quad K_f = \frac{2}{0.25} = 8 \text{ K kg mol}^{-1}$$

Example 20 *A solution of sucrose (molar mass = 342 g/mole) is prepared by dissolving 68.4 g in 1000 g of water. What is the*

(a) vapour pressure of the solution at 293 K?

(b) osmotic pressure at 293 K?

(c) boiling point of the solution?

(d) freezing point of the solution?

The vapour pressure of water at 293 K is 17.5 mm, $K_b = 0.52$, $K_f = 1.86$

Solution:

(a) Mole fraction of sucrose, $X_B = \frac{68.4/342}{68.4/342 + 1000/18} = \frac{9}{2509}$

$$\frac{p_A^\circ - p_A}{p_A} = X_B$$

Vapour pressure of water, $p_A^\circ = 17.5$ mm

Substituting the values, $\frac{17.5 - p_A}{17.5} = \frac{9}{2509}$

or $17.5 \times 2509 p_A = 9 \times 17.5$

$2509 p_A = 43750$

$p_A = 17.43$ mm

(b) $\pi V = nRT \quad V = 1$ litre $\quad n = \frac{68.4}{342}$

$$\pi \times 1 = \frac{68.4}{342} \times 0.0821 \times 293 \quad \text{or} \quad \pi = 4.8 \text{ atmospheres}$$

(c) $\Delta T_b = K_b \times m$ where m is the molality

$$\text{Molality } (m) = \frac{68.4}{342}, \; K_b = 0.52$$

Substituting the values,

$$\Delta T_b = 0.52 \times \frac{68.4}{342} = 0.104$$

Boiling point of the solution = 373 + 0.104 = 373.104

(d) $\Delta T_f = K_f \times m$

$$m = \frac{68.4}{342}; \; K_f = 1.86$$

$$\therefore \quad \Delta T_f = 1.86 \times \frac{68.4}{342} = 0.372$$

$\therefore$ Freezing point of the solution $= 273 - 0.372 = 273.628$ K

Example 21 *Calculate the freezing point of a solution containing 0.520 g glucose ($C_6H_{12}O_6$) in 80.2 grams of water. For water, $K_f = 1.86$ K kg mol^{-1}.*

Solution: Given

Weight of the solute (glucose), $w = 0.520$ g

Weight of solvent water, $W = 80.2$ g

Molar depression constant, $K_f = 1.86$ K kg mol^{-1}

Molecular weight of the solute $C_6H_{12}O_6$, $m = 180$

Calculation of molality

80.2 g of water contain glucose = 0.520 g

$$1000 \text{ g of water contain glucose} = \frac{1000 \times 0.520}{80.2}$$

$$\therefore \quad \text{Molality} = \frac{1000 \times 0.520}{80.2 \times 180}$$

$\therefore$ Applying the relation,

$$\Delta T_f = K_f \times \text{Molality}$$

$$= 1.86 \times \frac{1000 \times 0.520}{80.2 \times 180}$$

$$\therefore \quad \text{Freezing point} = 273 - 0.067$$

$$= 273.933 \text{ K} \qquad (\because \text{Freezing point of water} = 273 \text{ K})$$

Example 22 *A solution of 1.25 g of a certain non-electrolyte in 20 g of water freezes at 271.95 K. Calculate the molecular mass of the solute. (K_f = 1.86 K kg^{-1} mol^{-1})*

Solution: Here, we are given that

Weight of the solute, w = 1.25 g Weight of solvent W = 20 g

Molar depression constant K_f = 1.86 K kg mol^{-1}

Depression in freezing point ΔT_f = 273 – 271.95 = 1.05 K

Calculation of molality

20 g of water contain solute = 1.25 g

$\therefore$ 1000 g of water contain solute = $\frac{1000 \times 1.25}{20}$

Let the molecular mass of the solute = m

$$\therefore \quad \text{Molality} = \frac{1000 \times 1.25}{20 \times m}$$

Substituting the values in the relation,

$$\Delta T_f = K_f \times m \quad \text{or} \quad 1.05 = 1.86 \times \frac{1000 \times 1.25}{20 \times m}$$

or

$$m = \frac{1.86 \times 1000 \times 1.25}{20 \times 1.05} = 110.71$$

$\therefore$ Molecular mass of the solute (m) = 110.71

PROBLEMS FOR PRACTICE

1. The latent heat of fusion of ice is 79.7 cal/g. Calculate the molal depression constant of water.

[Ans. 1.86 K kg mol^{-1}]

2. The freezing point of pure benzene is 5.40°C. A solution containing 1 g of a solute dissolved in 50 g of benzene freezes at 4.40°C. Calculate the molecular mass of the solute. The molecular depression constant of benzene with reference to 100 g is 50°C.

[Ans. 100]

3. An aqueous solution freezes at – 0.2°C. What is the molality of the solution? Determine also

   (a) elevation in boiling point

   (b) lowering of vapour pressure at 25°C given that K_f = 1.86 K kg mol^{-1} and K_b = 0.512 K kg mol^{-1} and the vapour pressure of water at 25°C is 23.756 mm.

[Ans. Molality = 0.1075, ΔT_b = 0.055°C, lowering of vapour pressure = 0.046 m]

4. Naphthalene (f.p. 80.1°C) has molal freezing point constant of 6.82°C m^{-1}. A solution of 3.2 g in

100 g of naphthalene freezes at a temperature of 0.863°C less than pure naphthalene. What is the molecular formula of sulphur in naphthalene?

[Ans. S_8]

5. In the winter season, ethylene glycol is added to water so that water may not freeze. Assuming ethylene to be nonvolatile, calculate the minimum amount of ethylene glycol that must be added to 6.0 kg of water to prevent it from freezing at – 0.30°C. The molal depression constant of water is 1.86 K kg mol^{-1}.

[Ans. 60 g]

6. An aqueous solution contains 5% by weight of urea and 10% by weight of glucose. What will be its freezing point? Molal depression constant of water is 1.86°C/m

[Ans. –3.039°C]

CAUSE OF ABNORMAL MOLECULAR MASSES OF SOLUTES IN SOLUTIONS

In certain situations, we find that the value of the colligative property measured is greater or smaller than the value expected. Also, since molecular mass is inversely related to the observed colligative property, the molecular mass calculated from the observed value of colligative property by applying the relevant relation, comes out to be different from the calculated molecular mass. We express it by saying that the solute is showing abnormal molecular mass.

Abnormal molecular mass of a solute in solution is due to association or dissociation of molecules in the solution. These are explained as below.

1. Association If the molecules of the solute undergo association in solution, there will be decrease in the number of species. As a result, there will be proportionate decrease in the value of each colligative property. The experimental value of molecular mass of the solute will be higher in such a case. This is because molecular mass is inversely proportional to the value of any colligative property.

For example, acetic acid and benzoic acid both associate in benzene. Similarly, chloroacetic acid associates in naphthalene. The molecular mass of solute in such cases is higher than the molecular mass obtained from their molecular formulae. Thus, the molecular mass of acetic acid (CH_3COOH) in benzene, as determined from freezing-point depression, is 118 instead of 60.

2. Dissociation Inorganic acids, bases and salts dissociate or ionise in solution. As a result of this, the number of effective particles increases and, therefore, the value of colligative property is also increased. Therefore, the experimental value of molecular mass of the solute will be lower in such a case. This is because molecular mass is inversely proportional to the value of any colligative property as already discussed.

Evidently, the observed molecular mass will be higher in case of association and lower in case of dissociation.

25.14 | VAN'T HOFF FACTOR

To account for abnormal cases, van't Hoff introduced a factor i known as the ***van't Hoff factor***.

$$i = \frac{\text{Observed colligative property}}{\text{Calculated (normal) colligative property}}$$

Since colligative properties vary inversely as the molecular mass of the solute, it follows that

$$i = \frac{\text{Calculated (normal) molecular mass}}{\text{Observed molecular mass}}$$

Relation Between Degree of Association and van't Hoff Factor Consider the association of n molecules of a solute A to give one molecule of A_n

$$nA = A_n$$

Let the degree of association be α. If we start with one mole of A, the number of moles that associate is α and the number of moles that remain unchanged is $1 - \alpha$.

α mole on association will give α/n moles.

Total number of moles at equilibrium $= \frac{\alpha}{n} + (1 - \alpha)$ van't Hoff factor is the ratio of observed colligative property to calculated colligative property. And colligative property is proportional to the number of moles of the solute. Hence,



Fig. 25.30 *Jacobus van't Hoff was a Dutch physical and organic chemist and the first winner of the Nobel Prize in chemistry. He is best known for his works on chemical kinetics, osmotic pressure and stereochemistry.*

$$\text{van't Hoff factor } (i) = \frac{1 - \alpha + \frac{\alpha}{n}}{1}$$

Relation between Degree of Dissociation and van't Hoff Factor Let us consider the dissociation of a molecule to give n molecules or ions in the solution.

$$A \rightarrow nB$$

Let us start with 1 mole of A and let α be the degree of dissociation.
At equilibrium,
Number of moles of undissociated substance = $1 - \alpha$
Number of moles of dissociated substance = $n\alpha$
(one molecule dissociates to give n molecules)
Total number of moles of solute at equilibrium = $1 - \alpha + n\alpha$

Hence, Van't Hoff factor $(i) = \frac{1 - \alpha + n\alpha}{1}$

Example 23 *Calculate the osmotic pressure of 20% anhydrous calcium chloride solution at 273 K, assuming that the solution is completely dissociated. ($R = 0.082$ lit atm K^{-1} mol^{-1}).*

Solution: Molecular mass of $CaCl_2 = 40 + 71 = 111$

Since solution is 20%,

$\therefore$ weight of $CaCl_2$ per litre = 200 g, $V = 1$ litre, $T = 273$ K

$$n = \frac{\text{Wt. of solute}}{\text{Molecular mass of solute}} = \frac{200}{111}$$

Substituting the values in the relation,

$$\pi = \frac{n}{V} \times RT$$

we have $$\pi = \frac{200}{111} \times \frac{0.082 \times 273}{1} = 40.335 \text{ atm}$$

Since $CaCl_2$ dissolves to give 3 particles for each molecule on complete dissociation ($CaCl_2 \rightarrow Ca^{++} + 2Cl^-$)

$\therefore$ Observed osmotic pressure = Normal osmotic pressure × 3
= 40.335 × 3 = 121.00 atm

$\therefore$ Observed osmotic pressure = 121.00 atm

Example 24 *2.0 g of benzoic acid dissolved in 25.0 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant (K_f) of benzene is 4.9 K kg mol^{-1}. What is the percentage association of the acid?*

Solution Mass of the solute w_2 = 2.0 g

Mass of the solvent w_1 = 25.0 g

Observed ΔT_f = 1.62 K

$$K_f = \text{kg mol}^{-1}$$

$\therefore$ Observed molecular mass of benzoic acid (solute)

$$M_2 = \frac{1000 \times K_f \times w_2}{\Delta T_f \times w_1} = \frac{1000 \times 4.9 \times 2}{1.62 \times 25.0} = 242$$

Calculated molecular mass of benzoic acid (C_6H_5COOH)

(By adding atomic masses) = 72 + 5 + 12 + 32 + 1 = 122

Van't Hoff factor, $$i = \frac{\text{Calculated mol. mass}}{\text{Observed mol. mass}} = \frac{122}{242} = 0.504$$

If α is the degree of dissociation of benzoic acid then

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

Initial moles	1	0
After association	$1 - \alpha$	$\frac{\alpha}{2}$

$\therefore$ Total number of moles after association $= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$

or $$i = \frac{1 - \frac{\alpha}{2}}{1} = 0.504$$

or $$1 - \frac{\alpha}{2} = 0.504 \text{ or } \alpha = (1 - 0.504) \times 2$$
$$= 0.496 \times 2 = 0.992$$

or per cent association $= 0.992 \times 100 = 99.2$

Example 25 *0.1 M solution of KNO_3 has an osmotic pressure of 4.5 atmosphere at 300 K. Calculate the apparent degree of dissociation of the salt.*

Solution: π_{obs} = 4.5 atm C = 0.1 moles/litre

n = 2 because one KNO_3 molecule dissociates to give two ions, K^+ and NO_3^-.

T = 300

Substituting the values in the equation,

$$\pi = CRT = \pi = 0.1 \times 0.082 \times 300 = \pi = 2.46 \text{ atom}$$

$$i = \frac{\text{Observed osmotic pressure}}{\text{Calculated osmotic pressure}} = \frac{4.5}{2.46} = 1.83 \qquad \ldots(i)$$

Also, $$i = \frac{1 - \alpha + n\alpha}{1}$$

or $$i = 1 + \alpha(n - 1) \quad \text{or} \quad (n - 1) = i - 1$$

or $$\alpha = \frac{i-1}{n-1} \qquad \ldots(ii)$$

Substituting the value of i from (i) and (ii),

$$\alpha = \frac{1.83 - 1}{2 - 1} \quad \text{or} \quad \alpha = 0.83 = 83\%$$

PROBLEMS FOR PRACTICE

1. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 2×10^{-2} kg of phenol in 1.0 g of benzene has its freezing point depressed by 0.60 K. Calculate the fraction of phenol that has dimerised (K_f for benzene is 5.12 K kg mol^{-1}).

[Ans. 0.733 or 73.3%]

2. A certain number of grams of a given substance in 100 g of benzene lower the freezing point by 1.28°C. The same weight of solute in 100 g of water gives a freezing point of – 1.395°C. If the substance has normal molecular weight in benzene and is completely dissociated in water, into how many ions does a molecule of this substance dissociate when placed in water?

[Ans. 3]

3. 0.5 g of KCl (mol. mass 74.5) was dissolved in 100 g of water and the solution originally at 20°C froze at – 0.24°C. Calculate the percentage ionisation of the salt. K_f for 1000 g water =1.86°C.

[Ans. 92%]

4. 0.3015 g of silver nitrate, when dissolved in 28.40 g of water, depressed the freezing point by 0.212°. To what extent is silver nitrate dissociated? (Kf of water = 1.85°C mol^{-1})

[Ans. 83.5%]

5. A solution containing 2.2965 g of benzoic acid, C_6H_5COOH, in 20.27 g of benzene froze at a temperature 0.317°C below the freezing point of solvent. The freezing point of pure solvent is 5.5°C and the latent heat of fusion is 30.1 cal/g. Calculate

   (a) the apparent molecular mass of benzoic acid, and

   (b) its degree of association assuming that in this solution it forms double molecules.

[Ans. 184.2, 67.4%]

SOLVED CONCEPTUAL PROBLEMS

Example 26 *Of the following properties, which are colligative?*

(a) Refractive index

(b) Vapour pressure

(c) Boiling point
(d) Depression in freezing point
(e) Relative lowering of vapour pressure.

Solution: Depression in freezing point and relative lowering of vapour pressure.

Example 27 *How is relative lowering of vapour pressure related to osmotic pressure?*

Solution: $\frac{p^\circ - p_s}{p^\circ} = \frac{MP}{dRT}$. Hence, relative lowering of v.p. μ osmotic pressure

Example 28 *Molecular mass of benzoic acid was determined by using freezing-point measurements using (a) its solution in water, and (b) its solution in benzene. Will the results differ or not? Give reasons for your answers.*

Solution: The results will differ. In water, benzoic acid dissociates. Thus, number of particles increases. As a result, observed value of ΔT_f will be more than the expected value. Hence, observed molecular mass will be less than the actual value. In benzene, benzoic acid will associate. The situation is just the reverse. Number of particles decreases. Hence, observed ΔT_f will be less or molecular mass will be more.

Example 29 *What are isotonic solutions? How are their molar concentrations related to each other?*

Solution: Isotonic solutions are the solutions which have the same osmotic pressure. As π = CRT, at constant *T*, osmotic pressures will be equal when they have same molar concentration.

Example 30 *Which colligative property is used for finding the molecular masses of polymers and why?*

Solution: Polymers give very small values of colligative properties due to their large molecular masses. Δp, ΔT_b, ΔT_f, etc., are too small to be measured while osmotic pressure can be measured to acceptable level of accuracy.

Example 31 *Arrange the following in order of ascending values of their osmotic pressure:*

(a) 0.1 M Na_3PO_4 solution

(b) 0.1 M sugar solution

(c) 0.1 M $BaCl_2$ solution

(d) 0.1 M KCl solution

Solution: 0.1 M Na_3PO_4 solution = 0.3 moles of Na^+ and 0.1 moles of PO_4^{3-} = Total 0.4 moles.

0.1 M sugar solution = 0.1 M sucrose molecules = Total 0.1 moles

0.1 M $BaCl_2$ solution = 0.1 mole of Ba^{2+} and 0.2 mole of Cl^- = Total 0.3 moles

0.1 M KCl solution = 0.1 mole of K^+ + 0.1 mole of Cl^- = Total 0.2 mole.

All these values are per litre of the solution.

The solutions are arranged in the ascending order of their osmotic pressure as

0.1 M sugar solution < 0.1 M KCl solution < 0.1 M $BaCl_2$ solution < 0.1 M Na_3PO_4 solution

Example 32 *State whether the osmotic pressure of M/10 solution of glucose is the same as that of M/10 solution of sodium chloride.*

Solution: No. Colligative property of a solution depends upon the number of moles of the compound or ions present.

Example 33 *How can you justify that osmotic pressure is a colligative property*?

Solution: Osmotic pressure, $p = \frac{n}{V}RT$. Thus, it depends only on the number of moles of the solute dissolved in a definite volume of solution and there is no factor involving the nature of the solute. Hence, it is a colligative property.

Example 34 *What is meant by the statement "the osmotic pressure of a solution is 5.0 atmospheres?"*

Solution: This means that when the solution is separated from the solvent by a semipermeable membrane, there is a net flow of solvent molecules from solvent to the solution through the semipermeable membrane and that the pressure of the hydrostatic column set-up is 5.0 atmospheres.

Example 35 *How is elevation in boiling point related to (a) relative lowering of vapour pressure, and (b) osmotic pressure?*

Solution: The two relations are given as under:

(a) $\Delta T_b = \frac{1000 K_b}{M_1} \frac{\Delta p}{p^\circ}$, i.e. $\Delta T_b \propto \frac{\Delta p}{p^\circ}$

(b) $\Delta T_b = \frac{1000 K_b}{dRT} \pi$, i.e. $\Delta T_b \propto \pi$

Example 36 *Justify the statement that "dilute solutions behave in the same manner as gases " or "there exists an exact analogy between the dissolved state of the substance and its gaseous state".*

Solution: Dilute solutions obey the same equation as the ideal gas equation, i.e. $PV = nRT$. Thus, osmotic pressure of a dilute solution is equal to pressure which the solute would exert if it were a gas at the same temperature and occupied the same volume as the solution.

Example 37 *Explain why equimolar solutions of NaCl and cane sugar do not have the same osmotic pressure.*

Solution: NaCl is an electrolyte which dissociates to give Na^+ and Cl^- ions. As a result, the number of particles increases and so observed osmotic pressure is greater than expected. Cane sugar (sucrose) is a non-electrolyte. It does not undergo any association or dissociation. Hence, the expected osmotic pressure is observed.

Example 38 *A solution of 4 M HCl is expected to have osmotic pressure of 197 atmospheres. How is that bottles containing this solution in the laboratory do not break?*

Solution: Osmotic pressure has a meaning only when a solution is separated from the solvent by a semipermeable membrane. Thus, bottles containing this solution in the laboratory do not break.

Example 39 *Account for the following*:

(a) Camphor is used as a solvent in the Rast method.

(b) Benzoic acid in benzene shows less osmotic pressure than expected.

(c) Boiling point of 0.1 M NaCl is greater than 0.1 M glucose solution.

Solution:

(a) Camphor is used because it has high molal depression constant. We get a higher value of ΔT_b which helps in obtaining accurate results for molecular mass.

(b) Benzoic acid undergoes association in benzene.

(c) 0.1 M NaCl dissociates to form 0.2 M concentration of particles (Na+ and Cl- ions) whereas glucose remains as such.

SUMMARY

1. Properties of dilute solutions that depend upon the number of particles (concentration) of the solute and not on the nature of the solute are called *colligative* properties.
2. Vapour pressure of a solution or a solvent can be determined by manometric method while lowering of vapour pressure can be measured by *Ostwald and Walker* method.
3. According to *Raoult's law*, relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.
4. *Osmotic pressure* is the equilibrium hydrostatic pressure exerted by the solution column which just prevents the flow of solvent molecules into the solution through a semipermeable membrane.
5. *Osmosis* is a phenomenon by which the pure solvent molecules tend to diffuse through a semipermeable membrane into the solution.
6. *Van't Hoff theory* of dilution states: *A substance in solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would have exerted if it were a gas at the same temperature occupying the same volume as the solution.*
7. Osmotic pressure of a solution can be determined by one of the following methods: Pfeffer method, Morse and Frazer's method and Berkeley and Hartley method.
8. Solutions which have the same osmotic pressure at the same temperature are called *isotonic solutions*.
9. Different *theories* to explain the phenomenon of osmosis are membrane solution theory, membrane bombardment theory, molecular sieve theory and vapour pressure theory.
10. The osmosis taking place from solution to pure water by application of pressure greater than osmotic pressure on the solution is called *reverse osmosis*.
11. *Molal elevation constant* may be defined as the elevation in boiling point when the molality of the solution is unity.
12. Depression in freezing point of a solution can be measured by Beckmann's method or Rast camphor method.
13. *Molal depression constant* may be defined as the depression in freezing point when 1 mole of the solute is dissolved in 1000 g of the solvent.
14. When *association* or *dissociation* of the solute takes place in the solution, the mass of the solute calculated from the relevant equation is found to be different from the actual mass.
15. Van't Hoff factor *i* is the ratio of the observed colligative property to the normal colligative property.

KEY RELATIONS

$$\frac{p_A^\circ - p_A}{p_A^\circ} = \frac{n_2}{n_1 + n_2} \quad \text{and} \quad \frac{p_A^\circ - p_A}{p_A^\circ} = \frac{wM}{mW} \text{ (For a dilute solution)}$$

$$\pi V = nRT \quad \text{and} \quad M = \frac{wRT}{\pi V}$$

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W} \qquad \Delta T_b = K_b \times \text{Molality}$$

$$\Delta T_b = \frac{RT_a^2}{1000 l_v} m \qquad \Delta T_b = \frac{1000 K_b}{M_1} \frac{\Delta p}{p^\circ}$$

$$\Delta T_b = \frac{1000 K_b \pi}{dRT} \qquad \Delta T_f = \frac{K_f \times 1000 \times w}{W \times m}$$

$$\Delta T_f = K_f \times \text{molality}$$

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. The elevation in boiling point is given by the formula

$$\Delta T \quad K_b \times \frac{w}{m} \times \frac{1}{W}$$

where K_b is called

(a) boiling point constant

(b) ebullioscopic constant

(c) molal elevation constant

(d) all of these

2. The ratio of the colligative effect produced by an electrolyte solution to the corresponding effect for the same concentration of a non-electrolyte solution is known as

(a) degree of dissociation

(b) degree of association

(c) activity coefficient

(d) van't Hoff factor

3. Freezing-point depression is measured by

(a) Beckmann's method

(b) Rast's camphor method

(c) both

(d) none of these

4. The depression in freezing point is measured by using $\Delta T \quad K_f \times \frac{w}{m} \times \frac{1}{W}$ where K_f is called
   (a) molal depression constant
   (b) freezing point depression constant
   (c) cryoscopic constant
   (d) all of these
5. Molal elevation constant is the boiling point elevation when _____ of the solute is dissolved in one kg of the solvent.
   (a) one gram
   (b) one kg
   (c) one mole
   (d) none of these
6. Which of the following is a colligative property?
   (a) molar refractivity
   (b) optical rotation
   (c) depression in freezing point
   (d) viscosity
7. The law of the relative lowering or vapour pressure was given by
   (a) van't Hoff
   (b) Ostwald
   (c) Raoult
   (d) Henry
8. The study of depression in freezing point of a solution is called
   (a) osmotic pressure
   (b) ebullioscopy
   (c) cryoscopy
   (d) none of these

Answers

1. (d)
2. (d)
3. (c)
4. (d)
5. (c)
6. (c)
7. (c)
8. (c)

SHORT-ANSWER QUESTIONS

1. What are colligative properties? How can you say that 'relative lowering of vapour pressure' is a

colligative property?

2. Define osmotic pressure. How is it determined by Berkeley and Hartley's method?
3. Describe Ostwald and Walker's method (transpiration method) for the determination of lowering of vapour pressure.
4. What do you mean by molal elevation constant of a solvent? How is it related to the latent heat of vaporisation of the solvent? What are its units?
5. Briefly describe Rast's method for the determination of molecular mass of a solute.
6. What is the cause of elevation in boiling point? Explain clearly with the help of vapour-pressure temperature curve.
7. Using colligative properties, why are abnormal molecular mass observed in certain cases?
8. Derive the relation between elevation in boiling point and osmotic pressure.
9. What is molal depression constant or ebullioscopic constant? How is it related to the enthalpy of fusion? What are its units?
10. Derive the relation between depression in freezing point and lowering of vapour pressure.
11. Write the relationship between relative lowering of vapour pressure and osmotic pressure. Deduce Raoult's law from it.
12. What is Van't Hoff factor? How are the different expressions for colligative properties modified when the solute undergoes association or dissociation in the solvent?
13. Derive the relationship between the elevation in boiling point and relative lowering of vapour pressure.

GENERAL QUESTIONS

1. What are 'colligative properties'? Briefly explain how lowering of vapour pressure is used in the calculation of molecular masses of solutes. Explain one method for the experimental determination of lowering of vapour pressure.
2. Why is there a depression in freezing point when a nonvolatile solute is dissolved in a solvent. Derive thermodynamically the relation between the depression in freezing point and molecular mass of the solute.
3. Define osmotic pressure. How is it measured experimentally by Berkeley's and Hartley's? What are the advantages of this method over the other methods?
4. Derive thermodynamically the expression for the relative lowering of vapour pressure or derive Raoult's law thermodynamically.
5. Why do we observe abnormal molecular masses of solutes in certain cases when determined by studying colligative properties? What is van't Hoff factor? How is it used to determine the degree of association and degree of dissociation of a solute?
6. Derive the relationship between osmotic pressure and lowering of vapour pressure. Deduce Raoult's law from it.
7. Briefly describe the following methods for the determination of depression in freezing point:
   (a) Beckmann's method
   (b) Rast's method
8. Briefly explain van't Hoff theory of dilute solutions. How does it help in determination of molecular masses of solutes?
9. Derive thermodynamically the expression for osmotic pressure, $\pi = CRT$
10. Derive the relationship between
    (a) Depression in freezing point and lowering of vapour pressure

(b) Elevation in boiling point and osmotic pressure.

11. Why there is an elevation in boiling point when a nonvolatile solute is dissolved in a solvent? Derive thermodynamically the relation between elevation in boiling point and molecular mass of the solute. Describe one method commonly used for the determination of elevation in boiling point.



Adsorption

26

LEARNING OBJECTIVES

- Define adsorption, adsorbent and adsorbate
- Differentiate adsorption from absorption
- Study the factors that influence adsorption
- Differentiate between physical and chemical adsorption
- Define adsorption isotherm and study Freundlich isotherm and Langmuir isotherm
- Derive the BET equation and learn to calculate the surface area of an adsorbent with the help of this equation
- Differentiate between positive and negative adsorption
- Study the adsorption of liquids from solids and various factors that influence it
- Study Gibbs adsorption equation and correlate adsorption and surface tension
- Study the applications of Gibbs adsorption equation
- Explain adsorption isobars and adsorption isostere
- Study various applications of adsorption

26.1 INTRODUCTION

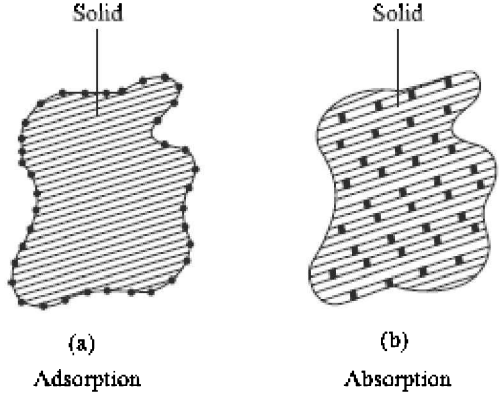


Fig. 26.1 *Adsorption vs absorption*

Consider a liquid in a vessel. A molecule in the interior of the liquid is being attracted by molecules around it. But all these forces of attraction get cancelled. Thus, there is no net force acting on molecules inside the liquid. However, the situation is different about molecules on the surface of the liquid. Such surface molecules are being attracted by molecules below it and inside the liquid. However, there are no molecules above the surface molecules. Hence, such molecules on the surface experience a net force of attraction downward.

Because of unbalanced force of attraction existing on the surface, liquids and solids have the property to attract and retain the molecules that come into contact at the surface.

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting into higher concentration of the molecules on the surface is called adsorption. The substance which is adsorbed on the surface in called ***adsorbate*** and the substance on which adsorption takes place is called ***adsorbent.*** Adsorption differs from the phenomenon of absorption, in that the former refers to the attraction and retention of the molecules of the substance on the surface only [Fig. 26.1 (a)] and the latter involves passing of the substance through the surface into the bulk of the liquid or the solid [Fig. 26.1 (b)] For example, ink is absorbed by the chalk whereas gases are adsorbed by charcoal.

Consider the following examples:

(i) Take a gas like CO, NH_3 or SO_2 in a closed vessel containing powdered charcoal. Note the pressure of the gas immediately by attaching the vessel to a manometer. After some time, it will be found that the pressure of the gas has fallen considerably.

(ii) Take the solution of a dye like methylene blue in a vessel and add to it powdered animal charcoal. Stir the solution with a glass stirrer. Filter the solution. It is observed that the filtrate that is obtained is colourless.

The above two examples illustrate the phenomenon of ***adsorption.*** In (i), the gas is adsorbed by powdered charcoal and in (ii), the dye is adsorbed by animal charcoal. The reverse of adsorption, i.e. removal of the adsorbate from the adsorbent, is called ***desorption.***

Both adsorption and absorption can take place simultaneously also. In such a case, we say that ***sorption*** is taking place.

1. Mechanism of Adsorption Particles on the surface are not surrounded by atoms or molecules above them and hence, they possess unbalanced or residual attractive forces. These forces are responsible for attracting the adsorbate particles on its surface. The extent of adsorption depends upon the surface area per unit mass of the adsorbent.

Another factor leading to adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface or there is a decrease in surface energy which appears as heat. It may be realised that adsorption is a kind of bond formation between the adsorbate and adsorbent and bond formation always evolves heat. Thus, adsorption is always an ***exothermic*** process. In other words, ΔH of adsorption is always negative. Also, there is a decrease in entropy when gas or liquid molecules are adsorbed because the freedom of movement of gas or liquid molecules is decreased, i.e. ΔS is negative.

For a spontaneous process, the thermodynamic requirement is that at a constant temperature and pressure, ΔG should be negative. On the basis of the equation $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH is sufficiently negative because $-T\Delta S$ is positive. As adsorption is a spontaneous process, a combination of these values makes ΔG negative.

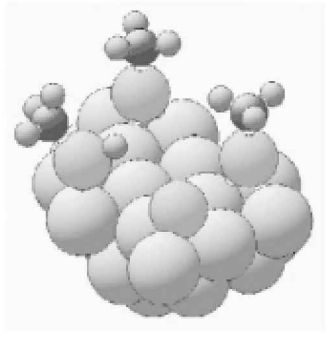


Fig. 26.2 *Representation of adsorption on the solid surface*

2. Factors Influencing the Adsorption of Gases by Solids The following factors influence the adsorption of gases by solids.

(a) Nature of the Gas being Adsorbed Different gases are adsorbed to different extents by the same adsorbent at the same temperature.

It is observed that higher the critical temperature of a gas, greater is the amount of that gas adsorbed. In other words, a gas which is more easily liquefiable or is more soluble in water is more readily adsorbed. This relationship is not surprising as the critical temperature of a gas is related to the intermolecular forces which are an important factor for adsorption too.

(b) Nature and Surface Area of the Adsorbent It is observed that the same gas is adsorbed to different extents by different solids at the same temperature. Further, the greater the surface area of the adsorbent, greater is the volume of the gas adsorbed. It is for this reason that substances like charcoal and silica gel are excellent adsorbents because they have highly porous structures and hence, large surface areas. The adsorbing power of these substances can be further increased by ***activating them*** in various ways. For example, wood charcoal can be activated by heating it in vacuum or some inert gas at temperatures between 625 K to 1275 K. As a result of this treatment, it appears that hydrocarbons and other gases are removed from charcoal and hence, the surface available for adsorption becomes larger.

(c) Temperature Studying the adsorption of any particular gas by some particular adsorbent, it is observed that adsorption decreases with increase of temperature and vice versa. For example, one gram of charcoal absorbs about 10 ml of N_2 at 273 K, 20 ml at 244 K and 45 ml at 195 K. The decrease of adsorption with increase of temperature may be explained as follows: Like any other equilibrium, adsorption is a process involving a true equilibrium. The two opposing processes involved are the ***condensation*** (i.e. adsorption) of the gas molecules on the surface of the solid and ***evaporation*** (i.e. desorption) of the gas molecules from the surface of the solid into the gaseous phase. Moreover, the process of condensation (or adsorption) is exothermic so that the equilibrium may be represented as

$$\text{Gas (Adsorbate)} + \text{Solid (Adsorbent)} \underset{\text{evaporation}}{\overset{\text{condensation}}{\rightleftharpoons}} \text{Gas absorbed on solid} + \text{Heat}$$

Applying Le Chatelier's principle, it can be seen that increase of temperature decreases the adsorption and ***vice versa.***

The amount of heat evolved when one mol of gas is adsorbed on the adsorbent is called the heat of adsorption.

(d) Pressure At constant temperature, the adsorption of a gas increases with increase of pressure. It is observed that at low temperature, the adsorption of a gas increases very rapidly as the pressure is increased from very small values.

26.2 | PHYSICAL ADSORPTION AND CHEMICAL ADSORPTION

1. Physical Adsorption, or van Der Waals Adsorption When a gas is held (adsorbed) on the surface of a solid by van der Waals forces (which are weak intermolecular forces of attraction) without resulting into the formation of any chemical bond between the adsorbate and the adsorbent, it is called ***physical adsorption*** or ***van der Waals adsorption.*** This type of adsorption involves low heats of adsorption, i.e. about 20-40 kJ per mol. Further, physical adsorption of a gas by a solid is generally reversible. Increase of pressure causes more gas to be adsorbed and the decrease of pressure frees the adsorbed gas. Similarly, decrease of temperature increases adsorption but the gas adsorbed at low temperature can be freed again by heating.

2. Chemical Adsorption of Chemisorption ***When a gas is held onto the surface of a solid by forces similar to those of a chemical bond, the type of adsorption in called chemical adsorption or chemisorption.*** This type of adsorption results into the formation of ***surface compound.*** That the forces involved are similar to those of a chemical bond is confirmed by the fact that the heats evolved during chemisorption are high (i.e. 40 to 400 kJ/mol) which are of the same magnitude as those involved in chemical reactions. Further, as chemisorption is something similar to a chemical change, it is usually irreversible. The efforts to free the adsorbed gas often gives some definite compound instead of the free gas. For example, oxygen adsorbed on tungsten or carbon is liberated as tungsten oxide or as carbon monoxide and dioxide. Physical adsorption takes place between every gas and a solid, i.e. it is not specific in nature (because it involves van der Waals force which exists among the molecules of every two substances), while chemisorption is specific in nature and occurs only where there is a tendency towards compound formation between the gas and the adsorbent. Further, unlike physical adsorption, chemisorption, like most chemical changes, increases with increase of temperature. For this reason, a gas may be physically adsorbed at low temperature but chemisorbed at higher temperature.

Table 26.1 Differences between physical adsorption and chemisorption

	Physical Adsorption		Chemisorption
1.	The forces operating in these cases are weak van der Waals forces	1.	The forces operating in these cases are similar to those of a chemical bond.
2.	No compound formation takes place in these cases	2.	Surface compounds are formed.
3.	The heats of adsorption are low, viz. 20—10 kJ mol^{-1}	3.	The heats of adsorption are high, viz. 40—100 kJ mol^{-1}
4.	The process is reversible, i.e. desorption of the gas occurs by increasing the temperature or decreasing the pressure	4.	The process is irreversible. Efforts to free the adsorbed gas give some definite compound.
5.	It is not specific in nature, i.e. all gases are adsorbed on all solids to some extent.	5.	It is specific in nature and occurs only when there is some possibility of compound formation between the gas being adsorbed and the solid adsorbent.
6.	This type of adsorption decreases with	6.	

	increase of temperature.	This type of adsorption increases the temperature
7.	Forms multimolecular layers	7. Forms unimolecular layer.
8.	The extent of adsorption is related to the ease of liquefaction of the gas	8. There is no such correlation.

3. Adsorption-Desorption Hysteresis We have learnt that chemisorption is not reversible. Therefore, the increase of adsorption with increase of pressure at a particular temperature is not exactly reversed when the pressure is deceased at that temperature. That is, adsorption and desorption do not follow the same path. This is expressed with the help of a curve called hysteresis curve.

26.3 ADSORPTION ISOTHERM

The amount of gas adsorbed by a given amount of the adsorbent depends upon both temperature and pressure. ***At constant temperature, there exist some definite relationships between the amount of the gas adsorbed and the equilibrium pressure. Such relationships are known as adsorption isotherms.***

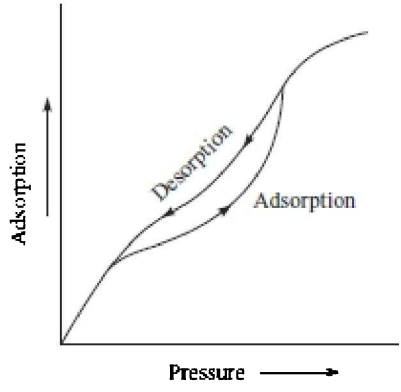


Fig. 26.3 *Adsorption-desorption hysteresis curve*

Five different general types of adsorption isotherms have been observed for the adsorption of gases or solids. These are shown in Fig. 26.4

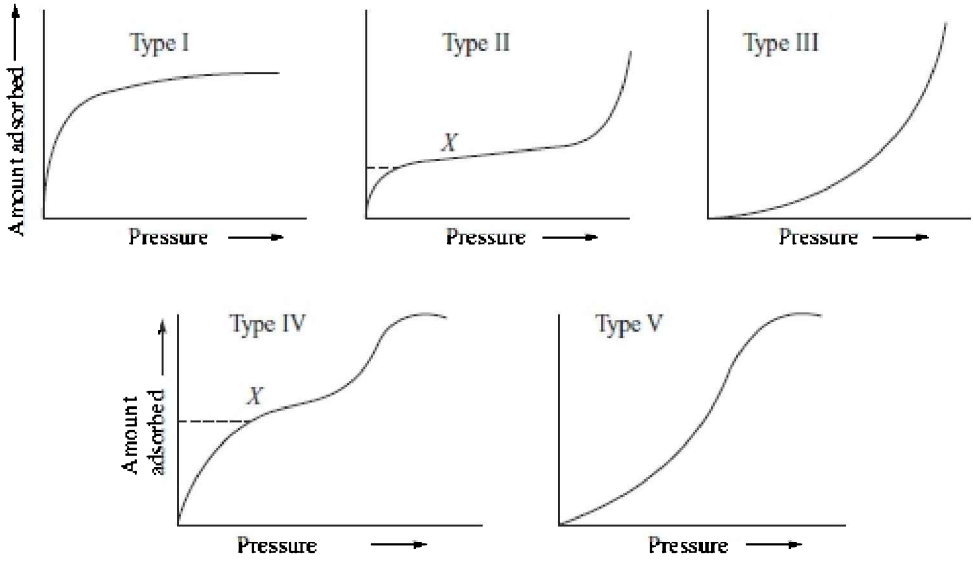


Fig. 26.4 *Types of adsorption isotherms*

26.4 FREUNDLICH ADSORPTION ISOTHERM

It is an empirical equation which states that at constant temperature,

$$\frac{x}{m} \propto P$$

where x is the mass of the gas adsorbed by m grams of the adsorbent at a pressure P, i.e. x/m is the amount of the gas adsorbed per gram of adsorbent. k and n are constants at a particular temperature and for a particular adsorbent and gas.

The quantity $1/n$ is generally less than 1 indicating that the amount of the gas adsorbed increases less rapidly than the pressure. Thus, the plots of the amount of the gas adsorbed against pressure are of the type shown in Fig. 26.5

At low pressures (say up to the point a), the graph is nearly linear. Hence, for low pressures,

$$\frac{x}{m} \propto P \qquad \ldots(26.1)$$

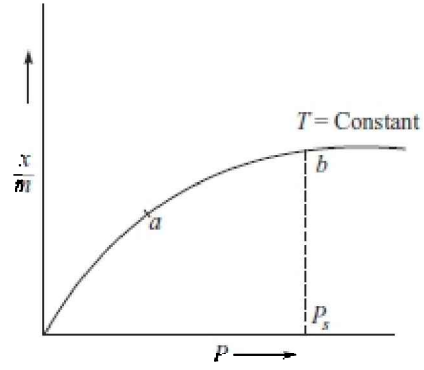


Fig. 26.5 *Freundlich adsorption isotherm*

For very high pressures (say beyond the point *b*), the adsorption becomes almost independent of pressure, i.e.

$$\frac{x}{m} \propto P^0 \qquad \ldots(26.2)$$

The state corresponding to the point *b* is called the ***saturation state,*** and the corresponding pressure *P* is called the ***saturation pressure.*** For intermediate pressure, obviously *x/m* will be proportional to *P* raised to the power lying between 0 and 1, i.e. fractions. Hence, we write

$$\frac{x}{m} \propto P^{1/n} \quad \text{or} \quad \frac{x}{m} = kP^{1/n}$$

To test Freundlich equation further logarithms of both sides of the equation may be taken, which gives

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

so that the plot of log *x/m* against log *P* should be a straight line with an intercept of log *k* on the *y*-axis and slope equal to 1/*n*. In actual practice, a reasonably straight-line plot is often obtained (Fig. 26.6).

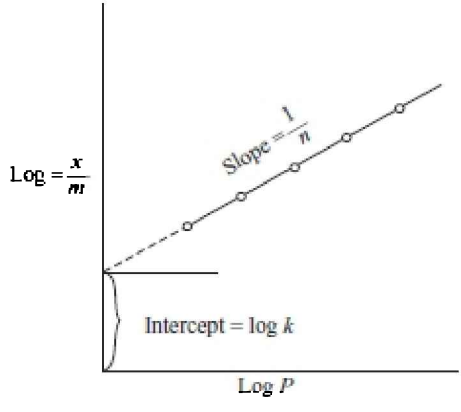


Fig. 26.6 *Plot of log x/m vs. log P.*

26.5 | LANGMUIR THEORY OF ADSORPTION

Langmuir put forward a ***theory of adsorption***, the main points of which are as follows:

1. Adsorption could take place on the surface of a solid only till the whole of the surface was completely covered with a ***unimolecular*** layer of gas molecules.
2. Adsorption consists of two opposing processes, namely ***condensation*** of the gas molecules on the solid surface and ***evaporation*** of the gas molecules from the surface back into the gaseous phase.
3. The rate of condensation depends upon the bare (uncovered) surface available for condensation. Initially, as the whole of the surface is bare, the rate of condensation is very high. As the surface is covered more and more, the rate of condensation decreases. On the other hand, the rate of evaporation depends upon the covered surface and hence, increases as more and more of the surface is covered. Ultimately, a stage is reached when the rate of condensation becomes equal to the rate of evaporation and equilibrium is said to have been attained.
4. The rate of condensation also depends upon the pressure of the gas, as according to the kinetic theory, the number of molecules striking per unit area is proportional to the pressure.

1. Deduction of Langmuir Adsorption Isotherm Equation The relationship was deduced by Langmuir as follows:

Suppose at any instant, the fraction of the surface covered by the adsorbed molecules = θ

The fraction of the surface bare and available for adsorption = $1 - \theta$

Suppose the pressure of the gas at that instant = P

Then according to Langmuir's theory of adsorption,

Rate of condensation $\propto (1-\theta) \times P = k_1 (1-\theta)P$ where k_1 is a constant of proportionality

Rate of evaporation $\propto \theta = k_2\theta$ where k_2 is another constant of proportionality

When the adsorption equilibrium is attained,

$$k_1(1-\theta)P = k_2\theta$$

or $$\theta(k_2 + k_1P) = k_1P \qquad \ldots(26.3)$$

or $$\theta = \frac{k_1P}{k_2 + k_1P} = \frac{(k_1/k_2)P}{1 + \frac{k_1}{k_2}P} = \frac{bP}{1+bP} \qquad \ldots(26.4)$$

where $\frac{k_1}{k_2} = b$, is another constant

As the gas molecules are assumed to form a one molecule thick layer, on the surface, the gas adsorbed per unit area or per gram of the adsorbent must obviously be proportional to the surface covered, i.e.

$$\frac{x}{m} \propto \theta$$

or $$\frac{x}{m} = k_3\theta \qquad \ldots(26.5)$$

where x is the mass of the gas adsorbed on m grams of the adsorbent and k_3 is a constant of proportionality.

$$\therefore \quad \frac{x}{m} = k_3 \cdot \frac{bP}{1+bP}$$

or
$$\boxed{\frac{x}{m} = \frac{aP}{1+bP}} \qquad \ldots(26.6)$$

where $k_3 b = a$ is another constant. Equation (26.6) is known as ***Langmuir adsorption isotherm.*** The constants a and b depend upon the nature of the gas adsorbate, the nature of the solid adsorbent and the temperature. Their values can be found from the experimental data.

To verify the validity of Langmuir adsorption equation divide both sides of Eq. (26.6) by P.

$$\frac{x/m}{P} = \frac{a}{1+bP}$$

Take the reciprocal

$$\frac{p}{x/m} = \frac{1}{a} + \frac{b}{a}P$$

As a and b are constants, a plot of $\frac{p}{x/m}$ vs. P should be a straight line with slope equal to b/a and intercept on the y-axis equal to $1/a$. This is actually found to be so.



Fig. 26.7 *Irving Langmuir was an American chemist. Among other works, he is known for his model of adsorption.*

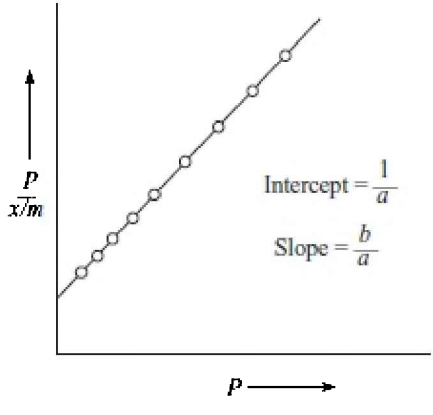


Fig. 26.8 *A general Langmuir adsorption isotherm*

2. Freundlich Isotherm is a Special Case of Langmuir Isotherm When the pressures are very low, adsorption is very little, i.e. a very small fraction of the surface is covered with molecules.

Thus, θ is very small so that $1 - \theta = 1$.

Equation (26.3), is reduced to $k_1, P = k_2\theta$

But from Eq. (26.5),

$$\theta = \frac{1}{k_3}\frac{x}{m}$$

$$\therefore \quad k_1 P = k_2 \frac{1}{k_3}\frac{x}{m} \quad \text{or} \quad \frac{x}{m} = \frac{k_1 k_3}{k_2} P$$

i.e.
$$\frac{x}{m} \propto P \qquad \ldots(26.7)$$

So, we get the equation 26.1 as given by Freundlich.

When the pressures are very high, there is considerable adsorption, i.e. the surface is almost completely covered with molecules.

Thus, $\theta = 1$ so that Eq. (26.3) becomes

$$k_1(1 - \theta)P = k_2 \quad \text{(Taking } \theta = 1 \text{ in the RHS of Eq. 26.3)}$$

or
$$1 - \theta = \frac{k_2}{k_1 P} \quad \text{or} \quad \theta = 1 - \frac{k_2}{k_1 P}$$

But from Eq. (26.5), as before,

$$\theta = \frac{1}{k_3}\frac{x}{m}$$

$$\therefore \quad \frac{1}{k_3}\frac{x}{m} = 1 - \frac{k_2}{k_1 P} \quad \text{or} \quad \frac{x}{m} = k_3 - \frac{k_3 k_2}{k_1 P}$$

When the pressures are very high, $1/P \approx 0$

so that we have

$$\frac{x}{m} = k_3$$

or it may be written as

$$\frac{x}{m} = k_3 P^0$$

i.e.
$$\frac{x}{m} \propto P^0 \qquad \ldots(26.8)$$

Thus, from equations (26.7) and (26.8), we have

At very low pressures, $\frac{x}{m} \propto P$

At very high pressures, $\frac{x}{m} \propto P^0$

Hence, for intermediate pressures, we must have

$$\frac{x}{m} \propto P^{1/n}$$

where $1/n$ has a value lying between 0 and 1,
i.e.

$$\frac{x}{m} = kP^{1/n}$$

which is the Freundlich isotherm.

26.6 BET EQUATION

To explain adsorption isotherms of Type II and Type III (refer Fig. 26.4), Brunauer, Emmett and Teller postulated that the adsorption is not unimolecular but ***multimolecular,*** i.e. at low pressure, a single adsorbed layer of molecules is formed but as the pressure is increased, many more layers of molecules are attached to the first layer. Based upon this principle, they derived an equation, called BET equation. The equation is

$$\frac{P}{v(P^{\circ} - P)} = \frac{1}{v_m C} + \left[\frac{C-1}{v_m C}\right]\frac{P}{P^{\circ}} \tag{26.9}$$

It can also be written in the form

$$v = \frac{v_m C f}{1-f}\,\frac{1}{1+(C-1)f} \tag{26.9a}$$

where v = Volume of the gas (reduced to STP) adsorbed at given pressure P and constant temperature T

v_m = Volume of the gas (reduced to STP) adsorbed when the surface is completely covered by a unimolecular layer

$f = \dfrac{P}{P^{\circ}}$ where P° is the vapour pressure (of the liquefied gas) at the experimental temperature T

C = A constant at the given temperature = $e^{(E_1 - E_L)/RT}$

E_1 = Heat of adsorption of the gas in the first layer

and E_L = Heat of liquefaction of the gas

If $E_1 > E_1$ so that C is considerably greater than 1, Eq. (26.9) gives a curve of the Type II. If $E_1 < E_L$, a curve of Type III is obtained.

In a special case, when a single unimolecular layer is supposed to be adsorbed on the surface, the BET equation reduces to the same form as Langmuir equation. Then it is able to explain the adsorption isotherm of Type I.

To explain adsorption isotherms of Type IV and Type V, it has been argued that in case of substances showing these types of adsorption, not only multimolecular adsorption takes place but also the condensation of the gas takes place in pores and the capillaries of the adsorbent. An isotherm of Type IV is obtained when the condition, as for Type II, is that $E_1 > E_L$, and an isotherm of Type V is obtained when the condition, as for Type III, is that $E_1 < E_L$.

To test the validity of the BET equation, Eq. (26.9a) may be rewritten in the form

$$\frac{f}{v(1-f)} = \frac{1+(C-1)f}{v_m C}$$

or

$$\frac{f}{v(1-f)} = \frac{1}{v_m C} + \frac{(C-1)}{v_m C} f$$

Thus, a plot of f/v $(1 - f)$ vs. f should be a straight line with a slope equal to $(C - 1)/v_m c$ and the intercept on the y-axis equal to $1/v_m c$.

1. Determination of Surface Area of an Adsorbent Using BET Equation The plot of f/v $(1 - f)$ versus f [i.e. P/v $(P ° - P)$ vs. $P/P°$] is a straight line with slope= $(C - 1)/v_m c$ and intercept on the y-axis $=1/v_m c$. From these two quantities, the valve of V_m, i.e. the volume of the gas required to completely cover the surface of the adsorbent with a unimolecular layer, can be calculated. As 22400 cc of the gas at STP contains Avogadro's number of molecules, therefore, the number of molecules in the volume V_m can be calculated. Further, as the area of cross section per single gas molecule used for adsorption is known; therefore, the total area occupied by the gas molecules gives the area of the definite weight of the adsorbent taken.

The calculation of surface area of the adsorbent is done as follows:

Volume V_m as obtained from the graph is reduced to NTP conditions by using the general gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

The surface area of the adsorbent may be calculated directly from the value of V_m as follows:

22400 cc of the gas at STP contain = 6.022 = 10^{23} molecules

$\therefore$ V_m cc. of the gas at STP will contain

$$-\frac{6.022 \times 10^{23} \times v_m}{22400} \text{ molecules}$$

If the area occupied by a single molecule is S then area occupied by i.e. the surface area of the adsorbent $\frac{6.022 \times 10^{23} \times v_m}{22400}$ molecules, i.e. the surface area of the adsorbent

$$= \frac{6.022 \times 10^{23}}{22400} \times v_m \times S$$

Suppose wg of the adsorbent was used in the experiment then specific surface area, i.e. area per unit gram of the absorbent is

$$\boxed{= \frac{6.022 \times 10^{23}}{W \times 22400} \times v_m \times S}$$

It may further be noted that for adsorption isotherms of the types I, II and IV, the volume V_m can be obtained directly from the plots of the adsorption isotherms; for Type I directly from the limiting adsorption and for types II and IV by extrapolating the middle flat portion (marked X) to zero pressure.

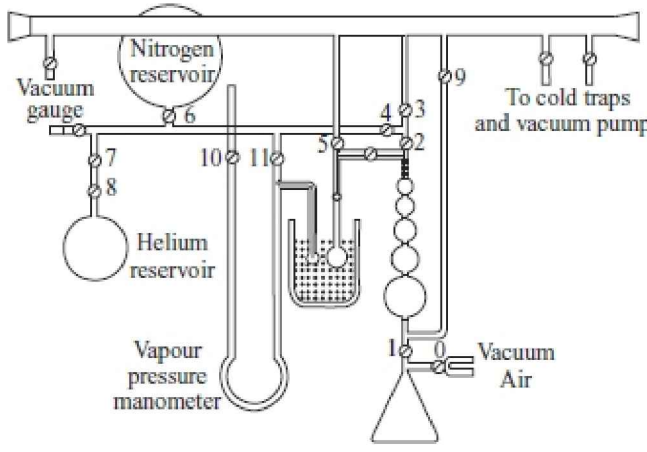


Fig. 26.9 *A schematic diagram of BET apparatus for the determination of surface area of a solid*

The gas most commonly used for surface-area determination is nitrogen gas at its normal boiling point (−195.8°C). At this temperature, the area occupied by a nitrogen molecule is taken to be 16.2 $Å^2$ (i.e. $16.2 \times 10^{-20}\ m^2$).

Example *The volume of nitrogen gas V_m (measured at STP) required to cover 1g of a sample of silica gel with a unimolecular layer is 129 $cm^3\ g^{-1}$ of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies $16.2 \times 10^{-20}\ m^2$.*

Solution Volume of N_2 at STP required to cover the gel with unimolecular layer, i.e.

$$v_m = 129 \text{ cc } g{-}1$$

Area occupied by each molecule of N_2 is

$$S = 16.2 \times 20\ m^2$$

22400 cc of N_2 at STP contains $= 6.022 \times 10^{23}$ molecules

$$\therefore \text{ 129 cc of } N_2 \text{ at STP will contain} = \frac{6.022 \times 10^{23} \times 129}{22400} \text{ molecules}$$

$$= 3.468 \times 10^{21} \text{ molecules}$$

Area occupied by a single molecule of $N_2 = 16.2 \times 10^{-20}\ m^2$

Area occupied by 3.468×10^{21} molecules of $N_2 = 16.2 \times 10^{-20} \times 3.468 \times 10^{21}$

$$561.8\ m^2$$

$\therefore$ surface area per gram of gel = $561.8\ m^2$

2. Positive and Negative Adsorption

(a) Positive Adsorption In most cases, the solute from the solution is adsorbed on the surface of the solid adsorbent so that the concentration of the solute on the surface of the solid is greater than in the bulk of the solution; this is called ***positive adsorption.***

(b) Negative Adsorption In a few cases involving solution of the electrolyte, the solvent from the solution is adsorbed by the adsorbent in preference to the solute, so that the concentration of the solute in the solution increases, i.e. becomes greater than the initial concentration. This is

called ***negative adsorption.*** For example, when a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption but with high concentrations of KCl, it shows positive adsorption.

PROBLEMS FOR PRACTICE

1. Adsorption of N_2 on a catalyst was carried out at − 195 °C (78 K). The BET plot of the data gave the value of v_m as 8.15 ml/g of the catalyst when reduced to NTP. Calculate the surface area of the catalyst assuming that the gas molecules adsorbed in the first layer are closely packed. Given that molecular area of nitrogen is 16×10^{-20} m^2

[Ans. 35.056 m^2/g]

2. The cross-sectional area of the nitrogen molecule is 16.2 $Å^2$. One gram of sample of activated charcoal requires 55 ml of nitrogen at STP to form a monomolecular layer. Calculate the surface area of the charcoal sample

[Ans. 239.5 m^2/g]

26.7 | ADSORPTION BY SOLIDS FROM SOLUTIONS

The adsorption by solids from the solution depends upon following factors:

(a) Nature of the Adsorbent Some adsorbents are more effective in attracting certain substances to their surfaces than others.

(b) Surface Area of the Adsorbent Greater the surface area of the adsorbent, greater the adsorption.

(c) Nature of the Solute and the Solvent Different solutes dissolved in the same solvent are adsorbed to different extents by the same adsorbent. For example, non-electrolytes are adsorbed much more than electrolytes from the aqueous solution by charcoal. Similarly, the same solute dissolved in different solvents is adsorbed to different extents.

(d) Effect of Temperature Increase of temperature results in the decrease of adsorption.

(e) Effect of Concentration The variation of the extent of adsorption with concentration is given by the Freundlich equation which for adsorption from solutions is written in the form

$$\frac{x}{m} = KC^{1/n}$$

where x is the amount of solute in grams adsorbed by m grams of the adsorbent, C is the equilibrium concentration of the solution in moles/litre. K and n are constants. The above equation is found to represent the adsorption from solutions much better then the adsorption of gases by solids.

To test the validity of the above equation for adsorption from solutions, take the logarithm of both the sides. We get

$$\log \frac{x}{m} = \log K - \frac{1}{n} \log C$$

Thus, a plot of log x/m vs. log C should be a straight line with slope equal to $1/n$ and intercept on the y-axis equal to log K.

Effect of Dissolved Substances on the Surface Tension ofa Solvent

Whenever a substance is dissolved in a solvent, the surface tension of the solvent changes. This is due to the facts that the concentration of the solute on the surface of the solution is different from the bulk of the solution. Based upon their effect on the surface tension, the various substances are divided into their types:

Type I ***Those Substances which Increase the Surface Tension, though the Increase is Generally not Large*** For example strong electrolytes when dissolved in water exhibit this type of behaviour. This is shown by Curve I in Fig. 26.10.

Type II ***Those Substances which Decrease the Surface Tension Regularly and Gradually with Increase in the Concentration*** For example, non-electrolytes or weak electrolytes when dissolved in water show this type of behaviour. This is in represented by Curve II in Fig. 26.10.

Type III ***Those Substances which Decrease the Surface Tension Considerably Even at Very Low Concentration*** For example, this type of behaviour is exhibited by aqueous solutions of soaps. Such substances are called ***surface active agents*** or ***surfactants.*** This type of behaviour is represented by Curve III in Fig 26.10.

If a solute brings about a ***decrease*** of surface tension, its concentration at the surface of the solution is ***more*** than in the bulk of the solution. This type of behaviour is called ***positive adsorption*** or the solute is said to exhibit positive surface activity. On the other hand, if a solute brings about an ***increase*** of surface tension, its concentration at the surface of the solution is found to be ***less*** than in the remainder of the solution. This type of behaviour is called ***negative adsorption*** or the solute is said to have negative surface activity.

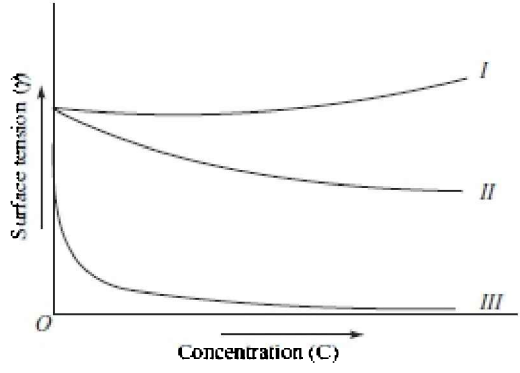


Fig. 26.10 *Effect of different type of dissolved substances on the surface tension of the solvent.*

26.8 | GIBBS ADSORPTION EQUATION

This equation gives relationship between adsorption and surface tension. Its derivation is based upon the concept of chemical potential which is nothing but ***partial molar free energy*** and pressure, keeping the composition of all other components constant.

Consider a system of two components (i.e. a solute and solvent). If n_1 and n_2 are the number of moles of the two components and μ_1 and μ_2 are their respective chemical potentials then the free energy of the system is given by

$$G = \mu_1 n_1 + \mu_2 n_2 \qquad \ldots(26.10)$$

However, when the two components are mixed, there is a change in the surface area of the solution and hence, there is a change in the surface energy of the system. To account for this, the total free energy of the system should also include the free energy of the surface. If γ is the

surface tension, i.e. surface energy per sq cm, and s is the surface area then

Free energy of the surface = γs

The free energy of the system will be given by

$$G = \gamma s + \mu_1 n_1 + \mu_2 n_2 \qquad \ldots(26.11a)$$

Differentiating this equation completely, we get

$$dG = \gamma ds + s d\gamma + \mu_1 dn_1 + n_1 \mu d_1 + \mu_2 dn_2 + n_2 d\mu_2 \qquad \ldots(26.11b)$$

The free energy change of a system can also be obtained in the form of a different expression as follows:

Free energy is a function of temperature, pressure and composition of the various components. It can be written as

$$G = f(T, P, n_1, n_2) \qquad \ldots(26.12)$$

If there is a small change in the temperature, pressure and the amounts of the two components, the change in the value of G will be given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} dn_2 \qquad \ldots(26.13)$$

But $\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \mu_1$

and $dG = \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} = \mu_2$

$\therefore$ $$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \mu_1 dn_1 + \mu_2 dn_2 \qquad \ldots(26.14)$$

According to total differential equation,

$$dG = VdP - SdT \qquad \ldots(26.15)$$

If temperature is kept constant, $dT = 0$, Eq (26.15) reduces to

$$(dG)_T = (VdP)_T$$

or $$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \ldots(26.16)$$

If pressure is kept constant, $dP = 0$, Eq (26.15) reduces to

$$(dG)_P = -(SdT)_P$$

or $$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \ldots(26.17)$$

Substituting the values from equations (26.16) and (26.17) in Eq. (26.14), we get

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 \qquad \ldots(26.18)$$

Total free energy change is obtained by adding the increase in free energy due to increase in the surface area. If ds is the increase in the surface area then free-energy change due to increase in surface area = $\gamma . ds$

$\therefore$ total free-energy change is given by

$$dG = -SdT + VdP + \gamma ds + \mu_1 dn_1 + \mu_2 dn_2 \qquad \ldots(26.19)$$

Comparing equations (26.11b) and (26.19), we get

$$s d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = S dT + V dP$$

or $$S dT - V dP + s d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0$$

But at constant temperature and pressure,

$$dT = 0, \quad dP = 0$$

$$\therefore \quad s d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad \ldots(26.20)$$

Now imagine that the system under consideration is divided into two parts, one part being that which is under the influence of the surface forces and the other is the remainder of the solution. The former may be called the ***surface phase*** and the latter the ***bulk phase*** as shown in Fig. 26.11.

If n°_1 and n°_2 are the number of moles of the two components in the bulk phase corresponding to n_1 and n_2 in the surface phase then since for the bulk phase, surface consideration are not involved. Eq. (26.20) for the bulk phase may be written as

$$n_1^\circ d\mu_1 + n_2^\circ d\mu_2 = 0 \qquad \ldots(26.21)$$

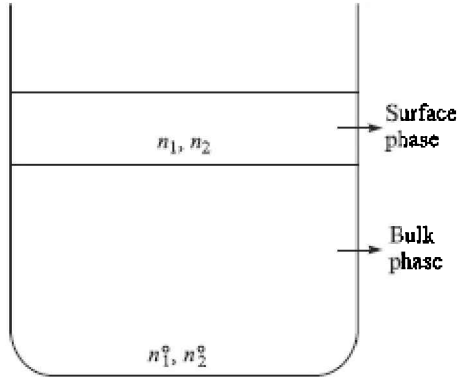


Fig. 26.11 *Surface and bulk phases*

Multiplying this equation by n_1/n°_1, we get

$$n_1 d\mu_1 + \frac{n_1 n_2^\circ}{n_1^\circ} d\mu_2 = 0 \qquad \ldots(26.22)$$

Subtracting this equation from Eq (26.20), we get

$$s d\gamma + n_2 d\mu_2 - \frac{n_1 n_2^\circ}{n_1^\circ} d\mu_2 = 0$$

or $$s d\gamma + d\mu_2 \left[n_2 - \frac{n_1 n_2^\circ}{n_1^\circ} \right] = 0$$

$$s d\gamma = - d\mu_2 \left(n_2 - \frac{n_1 n_2^\circ}{n_1^\circ} \right)$$

or $$-\frac{d\gamma}{d\mu_2} = \frac{n_2 - n_1 n_2^\circ / n_1^\circ}{s} \qquad \ldots(26.23)$$

If n_2 is the number of moles of one component, say the solute, associated with n_1 moles of

the solvent in the surface phase, $n_1 n_2^\circ / n_1^\circ$ is the corresponding numbers of moles associated with n_1 moles of the solvent in the bulk phase. This is because in the bulk phase, n_1° moles of the solvent are associated with n_2° moles of the solute.

$\therefore n_1$ moles of the solvent are associated with

$$\frac{n_2^\circ}{n_1^\circ} \times n_1 \text{ moles of the solute}$$

Thus, $n_2 - \dfrac{n_1 n_2^\circ}{n_1^\circ}$ is the excess concentration of the surface phase or $\dfrac{n_2 - n_1 n_2^\circ / n_1^\circ}{s}$ is the excess concentration of the surface phase per unit area of the surface.

Denoting this excess concentration of the surface phase by s_2, Eq. (26.23) can be written as

$$s_2 = -\frac{d\gamma}{d\mu_2} \qquad \ldots(26.24)$$

Further, we know that

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \qquad \ldots(26.25)$$

where a_2 is the activity of the component 2 and μ°_2 is the chemical potential of the component 2 in the standard state, i.e. when its activity is unity. Hence, at constant temperature,

$$d\mu_2 = RT\, d \ln a_2$$

$$= \frac{RT}{a_2} da_2$$

Substituting this valve in Eq. (26.24), we get

$$s_2 = -\frac{d\gamma}{RT\, da_2} \cdot a_2$$

$$s_2 = -\frac{a_2}{RT}\frac{d\gamma}{da_2} \qquad \ldots(26.26)$$

This equation is called ***Gibbs equation***

Although this equation is usually applied to solutes, it is equally applicable to either of the two components of a binary system.

Negative the subscripts, Eq. (26.26), therefore, can be written in the form

$$s = -\frac{a_2}{RT}\frac{d\gamma}{da_2} \qquad \ldots(26.27)$$

For dilute solutions, the activity may be replaced by concentration c so that Eq. (26.27) takes the form

$$\boxed{s = -\frac{C}{RT}\frac{d\gamma}{dc}}$$

26.9 APPLICATIONS OF GIBBS ADSORPTION EQUATION

1. In Predicting Negative Adsorption In the Gibbs equation, $d\gamma/dc$ gives the rate of variation of surface tension of the solution with concentration. If $d\gamma/dc$ is positive, s must be negative, i.e. the concentration of the solute in the surface is less than in the bulk of the solution. This is a case of negative adsorption.

If $d\gamma/dc$ is negative, s will be positive, i.e. the concentration of the solute is greater in the surface than in the bulk of the solution. This is a case of positive adsorption. This happens in the case of surface active agents like soaps.

2. In Calculation of the Excess Concentration ofa Dissolved Substance on the Surface of a Liquid (called Gibbs adsorption) knowing the concentration c of the solute in the solution and knowing the value of $d\gamma/dc$, i.e. the rate of variation of surface tension with concentration at temperature, T, the excess concentration of the dissolved substance on the surface of the liquid can be obtained.

3. In the Calculation of the Adsorption of an in Soluble Gas on the Surface of Liquid For example, the adsorption of saturated hydrocarbons (Component 2) on the surface of water (Component 1) can be determined by using Gibbs adsorption equation in a modified form as follows:

According to the Gibbs adsorption equation,

$$s_2 = -\frac{d\gamma}{d\mu_2} \qquad \ldots(26.28)$$

But for the gaseous Component 2,

$$\mu_2 = \mu_2^\circ + RT \ln p$$

where p is the vapour pressure of Component 2 over the liquid

$$d\mu_2 = RT\, d \ln p$$

$$= \frac{RT}{p} dp$$

Substituting this value in Eq. (26.28) above,

$$s_2 = -\frac{d\gamma}{RT\, dp} \cdot p$$

or

$$\boxed{s_2 = -\frac{p}{RT} \cdot \frac{d\gamma}{dp}}$$

Thus, knowing the value of $d\gamma/dc$, i.e. the rate of variation of surface tension with vapour pressure of the gaseous component, the adsorption of the vapour on the surface of the liquid can be calculated.

4. Adsorption Isobars ***The graphs obtained by plotting adsorption (x/m) vs temperature, keeping the pressure constant are called adsorption isobars.*** Studies show that in case of physical adsorption, the adsorption *(x/m)* decreases regularly with increase of temperature. [Fig. 26.12 (a)]. But in case of chemical adsorption, the adsorption first increases and then begins to decrease with increase of temperature [Fig. 26.12 (b)]. The increase in the beginning is evidently due to the fact that like any other chemical reaction, the heat supplied acts as the activation energy for the chemisorption.

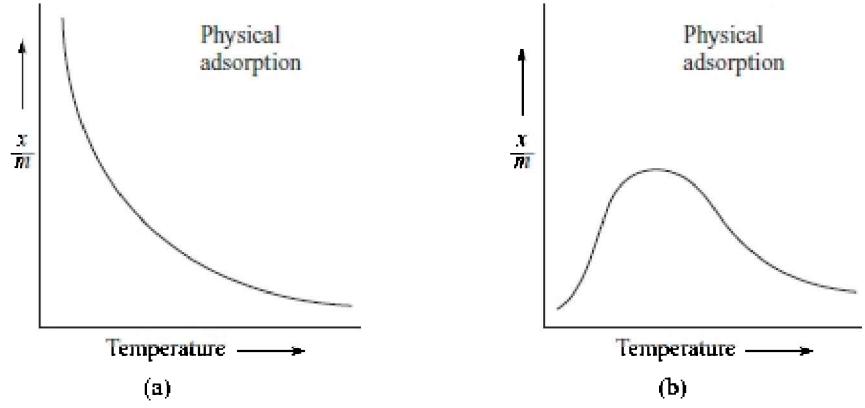


Fig. 26.12 *Adsorption isobars: (a) Physical adsorption (b) Chemisorption.*

5. Adsorption Isostere We have observed so far that the extent of adsorption increases with the increase of pressure but decreases with increase of temperature. Therefore, if the temperature is increased, leading to decrease of adsorption then pressure will have to be increased in order to keep the amount of adsorption constant. This means that for the same amount of adsorption, the plot between temperature and pressure is linear (Fig. 26.13).

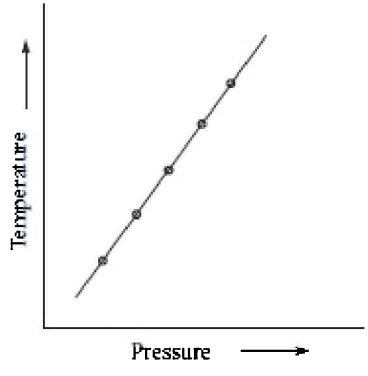


Fig. 26.13 *Adsorption isostere*

26.10 APPLICATIONS OF ADSORPTION

A few applications are described below:

1. In Gas Masks Gas masks are devices containing suitable adsorbents so that the poisonous gases present in the atmosphere are preferentially adsorbed and the air for breathing is purified.

Applying Chemistry to Life

Activated charcoal is embedded in a gas mask. Activated charcoal in a gas marsk attracts toxic gas molecules, allowing the person wearing the mark to breathe fresh air. These masks

may be used by persons moving through polluted areas and by miners.

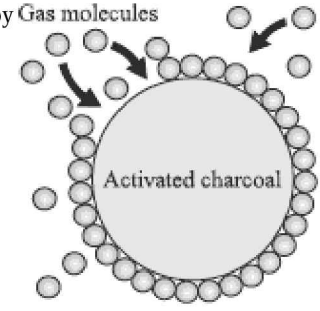


Fig. 26.14 *Activated charcoal*

2. In Chromatographic Analysis The selective adsorption of certain substances from a solution by a particular solid adsorbent has helped develop a technique for the separation of the components of a mixture. The technique is called chromatographic analysis.

3. In Preserving Vacuum In Dewar flasks, activated charcoal is placed between the walls of the flask so that any gas which enters into the annular space either due to glass imperfections or diffusion through glass is adsorbed.

4. In Cleaning of Sugar Sugar is decolourised by treating sugar solution with charcoal powder. The latter adsorbs the colour present.

5. In Adsorption Indicators Various dyes, which work on the principle of adsorption have been introduced as indicators, particularly in precipitation titration. For example, KBr is easily titrated with $AgNO_3$ using eosin as an indicator.

6. In Paint Industry Paint should not contain dissolved gases as otherwise the paint does not adhere well to the surface to be painted and thus, will have a poor covering power. The dissolved gases are, therefore, removed by suitable adsorbents during manufacture. Further, all surfaces are covered with layers of gaseous, liquid or solid films. These have to be removed before the paint is applied. This is done by suitable liquids which adsorb the films. Such/liquids are called ***wetting agents.*** The use of spirit as wetting agent in furniture painting is well known.

7. In Catalysis The action of certain solids as catalysts is best explained in terms of adsorption. According to the ***adsorption theory,*** the gaseous reactants are adsorbed on the surface of the solid catalyst. As a result, the concentration of the reactants increases on the surface and hence, the rate of reaction increases.

SUMMARY

1. The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into higher concentration of the molecules on the surface is called *adsorption.*
2. *Factors* that influence adsorption of gases on solids are nature of the gas, nature of the adsorbent, temperature and pressure.
3. When a gas is held on the surface of a solid by van der Waals (week) forces without resulting into the formation of any chemical bond, it is called *physical adsorption.*
4. When a gas is held on to the surface of a solid by forces similar to those of a chemical bond, the type of adsorption is called *chemical adsorption* or *chemisorption.*

5. At constant temperature, there exist some definite relationships between the amount of the gas adsorbed and the equilibrium pressure. Such relationships are known as *adsorption isotherms.*
6. According to Langmuir theory of adsorption, adsorption could take place on the surface of a solid only till the whole of the surface was completely covered with a unimolecular layer of gas molecules.
7. Brunauer, Emmett and Teller (BET) postulated that adsorption is unimolecular at low pressure of the gas, but as the pressure is increased, multimolecular adsorption takes place.
8. In a few cases involving solutions of electrolytes, the solvent from the solution is adsorbed by the adsorbent in preference to the solute, so that the concentration of the solute in the solution increases, i.e. it becomes greater than the initial concentration. This is called *negative adsorption.*
9. The Gibbs adsorption equation gives the relationship between adsorption and surface tension. Its derivation is based upon the concept of chemical potential or partial molar free energy.
10. The graphs obtained by plotting adsorption *(x/m)* vs temperature keeping the pressure constant are called *adsorption isobars.*
11. The phenomenon of adsorption finds applications in making gas masks, chromatographic analysis, preserving vacuum, cleaning of sugar, adsorption indicators, paint industry and catalysis.

KEY RELATIONS

Freundlich adsorption isotherm $\frac{x}{m} = k \times P^{1/n}$

Langmuir adsorption isotherm $\theta = \frac{aP}{1 + bP}$

BET equation $\frac{P}{v(P^\circ - P)} = \frac{1}{v_m C} + \left[\frac{C - 1}{v_m C}\right]\frac{P}{P^\circ}$

Area per unit g of the adsorption $= \frac{6.022 \times 10^{23}}{w \times 22400} \times v_m \times S$

Gibbs adsorption equation $s = -\frac{c}{RT}\frac{d\gamma}{dc}$

$$s_2 = -\frac{p}{RT}\frac{d\gamma}{dp}$$

EXERCISES

Based on Different University Papers

Multiple Choice Questions

1. The relationship between equilibrium pressure of a gas and its amount adsorbed on the solid adsorbent at constant temperature is called

(a) chemisorption

(b) adsorption isobars

(c) adsorption isotherms
(d) none of these
2. At low pressure, the amount of the gas adsorbed is _____ proportional to the pressure.
(a) directly
(b) inversely
(c) sometimes directly, sometimes inversely
(d) none of these
3. Physical adsorption occurs rapidly at _____ temperature
(a) low
(b) high
(c) absolute zero
(d) none of these
4. The process of adsorption is
(a) exothermic
(b) endothermic
(c) sometimes exothermic, sometimes endothermic
(d) none of the above
5. Chemisorption generally _____ with temperature.
(a) increases
(b) decreases
(c) remains the same
(d) none of these
6. Physical adsorption is a _____ process.
(a) reversible
(b) irreversible
(c) exothermic
(d) none of these
7. Multimolecular layers are formed in
(a) adsorption
(b) physical adsorption
(c) chemisorption
(d) reversible adsorption
8. Freundlich isotherms is not applicable at
(a) high pressure
(b) low pressure
(c) 273 K
(d) room temperature
9. Physical adsorption generally _____ with increasing temperature.

(a) decreases

(b) increases

(c) sometimes decreases, sometime increases

(d) none of these

10. The adsorption of gases on metal surfaces is called

(a) catalysis

(b) occlusion

(c) adsorption

(d) absorption

Answers

1. (c)
2. (a)
3. (a)
4. (a)
5. (a)
6. (a)
7. (c)
8. (a)
9. (a)
10. (b)

SHORT-ANSWER QUESTIONS

1. Explain the terms: adsorption and adsorbate giving an example.
2. Draw adsorption isobars for physical and chemical adsorption.
3. Give two points of Langmuir theory of adsorption.
4. Give two points of difference between physical and chemical adsorption.
5. Show that for a moderate range of pressures, the Langmuir adsorption reduces to Freundlich adsorption isotherm.
6. Write a note on chemisorption.
7. What are the factors that affect adsorption?
8. What are the different shapes of adsorption isotherms obtained for adsorption of gases on solids?
9. Give three applications of adsorption phenomenon.
10. Why does a finely powdered substance have greater adsorption capacity than coarsely powdered substance having the same mass?
11. What do we understand by unimolecular and multimolecular adsorption?
12. What is the effect of temperature and pressure on the adsorption of a gas on a solid?

13. What is adsorption-desorption hysteresis? Explain briefly.

GENERAL QUESTIONS

1. Explain the following terms:
   (a) Adsorption
   (b) Physical adsorption
   (c) Chemical adsorption
   (d) Freundlich adsorption isotherm
   (e) Langmuir adsorption isotherm
2. What is the effect of temperature on adsorption of gases on solids?
3. Write the assumptions of Langmuir adsorption isotherm and derive the equation pertaining to it.
4. (a) Write the main points of Langmuir's theory of adsorption.
   (b) Draw adsorption isobars for physical adsorption and chemical adsorption.
5. Write what you understand by the term adsorption. Give four points of difference between physical adsorption and chemical adsorption.
6. Distinguish between *adsorption* and *absorption*. Discuss the factors which affect the adsorption of a gas on a solid adsorbent. Discuss in brief the type of adsorption isotherms commonly observed for the adsorption of gases on a variety of adsorbents at different temperatures.
7. Derive Langmuir's adsorption isotherm stating the assumptions on which it is based. Show that for a moderate range of pressures, it reduces to Freundlich adsorption isotherm.
8. Discuss Langmuir theory of adsorption and derive the expression for Langmuir monolayer adsorption isotherm.
9. Derive Langmuir adsorption isotherm equation. Under what conditions does it become identical with Freundlich adsorption isotherm equation?
10. 100 ml of 0.3 M acetic acid is shaken with 0.8 g of wood charcoal. The final concentration of the solution after adsorption is 0.125 M. Calculate the weight of acetic acid adsorbed per gram of carbon.

[Ans. 1.31 g]

11. For an adsorbent-adsorbate system obeying the Langmuir adsorption isotherm, $a = 0.48$ bar^{-1} and $b = 0.16$ bar^{-1}. At what pressure will 50% of the surface be covered?

[Ans. 1.25 bar]

12. 10.0 g of oxygen is adsorbed on 2.5 g of metal powder at 273 K and 1 atm pressure. Calculate the volume of the gas adsorbed per gram of adsorbent.

[Ans. 2798.25 ml]

13. Four grams of a gas is adsorbed on 1.5 g of metal powder at 300 K and 0.7 atm. Calculate the volume of the gas at STP adsorbed per gram of adsorbent.

[Ans. 2052.5 m]

14. Five grams of a catalyst absorb 400 cm^3 of N_2 at STP to form a monolayer. What is the surface area per gram if the area occupied by a molecule of N_2 is 16 Å.

[Ans. 344 $m^2\ g^{-1}$]

15. What is an adsorption isotherm? Deduce Langmuir's adsorption isotherm.
16. Discuss Freundlich adsorption isotherm of a gas on a solid surface. How are the constants in the isotherm equation determined? How will you prove that Langmuir adsorption isotherm is superior to Freundlich adsorption isotherm?
17. What are the postulates of Langmuir adsorption isotherm? On the basis of these postulates, derive the Langmuir equation. How can it be used to determine the surface area of an adsorbent?
18. Write down the Langmuir's adsorption isotherm. Also write two objections in Langmuir's theory.
19. (a) In a particular experiment, it is required to have a large amount of gas absorbed on the surface of a solid. Suggest a few factors which may be helpful along with suitable explanations.

    (b) What signs of ΔH and ΔS in the case of physical adsorption are expected? Justify your answer.

(c) Write a note on chemisorption.

20. (a) What do you understand by the term *adsorption?* What are the factors which affect adsorption?

    (b) Discuss the effect of temperature and pressure on the adsorption of a gas on a solid surface.

21. (a) Show diagrammatically the different types of adsorption isotherms obtained for adsorption of gases on solids.

    (b) Discuss the behaviour of Langmuir adsorption isotherm at very low and very high pressures.

22. Deduce Gibbs adsorption equation thermodynamically.
23. Derive Freundlich adsorption isotherm from the Gibbs adsorption isotherm applied to a gas.
24. Draw the typical adsorption isotherms obtained in the case of unimolecular and multimolecular adsorption.
25. What are the postulates of Langmuir theory of adsorption? Derive Langmuir adsorption equation in the form $x = \frac{ap}{1 + bp}$. How is this equation verified?
26. (a) Distinguish between physisorption and chemisorption.

    (b) How is Langmuir adsorption isotherm related to Freundlich's isotherm? How are shapes of adsorption isotherms modified when multilayer adsorption takes place?

27. (a) Give two applications of adsorption.

    (b) Explain the reason why a finely powdered substance is more effective adsorbent?

28. (a) Derive Langmuir isotherm equation. How does this isotherm interpret the kinetics of unimolecular reactions catalysed by the solid surface?
29. (a) How is chemisorption distinguished from physisorption on the basis of number of adsorbed layers?

    (b) How can Langmuir adsorption isotherm equation be used to explain the observation: the decomposition of PH_3 gas on tungsten metal surface is first order at low pressure and zeroth order at high pressure?

30. What is the basic principle of BET equation? Write the BET equation. How is it used in the determination of surface area of the adsorbent?



Polymers 27

LEARNING OBJECTIVES

- Define degree of polymerisation
- Differentiate between high polymers and oligomers
- Differentiate between homopolymers and copolymers
- Understand natural and synthetic polymers
- Understand the terms *number-average* and *mass-average molecularmasses*
- Learn osmotic-pressure method for molecular-mass determination and the effect of Donnan membrane equilibrium
- Learn viscosity method for molecular mass determination
- Learn light-scattering method for molecular-mass determination.

27.1 INTRODUCTION

Polymers, or macromolecules, are long-chain high-molecular-mass compounds obtained by the combination of a large number of simple molecules. The simple molecules taking part in the formation of polymers are called ***monomers*** and this process of polymer formation is called ***polymerisation.***

The product formed is called a dimer, trimer or tetramer according as whether two, three or four molecules combine to give the product. If a large number of molecules (say n molecules) combine together, the product is called a polymer. Thus, n molecules of ethylene combine to produce polyethylene.

$$n\ CH_2 = CH_2 \longrightarrow [-CH_2 - CH_2 -]_n$$

Ethylene Polyethylene

In this chapter, we shall lay more emphasis on the physical properties of polymers, like molecular mass and its determination by different methods.

27.2 TERMS USED IN RELATION TO POLYMERS

The following terms are commonly used in the study of polymers:

1. Degree of polymerisation
2. High polymers and oligomers

3. Homopolymers and copolymers

These are briefly discussed as under:

1. The number of repeat units in the polymer chain is called ***degree of polymerisation.*** The product of degree of polymerisation (n) and the molecular mass of monomeric unit M_m is equal to the molecular mass of the polymer.

   Thus, molecular mass of the polymer = $n \times M_m$

2. ***High polymers and oligomers.*** Polymers with high degree of polymerisation are called ***high polymers*** while those with low degree of polymerisation are called ***oligomers.***

3. The polymer formed from only one kind of monomers is called a ***homopolymers*** while a polymer made from two or more different kinds of monomers is called a ***copolymer*** or ***mixed polymer.*** For example, polythene is an example of a homopolymer whereas Buna-S rubber is a example of copolymer formed from the monomers 1, 3-butadiene ($CH_2 = CH - CH = CH_2$) and styrene

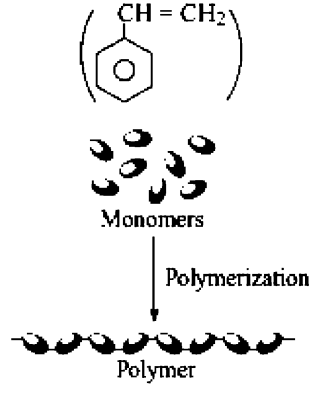


Fig. 27.1 *Polymerisation*

27.3 NATURAL AND SYNTHETIC POLYMERS

1. Natural Polymers Polymers obtained as such from a natural sources are called natural polymers. A few examples of the naturally occurring polymers include proteins, polysaccharides, gums, natural rubber, silk and wool. Proteins, silk and wool are polymers of amino acids, natural rubber is a polymer of isoprene, polysaccharides are polymers of glucose, fructose, etc.

2. Synthetic Polymers Polymers prepared by synthesis from simple substances are called synthetic polymers. A few examples of the polymers prepared synthetically include synthetic rubbers, polyethylene, polystyrene, nylon, etc.

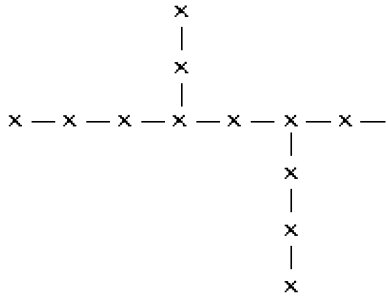
27.3.1 Characteristics of the Three Kinds of Polymers

1. Linear Polymers These are those polymers whose macromolecules contain the monomeric units linked together to form long and strong chains. Representing the monomeric units by x, a linear polymer may be represented as follows:

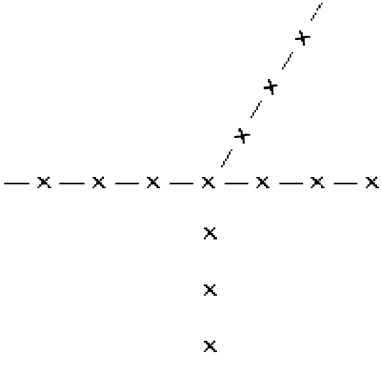
$$\cdots - X - X - X - X - X - X - \cdots$$

2. Branched Polymers These are those polymers in which the monomeric units are linked to

form long chains (called the **main chain)** with side branches (called the **side chains),** the number and length of which may vary widely from polymer to polymer. Branched polymers may be represented as shown alongside:



Cross-linked or Three-Dimensional Polymers When the monomers are linked together to form a three-dimensional network, the links involved are called cross-links and the polymer formed is called cross-linked polymer as represented below:



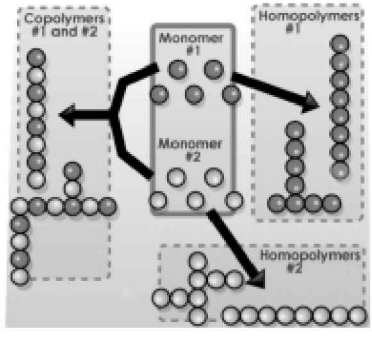


Fig. 27.2 *Homopolymers and copolymers*

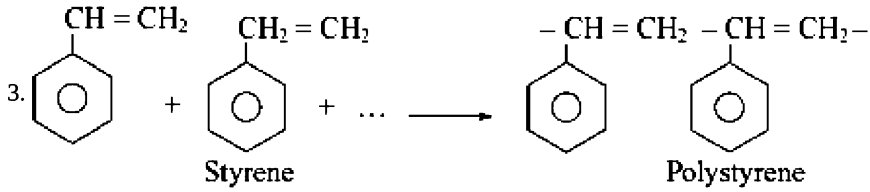
27.3.2 Addition Polymers and Condensation Polymers

1. Addition Polymers When the simple molecules (monomers) are linked together to form long chains without the elimination of any by-product molecules, the products formed are called addition polymers and the process involved is called addition polymerization.

As no by-product molecule is eliminated during the process, the molecular formula and, hence, the molecular mass of the polymer formed is an integral multiple of that of the monomer. A few examples of the addition polymerisation are given below:

1. $\ldots + CH_2 = CH_2 + CH_2 = CH_2 + \ldots \rightarrow \ldots CH_2 = CH - CH_2 = CH_2 \ldots$
   Ethene → Polyethane

2. $\ldots + CH_2 = \underset{\displaystyle Cl}{CH} + CH_2 = \underset{\displaystyle Cl}{CH} + \ldots \longrightarrow \ldots CH_2 - \underset{\displaystyle Cl}{CH} - CH_2 - \underset{\displaystyle Cl}{CH} \ldots$
   Vinyl chloride → Polyvinyl chloride (PVC)



2. Condensation Polymers When the monomers contain some active functional groups which can react together with the elimination of some molecules (usually water) and result into the formation of long chains, the process is called condensation polymersation and the product formed is called **condensation polymer.** In this case, as some by product molecule is eliminated, the molecular formula and, hence, the molecular mass of the polymer is not an integral multiple of that of the monomer. A few examples of the condensation polymerisation are given below:

$$H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH + H_2N-(CH_2)_6-NH_2$$

(a) Hexamethylene diamine + Adipic acid + Hexamethylene diamine ↓

$$-NH-(CH_2)_6-NHCO(CH_2)_4CONH(CH_2)_6-NH-$$

Nylon

$$OH-CH_2-CH_2-OH + HOOC-C_6H_4-COOH$$

(b). Ethylene glycol + Terephthalic acid $\xrightarrow{-H_2O}$

$$-\ldots O-CH_2-CH_2-O-CO-C_6H_4-CO-O\ldots$$

27.4 | NUMBER AVERAGE AND MASS-AVERAGE MOLECULAR MASSES

1. Number-average Molecular Mass ***When the total molecular mass of all the molecules of a sample is divided by the total number of molecules, the result obtained is called the average molecular mass.*** For example, suppose in a particular sample,

N_1 molecules have molecular mass M_1 each

N_2 molecules have molecular mass M_2 each

N_2 molecules have molecules mass M_3 each

and so on.

Then we have

Total molecular mass of all the N_1 molecules = N_1M_1

Total molecular mass of all the N_2 molecules = N_2M_2

Total molecular mass of all the N_3 molecules = N_3M_3 and so on

$\therefore$ Total molecular mass of all the molecules

$$= N_1M_1 + N_2M_2 + N_3M_3 + \ldots = \Sigma\, NiMi$$

Total number of all the molecules

$$= N_1 + N_2 + N_3 + \ldots = \Sigma \text{ Ni}$$

Hence, the number-average molecular mass will be given by

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \ldots}{N_1 + N_2 + N_3 \ldots} \quad \text{or} \quad \bar{M}_n = \frac{\Sigma N_1M_1}{\Sigma N_1}$$

2. Mass-average Molecular Mass When the total molecular mass of a group of molecules having a particular molecular mass are multiplied with their respective molecular mass, the products are added and the sum is divided by the total mass of all the molecules, the result obtained is called the mass average molecular mass. Supposing N_1, N_2, N_3, etc, molecules having molecular mass M_1, M_2, M_3, etc., respectively.

Total molecular mass of N_1 molecules = N_1M_1

Total molecular mass of N_2 molecules = N_2M_2

Total molecular mass of N_3 molecules = N_3M_3, and so on.

The products with their respective molecular masses will be $N_1M_1 \times M_1$, $N_2M_2 \times M_2$, $N_2M_3 \times M_3$, etc.,

i.e. $N_1M_1^2$, $N_2M_2^2$, $N_3M_3^2$, etc.

Sum of the products $= N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \ldots = \Sigma \text{NiMi}^2$

Total mass of all the molecules $= N_1M_1 + N_2M_2 + N_3M_3 + \ldots = \Sigma \text{NiMi}$

Hence, mass-average molecular mass is given by

$$\bar{M}_m = \frac{N_1M_1^2 + N_2M_2^2 + N_3N_3^2 + \ldots}{N_1M_1 + N_2M_2 + N_3M_3 + \ldots}$$

or

$$\bar{M}_m = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}$$

(a) Condition under which $M_n = M_m$

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + \ldots}{N_1 + N_2 + \ldots}$$

$$\bar{M}_m = \frac{N_1M_1^2 + N_2M_2^2 + \ldots}{N_1M_1 + N_2M_2 + \ldots}$$

If $\bar{M}_n = \bar{M}_m$ then

$$\frac{N_1M_1 + N_2M_2 + \ldots}{N_1 + N_2 + \ldots} = \frac{N_1M_1^2 + N_2M_2^2 + \ldots}{N_1M_1 + N_2M_2 + \ldots}$$

The two sides can be equal only if

$$M_1 = M_2 = \ldots$$

i.e. all molecules should have the same molecular mass. In that case, average has no significance.

(b) Polydispersity Index In polymers, we use a term polydispersity index which is given as under.

$$\text{Polydispersity index} = \frac{\text{Number average molecular mass}}{\text{Mass average molecular mass}}$$

Polydispersity index gives the width of molecular mass distribution.

Example 1 *A suspension contains equal masses of particles with molecular masses 20000 and 40000. Calculate $\bar{M}_n$ and $\bar{M}_m$*

Solution: Since the suspension contains equal masses of particles with molecular masses 20000 and 40000, we have

$$N_1M_1 = N_2M_2$$

Here, $M_1 = 20000$ and $M_2 = 40000$

Substituting the values in the equation above,

$$N_1 \times 20000 = N_2 \times 40000$$

or $$\frac{N_1}{N_2} = 2 \text{ or } N_1 = 2N_2$$

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2}{N_1 + N_2}$$

Substituting $2N_2$ for N_1 and putting the values of M_1 and M_2, we have

$$\bar{M}_n = \frac{(2N_2 \times 20000) + (N_2 \times 40000)}{2N_2 + N_2} = \frac{N_2(40000 + 40000)}{N_2(2+1)} = 26667$$

$$\bar{M}_m = \frac{N_1M_1^2 + N_2M_2^2}{N_1M_1 + N_2M_2}$$

Substituting 2 N_2 for N_1 and putting the values of M_1 and M_2,

$$\bar{M}_m = \frac{2N_2 \times 20000^2 + N_2 \times 40000^2}{2N_2 \times 20000 + N_2 \times 40000}$$

$$= \frac{N_2(2 \times 20000^2 + 40000^2)}{N_2(2 \times 20000 + 40000)}$$

$$= \frac{2 \times 2^2 \times 10^8 + 4^2 \times 10^8}{2 \times 2 \times 10^4 + 4 \times 10^4} = \frac{8 \times 10^8 + 16 \times 10^8}{4 \times 10^4 + 4 \times 10^4}$$

$$= \frac{24 \times 10^8}{8 \times 10^4} = 30000$$

Example 2 *Calculate $\bar{M}_m$ (mass-average molecular mass) for a system containing equal number of particles with molecular masses 10000 and 20000.*

Solution. In this case, $N_1 = N_2$

$$M_m = \frac{N_1M_1^2 + N_2M_2^2}{N_1M_1 + N_2M_2}$$

Substituteing N_1 for N_2, we have

$$M_m = \frac{N_1M_1^2 + N_1M_2^2}{N_1M_1 + N_1M_2} = \frac{N_1(M_1^2 + M_2^2)}{N_1(M_1 + M_2)} = \frac{M_1^2 + M_2^2}{M_1 + M_2}$$

Substituting for M_1 and M_2,

$$\bar{M}_m = \frac{10000^2 + 20000^2}{10000 + 20000} = \frac{10^8 + (4 \times 10^8)}{10^4 + (2 \times 10^4)}$$

$$= \frac{5 \times 10^8}{3 \times 10^4} = 16667$$

Example 3 *In a particular sample of a polymer, 100 molecules have molecular mass of 10^3 each, 200 molecules have molecular mass of 10^4 each and 200 molecules have molecular mass of 10^5. Calculate the number average and mass-average molecular mass.*

Solution.

$$\bar{M}_n = \frac{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5}{100 + 200 + 200} = \frac{10^5(1 + 20 + 200)}{500} = 4.4 \times 10^4$$

$$= 44{,}000$$

$$\bar{M}_n = \frac{100 \times (10^3)^2 + 200 \times (10^4)^2 + 200 \times (10^5)^2}{100 \times 10^3 + 200 \times 10^4 + 200 + 10^5}$$

$$= \frac{10^8(1 + 200 + 20000)}{10^5(1 + 20 + 200)} = \frac{10^3 \times 20201}{221} = 91000$$

Example 4 *A polymer consists of 40% by mass of macromolecules of molecular mass 10000 and 60% by weight of macromolecules of molecular mass 75000. Calculate the number average and massaverage molecular mass of the polymer.*

Solution: $M_1 = 10000 \quad M_2 = 75000$

Let N_1 and N_2 be the number of molecules of the two types.

$$\frac{N_1 M_1}{N_2 M_2} = \frac{4}{6} \quad \text{or} \quad \frac{N_1 M_1}{N_2 M_2} = \frac{2}{3} \quad \text{or} \quad N_2 M_2 = 1.5\, N_1 M_1$$

Also,

$$\frac{N_1 \times 10000}{N_2 \times 75000} = \frac{2}{3} \quad \text{or} \quad N_2 = \frac{N_1 \times 10000}{75000} \times \frac{3}{2} = 0.2\, N_1$$

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2} \text{ (substituting for } N_2 M_2) = \frac{N_1 M_1 + 1.5\, N_1 M_1}{N_1 + 0.2\, N_1}$$

$$= \frac{2.5\, N_1 M_1}{1.2\, N_1} = \frac{2.5}{1.2} \times 10000 = 20833$$

$$\bar{M}_m = \frac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2} = \frac{N_1 M_1 M_1 + N_2 M_2 M_2}{N_1 M_1 + N_2 M_2}$$

$$= \frac{(N_1 M_1 \times 10000) + (1.5\, N_1 M_1 \times 75000)}{N_1 M_1 + 1.5\, N_1 M_1} = \frac{N_1 M_1 (10000 + 112500)}{N_1 M_1 (1 + 1.5)}$$

$$= \frac{122500}{2.5} = 49000$$

27.5 | METHODS FOR THE DETERMINATION OF MOLECULAR MASSES

1. Osmosis Pressure Method Osmosis is the phenomenon of the passage of solvent molecules into the solution through a semipermeable membrane.

The hydrostatic pressure of the liquid column set up as a result of osmosis is called the ***osmotic pressure***, or osmotic pressure is the external pressure that has to be applied on the solution to prevent the entry of the solvent into the solution through the semipermeable membrane.

The solution of a polymer in a suitable solvent can be subjected to the phenomenon of osmosis because the size of the polymer molecules in the solution is not large enough to pass through the semipermeable membrane while the solvent molecules can easily pass through. If the solution were ***dilute***, the osmotic pressure is given by the van't Hoff equation, viz.

$$PV = nRT$$

or

$$P = \frac{n}{V} RT \qquad \ldots(27.1)$$

where P = Osmotic pressure

n = Number of moles of the polymer

V = Volume of the polymer solution

T = Absolute temperature at which measurements are made

R = Solution constant or the gas constant

Substituting, $n = \frac{w}{M}$, Eq. (27.1) reduces to

$$P = \frac{w}{M} \times \frac{1}{V} RT = \frac{w}{V} \frac{RT}{M} = C \frac{RT}{M} \qquad \ldots(27.2)$$

where $C = \frac{w}{V}$ is the concentration of the solution in grams litre.

Equation (27.2) may be rewritten as

$$\frac{P}{C} = \frac{RT}{M} \qquad \ldots(27.3)$$

According to this equation, $\frac{P}{C}$ should be a constant at a constant temperature, i.e. a plot of $\frac{P}{C}$ vs C should be a straight line.

However, this result is found to hold good only for dilute solutions of low-molecular-weight polymers. For high-polymer solutions, it is observed that the osmotic pressure varies with concentration according to the following relationship:

$$\frac{P}{C} = \frac{RT}{M} + AC + BC^2 + \ldots \qquad (27.4)$$

where A, B, etc., are constants. The quantity $\frac{P}{C}$ is called reduced **osmotic pressure.**

From Eq. (27.4), it is evident that

$$\frac{P}{C} = \frac{RT}{M} \text{ if } C = 0$$

i.e.

$$\text{limit} \left(\frac{P}{C}\right)_{C \to 0} = \frac{RT}{M}$$

Thus, if $\frac{P}{C}$ values are plotted against C and the graph is extrapolated to $C = 0$ then the intercept on the Y-axis is equal to $\frac{RT}{M}$ (Fig. 27.3).

From this, the value of M can be calculated as

$$M = \frac{RT}{\left(\frac{P}{C}\right)_{C \to 0}}$$

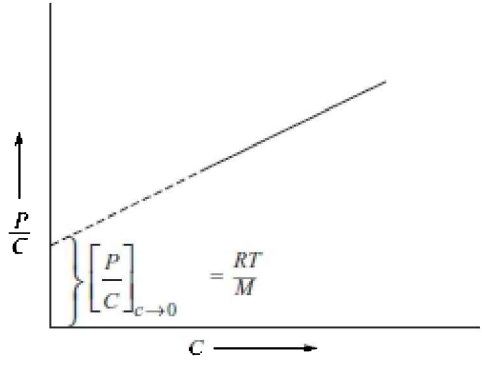


Fig. 27.3 *Variation of reduced osmotic pressure with concentration*

As osmotic pressure is a colligative property, i.e. it depends upon the number of particles present; therefore, the molecular mass obtained by this method is the ***number average molecular***

mass.

Thus, to determine the molecular mass of a polymer, it is required to measure the osmotic pressure of solutions of several concentrations and extrapolate the line to zero concentration.

The instruments used for determining the molecular weight by this method are called ***osmometers.*** A simple design of an osmometer is shown in (Fig. 27.4). Two different techniques are used:

(a) Static Method The solvent is allowed to enter the polymer solution through the semipermeable membrane till the level in the capillary tube stops rising.

(b) Dynamic Method In this method, the rate of penetration of the solvent into the solution through the semipermeable membrane is noted under a known applied pressure.

The dynamic method is preferred because it gives quick results.

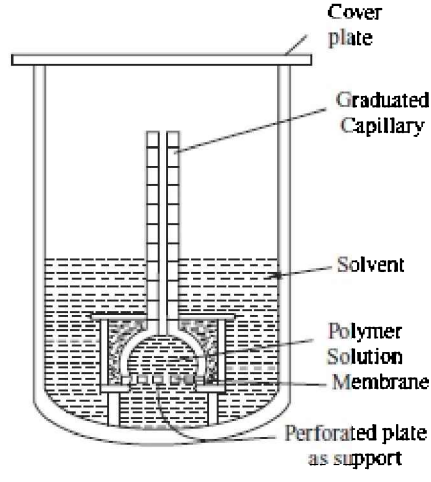


Fig. 27.4 *A general design of osmometer*

2. Molar Mass of Charged Polymers (Effect of Donnan Membrane Equilibrium) It has been observed that molecular mass of charged polymers like proteins, as determined by osmotic-pressure method, is considerably smaller than that determined by other methods. This was found to be due to an electrical phenomenon, known as Donnan membrane equilibrium, which takes place when a large, nondiffusible charged ion like a protein ion, is separated from a diffusible salt by a semipermeable membrane.

Suppose a solution of salt $Na^+ P^-$ of concentration C_1 is separated by a semipermeable membrane from a solution of sodium chloride of concentration C_2. Here, P^- is the protein particle carrying a negative charge. During osmosis, the chloride ions have a tendency to diffuse from a region of higher concentration C_2 on the RHS to a region of lower concentration C_1 on the LHS. However, the protein ion P^- cannot pass through the membrane. To maintain electrical neutrality, an equal number of Na^+ would pass from RHS to LHS. This is shown diagrammatically as under:

Na^-	P^-	$\|\|$	Na^-	Cl^-	Initial state
C_1	C_1	$\|\|$	C_2	C_2	
Na^-	P^-	Cl^-	Na^+	Cl^-	At equilibrium
C_1+x	C_1	x	C_2-x	C_2-x	

The osmotic pressure measurement would get complicated by additional particles on LHS.

If the solution behaves ideally, the osmotic pressure can be obtained with the help of van't Hoff equation $P = RTC$. The concentration term C in the present case would be the difference in molar concentrations on the two sides of the membrane. Therefore, at equilibrium, we have

$$P = RT\{(C_1 + x) + (C_1 + x)\} - \{(C_2 - x) + (C_2 - x)\} \quad \ldots(27.5)$$

or

$$P = 2RT\{C_1 - C_2 + 2x\} \quad \ldots(27.6)$$

If the concentration of the salt C_2 is low compared to the concentration C_1 of the nondiffusible ion, the osmotic pressure would be given by

$$P = 2RT(C_1 + 2x) \quad \ldots(27.7)$$

Evidently, this pressure is higher than the pressure which should have been given by the relation $P = 2\ RTC_1$. The molecular mass of the solute and osmotic pressure are inversely related.

Therefore, molecular mass determined from osmotic-pressure method would come out to be smaller than the actual value. If the concentration of the salt C_2 is high compared to the concentration C_1 of the nondiffusible ion then Eq. (27.6) takes the form

$$P = 2RTC_1 \quad \ldots(27.8) \quad \left[\begin{array}{l}\text{calculations involving activity}\\ \text{coefficients show that } 2x = C_2\end{array}\right]$$

This equation is free from the concentration of chloride ion.

In other words, we can eliminate the effect of Donnan equilibrium on the osmotic pressure by taking a high concentration of salt in the solution.

3. Sedimentation or Ultracentrifugation Method Sedimentation is the process of setting down of the particles in a solution. Polymers, because of large size of their molecules, start settling down due to the force of gravity, through very very slowly. Based upon this idea, a method has been developed for the determination of molecular weight of polymers.

This method is based upon the principle that the rate of sedimentation depends upon the size of the particles. Thus by measuring the rate of sedimentation, the size of the particles can be calculated from which the mass of particles and then the molecular mass can be calculated. The rate of sedimentation can be followed from the fact that if the solution is kept undisturbed for quite some time, the solvent forms a separate layer at the top. As time passes, the level B of the solution moves downwards which can be located either directly or by optical method. The mathematical expression for the calculation of the result is obtained as follows:

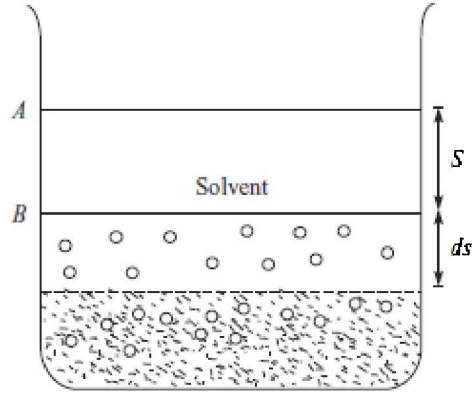


Fig. 27.5 *Sedimentation under gravity*

For any sedimenting particle, there are two forces acting on it. These are

(a) **The gravitational force acting downwards**

$$= \frac{4}{3}\pi r^3 (d - d')g \qquad (27.9)$$

where r = Radius of the particle
d = Density of the particles
d' = Density of the solvent (medium)
g = Acceleration due to gravity

(b) **Opposing frictional force** = $6\pi r\eta V$(Stokes Law)

where r = Radius of the particles, as mentioned above
η = Coefficient of viscosity of the medium
V = Velocity of sedimentation of the particle

When the two opposing forces become equal, the particle falls with a constant velocity V, i.e. for a constant sedimentation rate,

$$6\pi r\eta V = \frac{4}{3}\pi r^3 (d - d')g$$

or
$$V = \frac{2r^2 g(d - d')}{a\eta} \qquad (27.10)$$

If the level B (at a distance x from the top) travels a distance dx in a small interval of time dt the velocity of sedimentation = $\frac{dx}{dt}$

$\therefore$
$$\frac{dx}{dt} = \frac{2r^2 g(d - d')}{a\eta}$$

or
$$dx = \frac{2r^2 g(d - d')}{a\eta}\, dt \qquad (27.11)$$

Integrating this equation between the limits x_1 at t_1 and x_2 at t_2, we get

$$\int_{x_1}^{x_2} dx = \frac{2r^2 g(d-d')}{a\eta} \int_{t_1}^{t_2} dx$$

i.e. $$x_2 - x_1 = \frac{2r^2 g(d-d')(t_2 - t_1)}{a\eta} \qquad (27.12)$$

Thus, by knowing d and d' and by measuring the distances x_1 and x_2, at two different times t_1 and t_2, the radius of the sedimenting particles can be calculated. Then we have

$$\text{Mass of the particle, } m = \frac{4}{3}\pi r^3 d \qquad (\text{Mass} = \text{Volume} \times \text{Density})$$

and molecular mass of the polymer = Nm where $N$is Avogadro's number.

A limitation of this method is that sedimentation under gravity is very very slow. This difficulty was solved by performing the experiment in an ultracentrifuge. Thus, gravity is substituted by the centrifugal force of rotation. The solution is taken in a cell placed in a specially designed rotor. The force exerted on the particles in this machine may be as high as one million times the force of gravity or even more. Thus, the time of sedimentation is reduced considerably. The rate of sedimentation can be observed by optical methods without stopping the ultracentrifuge. Thus, by using this technique, the acceleration due to gravity g in expression (27.11), is replaced by the acceleration due to centrifugal field. The latter at a distance x from the axis of rotation is given by $\omega^2 x$ where ω is the angular velocity of rotation. Thus, Eq. (27.11) is modified to

$$\frac{dx}{dt} = \frac{2r^2\omega^2 x(d-d')}{a\eta} \quad \text{or} \quad \frac{1}{x}dx = \frac{2r^2\omega^2 x(d-d')}{a\eta}dt \qquad (27.13)$$

Integrating between the limits x_1 at t_1 and x_2 at t_2, we get

$$\ln\frac{x_2}{x_1} = \frac{2r^2\omega(d-d')}{a\eta}(t_2 - t_1) \qquad (27.14)$$

Using this equation, the radius r of the particle and hence, the mass m and then the molecular mass can be calculated as explained before.

The molecular mass obtained by sedimentation method is called sedimentation average molecular mass ($\overline{M}_g$). It is nearly equal to the mass average molecular mass ($\overline{M}_m$).

4. Viscosity Method This method requires the measurement of viscosities of polymer solutions of different concentrations which can be done easily with the help of an Ostwald viscometer. However, this method is not an absolute method because it requires calibration using certain other substances of known molecular masses. The theory of the method is discussed below:

If η is the viscosity of a solution and η_o that of pure solvent at the same temperature, the ratio η/η_o is called the relative viscosity of the solution and is usually represented by η_r i.e.,

$$\frac{\eta}{\eta_o} = \eta_r \qquad \ldots(27.15)$$

Another quantity ***specific viscosity*** η_{sp} is given by

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \qquad \ldots(27.16)$$

Further, it is observed that the ratio η_{sp}/C where C is the concentration of the solution, generally expressed in grams per 100 ml of the solution, varies linearly with concentration. The extrapolation of η_{sp}/C value to zero concentration gives what is known as ***intrinsic viscosity***, represented usually by $[\eta]$, i.e.

$$[\eta] = \left(\frac{\eta_{sp}}{C} \right)_{C \to 0} \quad \ldots(27.17)$$

The intrinsic viscosity is found to be related to the molecular mass M by the expression

$$[\eta] = RM^a \quad \ldots(27.18)$$

where R and a are constants for the given polymer series in a particular solvent.

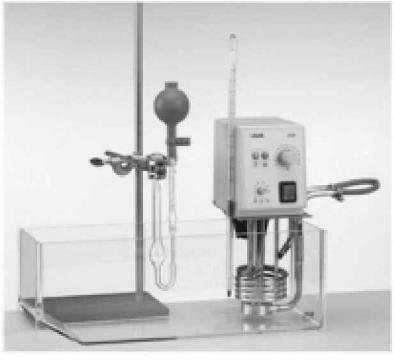


Fig. 27.6 *Set up of an apparatus consisting of thermostatted capillary viscometer for the determination of mean molecular mass of a polymer*

Thus, if k and a are known for a particular polymer series in a particular solvent, the value of M can be determined by finding $[\eta]$ for the polymer under investigation.

$[\eta]$ for the polymer under investigation can be found by plotting η_{sp}/C vs C and extrapolating the result to zero concentration as shown in Fig. 27.7 for polyvinyl chloride in cyclohexane at 25°C.

To determine k and a, a number of samples of the same polymer series are taken whose molecular masses have been determined by other methods like osmometry or light scattering. Writing Eq. (27.18) in the form

$$\log \eta = \log R + a \log M$$

a plot of log η, log M will be straight line with slope a and intercept log k. Thus, the values of k and a can be obtained for the given polymer series in a particular solvent.

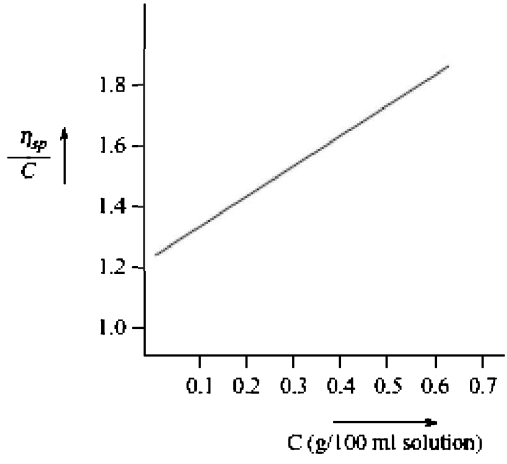


Fig. 27.7 *Plot of η_{sp}/C vs C for polyvinyl chloride in cyclohexane at 25°C*

The molecular mass obtained by this method is called ***viscosity-average molecular*** mass ($\overline{M}_V$). If a = 1, it is equal to the mass average molecular mass. However, as a usually lies between 0.5 to 1, the viscosity-average molecular mass ($\overline{M}_V$) usually lies between number-average molecular mass ($\overline{M}_n$) and mass-average molecular mass ($\overline{M}_m$).

Example 5 *Write intrinsic viscosity-molecular weight relationship. Determine the values of two constants appearing in the above relation when a fraction of a polymer of molecular weights 34000, 61000 and 130000 dissolved in an organic solvent gave the intrinsic viscosities as 1.02, 1.60 and 2.75 respectively at 25°C.*

Solution: Intrinsic viscosity-molecular mass relation is

$$[\eta] = kM^a$$

Substituting the values in the equation above

$$1.02 = k\,34000^a \quad \ldots(i)$$

$$1.60 = k\,61000^a \quad \ldots(ii)$$

Divide Eq. (ii) by (i),

$$\frac{1.60}{1.02} = \left(\frac{61000}{34000}\right)^a \text{ or } \frac{1.60}{1.02} = \left(\frac{61}{34}\right)^a$$

Taking logarithm of both sides,

$$a \log 1.794 = \log 1.568$$

or

$$a = \frac{\log 1.568}{\log 1.794} = \frac{0.1953}{0.2539} = 0.769$$

Substitute the value of a in (i),

$$1.02 = k\,34000^{0.769}$$

Taking logarithm of both sides,

$$\log 1.02 = \log k + 0.769 \log 34000$$
$$0.0086 = \log k + 0.769 \log (3.4 \times 10^4)$$
$$0.0086 = \log k + 0.769 (0.5315 + 4)$$
$$0.0086 = \log k + 0.769 \times 4.5315$$
$$0.0086 = \log k + 3.4847$$

or $$\log k = \bar{4}.5239$$

or $$k = 3.341 \times 10^{-4}$$

5. Light-Scattering Method This method is based upon the phenomenon of 'scattering of light' by colloidal solutions because polymers are macromolecular colloids. The amount of light scattered depends directly on the size and number of particles present in the solution.

When a light of intensity I_o is passed through the solution contained in a cell of length l, the intensity of the transmitted light is reduced to I due to scattering. The relationship between I and I_o is given by

$$\tau = \frac{1}{l} \log \frac{I_o}{I} \qquad \ldots(27.18)$$

when τ is called the turbidity of the scattering medium.

The turbidity τ is related to the apparent molecular mass of the polymer in the solution according to the following equation, given by Debye

$$\frac{HC}{\tau} = \frac{1}{M'} + AC + BC^2 + \ldots \qquad \ldots(27.19)$$

where C = concentration of the solution in g/cm^3, h is a constant for a given polymer and a given dispersion medium

A, B, etc., are constants and M' is the apparent molecular mass of the polymer

H is given by the following relation

$$H = \frac{32 \pi^3 \eta_o^2 (d\eta/dc)^2}{25 N \lambda_o^4} \qquad \ldots(27.20)$$

where η_o= Refractive index of the solvent

$d\eta/dc$ = Variation of refractive index of the solution with concentration

λ_o = Wavelength (in vacuum) of the light used

N = Avogadro's Number

Equation (27.19) leads to the following result:

$$\text{limit} \left(\frac{HC}{\tau} \right)_{C \to 0} = \frac{1}{M'} \qquad \ldots(27.21)$$

Thus, to get M', we should plot $\frac{HC}{\tau}$ versus C and then extrapolate the plot to zero concentration.

Intercept gives $1/M'$ from which M' can be calculated.

To get the value of $\frac{HC}{\tau}$ corresponding to different concentrations C, solutions of experimental polymers in a particular suitable solvent are prepared. In each case, the turbidity τ is measured and the quantity H is calculated. To measure turbidity τ [using Eq. (27.18)], the intensity of the light scattered at 90° to the direction of the incident beam is measured with a simple photometer. To get the value of H, the quantities involved in Eq. (27.20) have to be

measured. The refraction index η_o of the solvent is measured with a refractometer, $d\eta/dc$ is measured with special differential refractometers.

Further, the apparent molecular mass M' is related to a the correct molecular mass M by the relation

$$M = M' \alpha\beta \qquad \ldots(27.22)$$

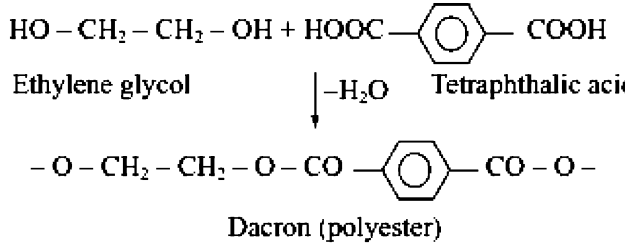
where α and β are corrections depending upon the size and the nature of the solute particles. α is called ***dissymmetry correction*** and β is called ***dipolarisation correction.*** The correction factor α is obtained by measuring the intensities of scattered light at angles, of 45° and 135° to the primary beam and β is obtained from the ratio of the horizontal to the vertical components of the light scattered by the solute at 90° to the direction of the incident beam.

It may be pointed out that the molecular mass obtained by this method is the ***mass-average molecular mass*** M_w.

27.6 | STEP POLYMERISATION

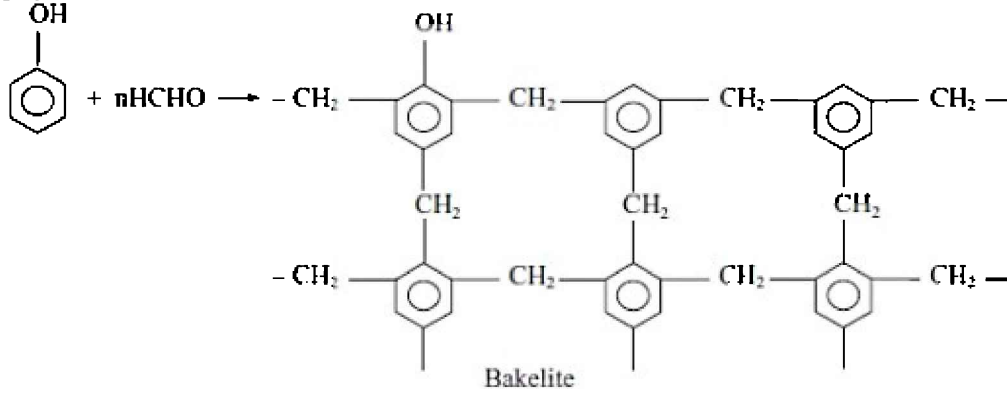
When the monomers contain some active functional groups which can react together with the elimination of some simple molecules like H_2O, HCl, etc., and result into the formation of long chains, we obtain step-growth polymers and this process is called step-growth polymerisation.

Example



Dacron (polyester)

Phenol and formaldehyde form Bakelite as given below. It is an example of cross-linked polymer



Bakelite

Cross-linked polymers are generally obtained where there is a possibility of chemical reaction at more than one point in the molecule. In the absence of such an opportunity, linear polymers are formed.

Example 6 *Equal number of molecules with M_1 = 10000 and M_2 = 100000 are mixed. Calculate the number-average and mass-average molecular mass of the polymer. Also calculate the polydispersity of the polymer sample.*

Solution: Number average molecular mass

$$\bar{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{N \times 10000 + N \times 100000}{N + N} = \frac{N \times 110000}{2N} = 55000$$

Mass-average molecular mass $\bar{M}_m = \frac{\Sigma N_1 M_1^2}{\Sigma N_1 M_1}$

$$= \frac{N \times (10000)^2 + N \times (100000)^2}{(N \times 10000) + (N \times 100000)} = \frac{10000^2 + 100000^2}{110000}$$

$$= \frac{10^8 + 10^{10}}{11 \times 10^4} = \frac{10^8 (1 + 10^2)}{11 \times 10^4} = \frac{10^4 \times 101}{11} = 0.919 \times 10^4$$

$$\text{Polydispersity index} = \frac{\text{Number-average molecular mass}}{\text{Mass-average molecular mass}}$$

$$= \frac{55 \times 10^3}{0.919 \times 10^4} = \frac{5.5 \times 10^4}{0.919 \times 10^4} = 5.98$$

Polydispersity index gives the width of molecular mass distribution.

SUMMARY

1. *Polymers* are long-chain high-molecular mass compounds obtained by the combination of a large number of simple molecules
2. Simple molecules taking part in the formation of polymers are called *monomers.*
3. The number of repeat units in the polymer chain is called *degree of polymerisation.*
4. Polymers obtained as such from natural sources are called *natural polymers,* for example, silk, wool, natural rubber, etc. Polymers prepared by synthetic methods from simple substances are called *synthetic polymers,* for example, nylon, polystyrene, etc
5. When simple molecules are linked together to form long chains without the elimination of any by-product molecules, the products formed are *addition polymers.*
6. When the monomers react with the elimination of some simple molecules to give a polymer, the product is called condensation polymer.
7. When the total molecular mass of all the molecules of a sample is divided by the total number of molecules, the result obtained is called *number average* molecular mass.
8. When the total molecular mass of group of molecules having particular molecular masses are multiplied with their respective molecular mass, the products are added and the sum is divided by the total mass of all the molecules, the result obtained is called *mass-average* molecular

mass.

9. Molecular mass of a polymer can be determined by one of the following methods:
   (a) Osmotic pressure method
   (b) Sedimentation or ultracentrifugation method
   (c) Viscosity method
   (d) Light-scattering method
10. Molecular mass of charged polymers like proteins as determined by osmotic-pressure method is considerably smaller than that determined by other methods. This is due to an electrical phenomenon known as Donnan membrane equilibrium.

KEY RELATIONS

$$\bar{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad \bar{M}_m = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

$$M = \frac{RT}{\left[\frac{P}{C}\right]_{C \to 0}} \text{ (osmoticpressure method)}$$

$$\ln \frac{x_2}{x_1} = \frac{2r^2\omega(d - d')}{a\eta}(t_2 - t_1) \quad \text{(sedimentation method)}$$

$$[\eta] = \left[\frac{\eta_{sp}}{C}\right]_{C \to 0} \text{ (viscosity method)}$$

$$\text{limit}\left[\frac{HC}{\tau}\right]_{C \to 0} = \frac{1}{M}, \quad \text{(light scattering method)}$$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. Polymers with low degree of polymerisation are called
   (a) polymers
   (b) monomers
   (c) oligomers
   (d) tetramers
2. Examples of natural polymers are

(a) silk, wool

(b) natural rubber, nylon

(c) polyethylene, polystyrene

(d) glucose, nylon

3. Which of the following are example of addition polymerisation?

(a) Hexamethylene + Adipic acid → Hexamethylene diamine

(b) Ethylene glycol + Terephthalic acid → Dacron

(c) Styrene → Polystyrene

(d) None of the above

4. Number average molecular mass is given by the formula

(a) $\bar{M}_n = \frac{\Sigma M_i}{\Sigma N_i}$

(b) $\bar{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i}$

(c) $\bar{M}_n = \frac{\Sigma N_i M_i^2}{\Sigma M_i}$

(d) $\bar{M}_n = \frac{\Sigma N_i M_i^2}{\Sigma M_i}$

5. Mass average molecular mass is given by the formula

(a) $\bar{M}_m = \frac{\Sigma N_i M_i}{\Sigma N_i M_i^2}$

(b) $\bar{M}_m = \frac{\Sigma N_i M_i^2}{\Sigma N_i}$

(c) $\bar{M}_m = \frac{\Sigma N_i M_i^2}{\Sigma M_i}$

(d) $\bar{M}_m = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$

6. Which of the following is not a method for the determination of molecular mass of a polymer?

(a) Viscosity method

(b) Sedimentation method

(c) Boiling point method

(d) Osmotic pressure method

7. Scattering of light can be used to determine the molecular mass of a polymer. The amount of light scattered depends directly on the

(a) size of particles

(b) number of particles

(c) size and number of particles

(d) size and density of particles

Answers

1. (c)
2. (a)
3. (c)
4. (b)
5. (d)
6. (c)
7. (c)

SHORT-ANSWER QUESTIONS

1. Differentiate between monomer and polymer giving examples.
2. What is meant by degree of polymerisation? What is the relation between the molecular mass of the polymer and the molecular mass of the monomeric unit?
3. Write briefly about

   (a) homopolymer

   (b) copolymer
4. Give two examples each of addition polymerisation and condensation polymerisation.
5. Give the relations for number-average molecular mass and mass-average molecular mass explaining the meaning of each symbol.
6. Draw a labelled design of an osmometer for the determination of molecular mass of a polymer.
7. What is the limitation of the sedimentation method of determination of molecular mass of a polymer? How is this difficulty overcome?
8. How is intrinsic viscosity related to specific viscosity? How is the relation between the two helpful in the determination of molecular mass of a polymer?
9. What is meant by polydispersity index of a polymer?
10. Describe the formation of bakelite from its monomers

GENERAL QUESTIONS

1. What are polymers and polymerisation? Explain with examples.
2. Differentiate between

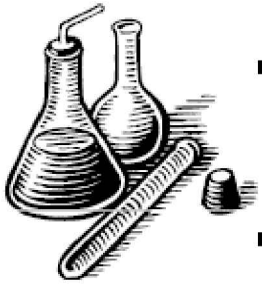
   (a) high polymers and oligopolymers

   (b) natural polymers and synthetic polymers
3. What is meant by number average and mass-average molecular masses of polymers. Derive the relations for the two types of molecular masses. Under what circumstances, the two become the same.

4. Describe the osmotic-pressure method for the determination of molecular mass of a polymer. Explain the calculation of molecular mass with the help of a graph.
5. What is sedimentation? How is this phenomenon used in the calculation of molecular mass of a polymer? What is the limitation of this method?
6. Describe the viscosity method for the determination of molecular mass of a polymer. Explain the computation of the molecular mass from the graph
7. What is the utility of scattering of light in the determination of molecular mass of a polymer?
8. Write notes on

   (a) Polydispersity

   (b) High polymers and oligomers
9. What is Donnan membrane equilibrium? Why do we obtain lower values of molecular mass of charged polymers?



Nuclear Chemistry

28

LEARNING OBJECTIVES

- Define isotopes, isobars and isotones
- Learn different methods for separation of isotopes
- Study the characteristics offundamental particles of nucleus
- Define atomic number and mass number
- Study different theories for the stability of a nucleus
- Understand the terms *binding energy* and *mass defect*
- Use Einstein mass-energy relationship
- Appreciate the importance of binding energy curve and packing fraction
- Study different methods for detection and measurement of radioactivity
- Learn the theory of radioactive disintegration
- Identify K-electron capture, neutrino and antineutrino
- Study artificial disintegration
- Learn artificial or induced radioactivity
- Learn different types of nuclear reactions
- Define Q-value of nuclear reaction
- Study nuclear fission and nuclear fusion
- Study hydrogen bomb, plutonium bomb and cobalt bomb
- Learn applications of radioactivity
- Design a nuclear reactor

28.1 | ISOTOPES

Isotopes are different atoms of the same element having the same atomic number and hence, the same chemical properties and the same position in periodic table but differing in atomic weight (mass number).

The existence of isotopes was first discovered by Soddy in 1916.

28.1.1 Representation of Isotopes

Each isotope is represented by its appropriate symbol along with its mass number at the left upper end (superscript) and the atomic number at its lower left end. Thus, three isotopes of oxygen are written as

$^{16}_{8}O$, $^{17}_{8}O$ $^{18}_{8}O$

Similarly, two isotopes of carbon of mass numbers 12 and 13 are written as $^{12}_{6}C$ and $^{13}_{6}C$ respectively.

Soddy recognised the presence of such particles which are identical in every respect, except mass and radioactive properties. They have different atomic weights but same atomic number and, therefore, occupy the same place in the periodic table.

Lead was the first nonradioactive element which was shown to exhibit isotropy. The end product of each radioactive series was found to be an isotope of lead with mass number 206 (uranium series), 207 (actinium series) and 208 (thorium series) as shown in Table 28.1. Thus, ordinary lead (At. wt. = 207.2) is merely a mixture of the three isotopes.

Table 28.1 Radioactive series

S.No	Series	Parent	Stable end Product
1.	Uranium series	$^{238}_{92}U$	$^{206}_{82}Pb$
2.	Actinium series	$^{235}_{92}U$	$^{207}_{82}Pb$
3.	Thorium series	$^{232}_{90}Th$	$^{208}_{82}Pb$

Chlorine has two isotopes with mass numbers 35 and 37. The former contains 17 protons and 18 neutrons in the nucleus while the latter contains 17 protons and 20 neutrons. The atomic number in each case is 17 and so their electronic configuration is also the same. They differ only in the number of neutrons contained in their respective nuclei. Two isotopes of chlorine are shown in Fig. 28.1.

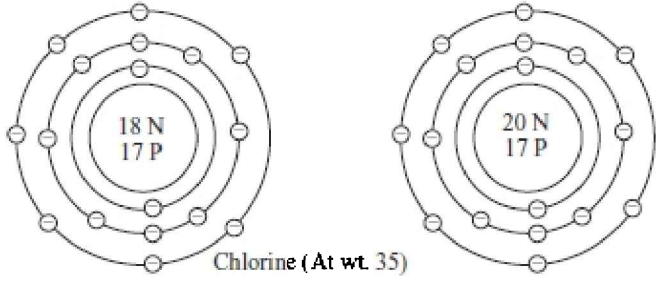


Fig. 28.1 *Isotopes of chlorine*

Similarly, hydrogen has three isotopes of mass numbers 1, 2 and 3. Isotopes of hydrogen are represented in Fig. 28.1.

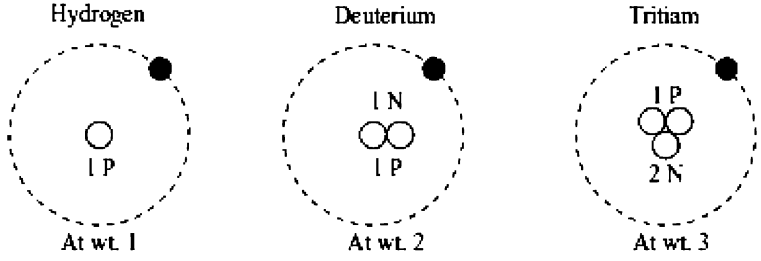


Fig. 28.2 *Isotopes of hydrogen*

1. Isobars Isobars are atoms of different elements having the same mass number but different atomic numbers. In other words, nuclei of two isobars contain the same total numbers of nucleons (protons + neutrons) but have unequal number of protons. For example, argon, potassium and calcium having atoms of the same mass number 40: $^{40}_{18}Ar$, $^{40}_{19}K$, $^{40}_{20}Ca$, where 18, 19 and 20 shown as subscripts are the atomic numbers of the three elements respectively, are isobars. Since the atomic numbers are different, their chemical properties are also different. A few more examples of isobars are given below:

(i) $^{76}_{32}Ge$ and $^{76}_{34}Se$

(ii) $^{210}_{82}Pb$, $^{210}_{83}Bi$ and $^{210}_{84}Po$

(iii) $^{228}_{88}Ra$, $^{228}_{89}Ac$ and $^{228}_{90}Th$

A radioactive element on emission of a β-particle produces an isobar.

The structures of isobars of argon $^{40}_{18}Ar$, potassium $^{40}_{19}K$ and calcium $^{40}_{20}Ca$ are given below in Fig. 28.3.

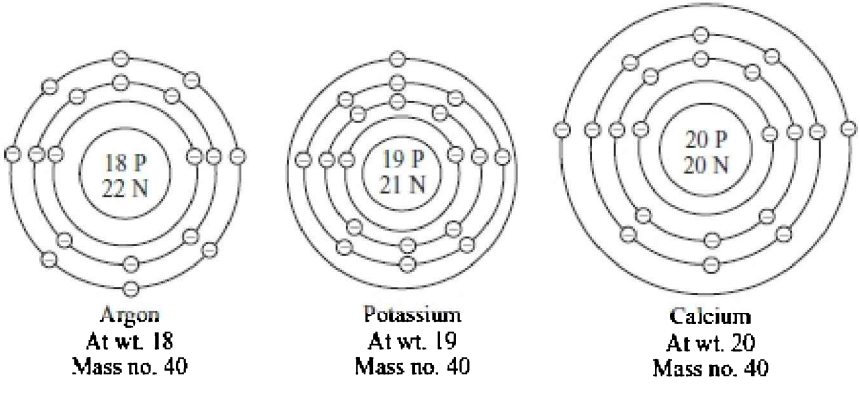


Fig. 28.3

2. Isotones Isotones are the atoms of different elements having the same number of neutrons but different atomic numbers. In other words, the atomic species possess different numbers of protons and also different mass numbers.

$^{30}_{14}Si$, $^{31}_{15}P$, $^{32}_{16}S$ are isotones since they all contain 16 neutrons. Table 28.2 shows distinction between isotopes, isobars and isotones.

Table 28.2 *Distinction between isotopes, isobars and isotones*

Atomic spaces	At. no.*Z*	Mass numbers *A*	Neutrons *N*	Examples
Isotope	Same	Different	Different	$^{35}_{17}Cl$, $^{37}_{17}Cl$
Isobar	Different	Same	Different	$^{3}_{1}H$, $^{3}_{2}He$
Isotone	Different	Different	Same	$^{2}_{1}H$, $^{3}_{2}He$

28.1.2 Methods used for Separation of Isotopes

Different methods used for isotopes separation are described as under:

1. Thermal Diffusion The method is based essentially on the principle that if two gases of different molecular masses are enclosed between two surfaces at different temperatures, the heavier gas will tend to diffuse to the cooler end and the lighter gas, towards the hotter end. This effect occurs side by side with ordinary diffusion which tends to restore the uniform concentration in the gaseous mixture.

The apparatus used in this method consists of a vertical tube about 3 metres in length and 1 cm in diameter. It is cooled by water on the outside and heated electrically on the inside by means of a platinum wire stretched axially along the tube. When a temperature gradient is set up between the wire and the cooled walls of the tube the lighter isotopic species diffuse preferentially to the hotter centre of the tube. The convection currents in the tube carry the lighter species upwards and the heavier cold species downwards (Fig. 28.4). The convection currents thus further enhance the isotopic separation. With a column of 60 metres and a temperature difference of 873 K, Clausius and Dickel accomplished an almost complete separation of Cl-35 and Cl-37.

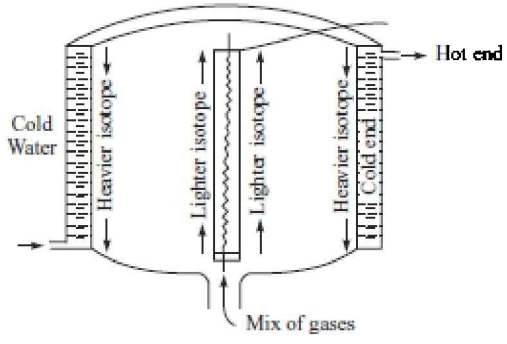


Fig. 28.4 *Thermal diffusion of gases*

2. Fractional Distillation This method of separation isotopes is based upon the difference in the vapour pressures or boiling points of liquids. The rate at which an isotope evaporates is inversely proportional to the square roots of its mass so that on fractional distillation, the ***condensate*** tends

to become richer in the higher isotopes and the residual liquid in the heavier isotopes.

Bronsted and Hevesy (1921) used this principle to partially separate the isotopes of mercury by distillation in high vacuum. The apparatus used by them is shown in Fig. 28.5.

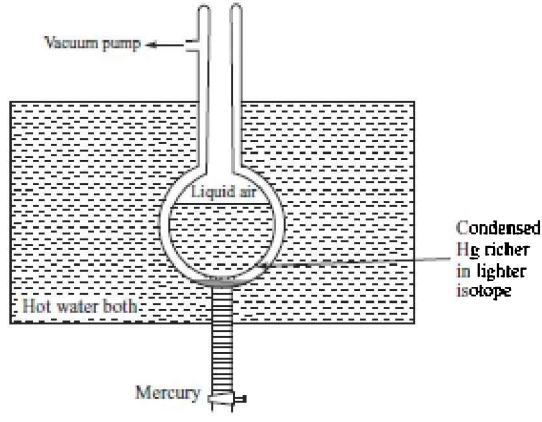


Fig. 28.5 *Apparatus for the separation of mercury isotopes*

Mercury is evaporated in partial vacuum at 313 to 333 K between the walls of a Dewar flask. The inner vessel is cooled with liquid air placed about 1 to 2 cm above mercury. The lighter isotopes evaporate preferentially and condense on the cold surface. After about one-fourth of mercury has evaporated, the condensate and residue are separated again. The condensate is melted and then partially evaporated. On repeating the process several times, a slight enrichment of the lighter isotopes of mercury occurs in the condensate and of the heavier isotopes in the liquid.

3. Chemical Exchange Method Although the chemical properties of the isotopes of an element are similar, the rate at which the reactions occurs can differ appreciably. The principle of chemical exchange has been employed for the separation of isotopes. Thus, when ammonia gas containing N^{15} isotope is bubbled upwards through a column in which ammonium nitrate solution is flowing downwards, the following exchange reaction takes place.

$$N^{15}H_3(gas) + N^{14}H_4NO_3\ (solution) \rightarrow N^{14}H_3(gas) + N^{15}H_4NO_3\ (solution)$$

An enrichment of about 70% of N^{15} has been achieved by Thode and Urey (1939) using the above exchange reaction.

4. Electromagnetic Separation The principle of mass spectrograph can be applied to large-scale separation of isotopes. The Aston mass spectrograph is used to bring about separation.

The usual photographic plate is replaced by receptacles placed in proper position to receive the streams of isotopes of the element (Fig. 28.6).

The electromagnet method is the only method which achieves 100% separation of isotopes. Appreciable amounts of U^{235} required for experiment purposes were separated electromagnetically by Nier in 1940. Nowadays we utilize this method for the separation of isotopes of a large number of elements. In all the methods of separation other than electromagnetic, a single process produces two fractions of the material with different concentrations.

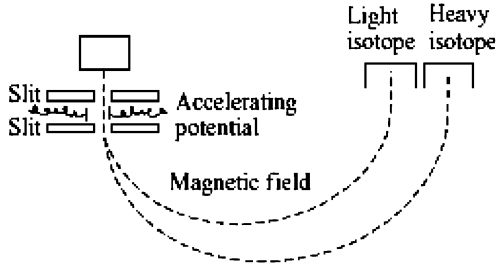


Fig. 28.6 *Mass spectrographic method separation of isotopes*

The extent to which a mixture of two isotopes may be separated in one stage of a particular process is called the separation factor. It is the ratio of the relative concentration of the desired isotopes after processing to its relative concentration before processing. If n_1 and n_2 are the numbers of light and heavy species in a mixture before processing and N_1 and N_2 are the corresponding numbers after processing in a one-stage process, the separation factor S may be represented mathematically as

$$S = \frac{N_1/N_2}{n_1/n_2}$$

The higher the value of S, the greater is the efficiency of separation. In most of the processes available for the separation of isotopes, S is only slightly greater than unity and consequently, the given process has to be carried out in several single-separation stages to achieve the desired extent of separation.

5. Centrifugal Method If a mixture of two isotopes of the same element in gaseous or liquid state is subjected to a gravitational field, the heavier isotope will tend to concentrate in the direction of the field and consequently, separation of the isotopes will occur provided there is no mixing to counteract this movement. This is the underlying principle of this method. The extent of separation in this method depends on the mass difference between two isotopes whereas in the diffusion method, it is dependent upon the square of the ratio of the masses. The separation factor is, therefore, better in the centrifugal method than in the diffusion method.

6. Gaseous Diffusion This method is applicable to gases. Two gaseous molecules of molecular masses M_1 and M_2 can be separated by gaseous diffusion (Fig. 28.7). According to Graham's law of gaseous diffusion, the rates of diffusion of the two gaseous species are given by the relation

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

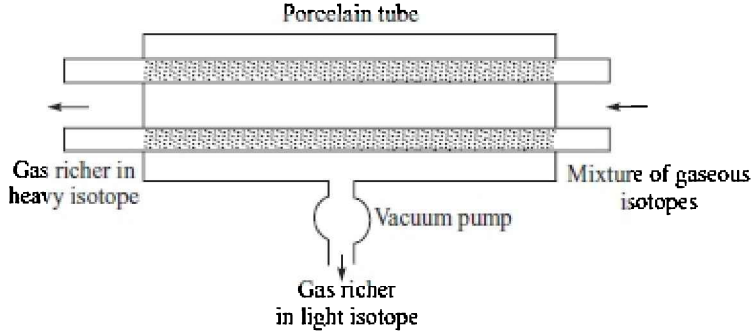


Fig. 28.7 *Apparatus for the separation of gaseous isotopes*

Applied to isotopes, this would be given by an ideal separation factor of

$$S = \sqrt{\frac{M_2}{M_1}}$$

where M_1 and M_2 are molecular masses of the two isotopes or of the compounds in which they occur. Astron used this principle first for the partial separation of isotopes of neon. Harkins applied the same principle of gaseous diffusion for separating the isotopes of chlorine from hydrogen chloride gas. After a laborious series of experiments, a slight enrichment of the heavier chlorine isotopes was achieved. Thus, chlorine of atomic mass 35.498 was obtained as compared to the normal value of 35.467. Har-kin's method of diffusion at atmospheric pressure is less effective in the separation of isotopes than the method of diffusion at low pressure first applied successfully by Hertz. Hertz also introduced the cascade system (many successive diffusion stages) with a view to further improve the rate of separation.

7. Electrolytic Method Urey and Washburn (1932) observed that the residual water becomes enriched in the heavier isotopes on continuous electrolysis of water. Lewis and co-workers succeeded in preparing about 1 cc of water containing only heavier isotopes of hydrogen of mass 2 by continuous electrolysis of a large amount of water using an old commercial electrolytic cell. The electrolytic production of O^{18} and D_2O are now carried out commercially where electric power is cheap. The electrolytic method has not been very successful in separating the isotopes of the elements other than hydrogen.

Size of the Nucleus vs that of the Atom

Rutherford calculated that the nucleus of an atom has effective diameter of 10^{-15} m whereas the diameter of an atom itself is about 10^{-10} m. It follows that the diameter of a nucleus is approximately $\frac{10^{-15}}{10^{-10}}$, i.e. 10^{-5} or $\frac{1}{10,000}$ of the diameter of an atom.

28.2 FUNDAMENTAL PARTICLES OF THE NUCLEUS

The most important particles of the nucleus are the proton which has +1 charge and mass of

1.00758 a.m.u. and the neutron which has zero charge and mass of 1.00893 a.m.u. The nuclear constituents are known collectively as ***nucleons.*** There are a number of other fundamental particles such as electron, anti-proton, positron (all mass particles) and neutrino, photons and gravitation (energy particles) which are stable. Their characteristics are given in Table 28.3. Among unstable fundamental particles are mesons and V-particles besides neutrons. They are listed in Table 28.4.

Table 28.3 Characteristics ofcertain stable fundamental particles

Particles	Symbol	Charge	Mass (a.m.u.)
Proton	P_1, H^1	+	1.00758
Electron	e^-, β^-	−	0.0005486
Positron	e^+, β^+	+	0.0005486
Anti-proton	P^-	−	1.00758
Neutrino	ν	0	< 0.00002
Photon	γ	0	0
Gravitation	G	0	0

Table 28.4 Characteristics ofcertain unstable fundamental particles

Particles	Symbol	Charge	Mass a.m.u.
Neutron	*n*, on′	0	1.00893
Negative mu meson	μ^-	−	0.1152
Positive mu meson	μ^+	+	0.1152
Negative Pi meson	π^-	−	0.1514
Positive Pi meson	π^+	+	0.1514
Neutral Pi meson	π°	0	0.1454
Tau meson	τ	±	0.5349
Kappa meson	κ	±	0.6035
Zeta meson	ζ	±	0.3018
Negative Chi meson	χ	−	0.7680

Positive Chi meson	χ	+	0.7680
Negative V-particle	V^-	−	1.2069
Positive V-particle	V^+	+	1.2069
Neutral V-particle	V^0_1	0	1.2014
Neutral V-particle	V^0_2	0	0.4643

28.2.1 Atomic Number and Mass Number

(a) Atomic Number It is the number of protons in the nucleus of an atom.

(b) Mass Number It is the sum of the number of protons and neutrons in the nucleus of an atom.

Z = Number of protons in the nucleus
= Atomic number

A = Total number of nucleons, i.e. protons and neutrons
= Mass number

N = Number of neutrons in the nucleus = $A - Z$

Mass number A is an integer with a value close to the atomic mass.

Thus, a nuclide is a nucleus containing a particular number of neutrons and protons. The total number of protons and neutrons together represent the mass of the nuclide and is known as mass number.

Mass number = No. of Protons + No. of neutrons

Example 1 *The average mass of chlorine is 35.5. The mass numbers of two isotopes are 35 and 37. Give the proportion in which two isotopes are present in ordinary chlorine.*

Solution: Let the proportion of Cl-35 and Cl-37 be 1: x

Then the average atomic mass would be

$$= \frac{(35 \times 1) + (37 \times x)}{1 + x}$$

But this is given to be 35.5

Hence,
$$\frac{(35 \times 1) + (37 \times x)}{1 + x} = 35.5 \quad \text{or} \quad \frac{35 + 37x}{1 + x} = 35.5$$

$$35 + 37x = 35.5\,(1 + x)$$

$$35 + 37x = 35.5 + 35.5x \quad \text{or} \quad 1.5x = 0.5 \quad \text{or} \quad x = 1/3$$

Therefore, the ratio is 1 : 1/3 or 3 : 1

28.2.2 Meson Theory of Stability of Nucleus

Protons have positive charge. In any nucleus containing two or more protons, there will be electrostatic repulsion between the like charges. In a stable nucleus, the attractive forces are greater than the repulsive forces. In an unstable nucleus, the repulsive forces exceed the attractive forces and spontaneous fission occurs.

The first successful attempt for explaining the nuclear forces was made by Yukawa of Japan in 1935. He put forward his ***meson theory*** and postulated the existence of a nuclear particle π-meson (called pion) which acts as a glue binding the protons and neutrons together in the nucleus. The π-meson may be positive (π^+) negative (π^-) or neutral (π°). The charged π-meson has a mass 273 times that of an electron and a charge of +1 or −1. These mesons hold the protons

and neutrons together by continuously exchanging positions between neutrons and protons in the nucleus. Exchange of π^- –and π^+-meson accounts for binding energy between neutrons and protons. Thus, a proton would release a π^+-meson and would become a neutron, whereas a neutron would release a –ve π-meson and become a proton or vice versa. This exchange process is represented by

$$p \rightleftharpoons n + \pi^{+1}$$

Proton neutron

and

$$n \rightleftharpoons p + \pi^-$$

The exchange of π meson between neutrons and protons occurs at the rate of 10^{24} transfers/second.

This concept of exchange force is similar to the exchange forces resulting in the formation of a covalent bond.

The neutral π-meson is an uncharged particle with a mass 264 times that of an electron. The binding force between like particles, i.e. exchange of neutron-neutron *(n-n)* and proton-proton *(p-p)* involves neutral π-mesons. The exchange reaction involving neutral π mesons are shown below:

$$p \rightleftharpoons p + \pi^0$$

$$n \rightleftharpoons n + \pi^0$$

Thus, the two protons and two neutrons are held together by the exchange of π°.

The attractive force between *p-n*, *n-n* and *p-p* are probably all similar in strength. The continual transfer of mesons means that the particles representing neutrons and protons are constantly changing. The transformation of neutrons into protons and vice versa are first-order reactions. The rates of the reactions depend on the relative numbers of neutrons and protons present. In a stable nucleus, these two changes are in equilibrium.

28.2.3 n/p Ratio for Stability of Nucleus and Zone of Stability

The stability of the nucleus depends on the number of protons and neutrons present. Nuclei with even number of protons and even number of neutrons seem to be particularly stable.

Light elements up to atomic number 20 form most stable nuclei when the number of protons *p* in the nucleus is equal to the number of neutrons n, i.e. *n/p* = 1. However, as the nuclear charge exceeds 20, the ratio *n/p* for stability exceeds unity. In such a case, the number of neutrons is greater than that of protons. With increase in the number of protons, the force of repulsion between them increases and this tends to lower the stability of nucleus. The force of repulsion can be diminished to some extent if the number of neutrons is more.

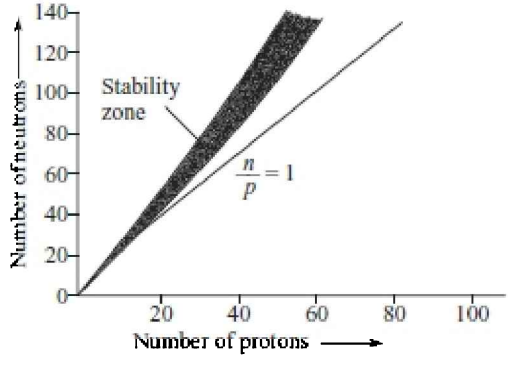


Fig. 28.8 *The relation between number of neutrons and protons in stable nuclei.*

This would increase the size of the nucleus and hence, the proton would lie farther apart and suffer from smaller repulsion.

As the value of *n/p* increases beyond 1.6, i.e. beyond atomic number 92, the nuclei become so large that they undergo spontaneous fission.

The variation in the number of neutrons with number of protons in stable non-radioactive nuclei is shown in Fig. 28.8. The stable nuclei lie within the shaded area which is called the ***zone of stability.*** Nuclei that lies outside the zone of stability will, therefore, be unstable. Nuclei that fall above the stability zone have more neutrons while those lying below have more protons. Both these situations cause instability. Such nuclei would attain stability by undergoing change that would produce a nucleus with *n* to *p* ratio within the stability zone. Two cases arise depending on the *n/p* ratio of nuclei.

1. ***A nucleus that possesses a higher n/p ratio would involve a decrease of neutrons, an increase of proton or a simultaneous alteration of both particles to attain stability.***
2. ***A nucleus that possesses a lower n/p ratio would achieve stability by an increase of neutrons or decrease of protons or both simultaneously.***

The nuclei of radioactive elements lie above and below the zone of stability (also known as stability belt). Hence, they undergo spontaneous disintegration to emit α-and β-particles. Loss of each α-particles is equivalent to loss of two protons and two neutrons and loss of each β-particle is equivalent to increase of one proton and decrease of one neutron.

28.2.4 Liquid Drop Moded (LDM) to Explain Stability of Nucleus

This model introduced by Niels Bohr is based on the following assumptions.

1. ***Nucleus is like a droplet of incompressible and homogeneous liquid and all nuclei have the same density.***
2. ***Attraction within nucleus is strong.***
3. ***Nuclear force is independent of spin and charge, i.e. there is no difference in the magnitude of the force between n-n, p-p and n-p.***
4. ***Nucleus force has a short range character and is effective between nearest neighbours. The nucleus is described in terms ofa liquid drop. A small liquid drop is almost spherical. It is held together by short-range forces, i.e. the attraction between neighbours. Molecules at the edge of a drop feel the attractive force on one side only which is known as the surface tension effect. A large liquid drop feels the attractive force on one side only which is known as the surface-tension effect. A large liquid drop becomes elongated and with a little disturbance, breaks into pieces.***

In a similar way, a nucleus is held together by short range forces (the exchange of π-mesons). The surface-tension effect ensures that small nuclei are spherical. As the mass of nucleus increases, the repulsion between protons increases more rapidly than the attractive forces. To minimise the repulsive force, the shape of the nucleus is deformed just like the elongation of a large liquid drop. The two ends of the drop will have positive charge leading to a dumb-bell shaped structure, finally breaking into two parts as shown in Fig. 28.9.



Fig. 28.9 *Liquid drop model.*

Nuclear fission of heavy nuclei can be explained by taking the example of uranium. Uranium (Z-92) of mass number 235. $^{235}_{92}U$ is so deformed that the addition of a little extra energy by absorption of a neutron causes the nucleus to break into two smaller nuclei (nuclear fission) with a release of large amount of energy. Nuclei with mass numbers larger than that of uranium are so deformed that they undergo spontaneous fission. This means that the nuclei disintegrate (break up on their own) without any external perturbation.

The density of all nuclei except the very light is almost constant; thus the volume of nucleus is directly proportional to the number of nucleons present.

28.2.5 Shell Model to Explain Stability of Nucleus

Nuclear shell model is based on the assumption that each nucleon moves independently in an average potential generated by the remaining nucleons.

This means that the interaction among the nucleons is weak so that mean free path of nucleons is larger than the nuclear dimension. In other words, nucleons move inside the nucleus without any collision. This goes against the assumption of LDM that interactions among nucleons are strong so that mean free path of the nucleons is smaller than the nuclear dimension.

The electrons are arranged in different shells and orbitals which may be described by four quantum numbers. The nucleons are similarly thought to be arranged in shells, corresponding to different energy levels. When the nucleons occupy the lowest energy levels, this corresponds to the ground state. Under different conditions, the nucleons may occupy different (higher or excited) energy levels. Usually, the population of these higher nuclear energy ***levels*** is so short-lived that it cannot be observed. Thus, the properties of the nucleus depend only on the number of neutrons and protons and not on the energy levels they occupy.

In a few cases, the excited nuclear states have a measurable life and when this occurs, nuclear isomers are said to be exist. Nuclear isomers are simple nuclei with the same number of neutrons and protons but whose energies differ. It follows that the masses of the isomers differ by a very small amount corresponding to the difference in energy. Many nuclei are unstable even when they correspond to the ground state. Unstable nuclei decompose by emitting various particles and electromagnetic radiations and this is called radioactive decay. Over 1,500 unstable nuclei are known. If no radioactive decomposition can be detected, the nucleus is said to be stable.

The shell model is supported by a periodicity in nuclear properties. Certain combinations of neutrons and protons are particularly stable.

1. ***Elements of even atomic numbers are more stable and more abundant than neighbouring elements of odd atomic number.*** This is known as Harkin's rule. The rule applies almost universally but H is an exception.
2. ***Elements of even atomic numbers are richer in isotopes and never have less than three stable isotopes. Elements with odd atomic numbers often have only one stable isotope and never have more than two.***
3. ***There is a tendency for the number of neutrons and the number of protons in the nucleus to be even.***

This suggests that nucleons may be paired in the nucleus analogous to the pairing of electrons in atomic and molecular orbitals. If two protons spin in opposite directions, the magnetic fields they produce will mutually cancel each other and develop attractive forces. The small amount of binding energy thus generated is sufficient to stabilise the nucleus. However, this is not the most important source of energy in the nucleus.

This model gains acceptability because we find that certain nuclei are extra stable and this is attributable to a filled shell. Nuclei with 2, 8, 20, 28, 50, 82 or 126 neutrons or protons are particularly stable and have a large number of isotopes. These numbers are termed ***magic numbers.*** The numbers 114, 164 and 184 should also be included in the series of magic numbers. When both the number of protons and the number of neutrons are ***magic numbers,*** the nucleus is very stable, for example, Pb is very stable and has 82 protons, and 208 − 82 = 126 neutrons. The

emission of y-rays by the nucleus is readily explained by the shell model. If nucleons in an excited state fall to a lower nuclear energy level, they will emit energy as γ-rays.

28.2.6 Binding Energy and Mass Defect

1. Binding Energy When a nucleus is formed from its constituent protons and neutrons, a large amount of energy is released. This energy is equal in magnitude to the binding energy of the nucleus, since the binding energy is defined as the 'energy required to break up a nucleus into its individual nucleons, i.e. its protons and neutrons.

2. Mass Defect The mass atomic nucleus is always less than the combined masses of the protons and the neutrons from which it is formed. The difference is called the mass defect. The mass defect is related to the binding energy holding the neutrons and protons together in the nucleus. The energy equivalent to the loss in mass is known as the binding energy of the nucleus.

Helium nucleus consists of two protons and two neutrons. It is found that the mass of helium is smaller than the combined mass of two protons and two neutrons by an amount δm where δm is the mass defect. δm can be calculated by substituting the masses of the helium nuclei, protons and neutrons. Binding energy can be obtained by using the relationship

$$E = (\Delta m) \times c^2$$

where c is the velocity of light.

3. Einstein's Mass-Energy Relation Einstein in 1905 proposed that mass can be converted into energy and the mass-energy equivalence is given by the relation

$$E = mc^2$$

where E is energy in ergs, m is the decrease in mass of a body in grams and c is the velocity of light 2.9979×10^{10} cm/s. Thus, loss of mass results in the liberation of energy. Since the velocity of light has a very high value, a small amount of mass can be converted into a large amount of energy.

The energy equivalent of 1 g of matter

$$E = 1 \times (2.9979 \times 10^{10})^2 = 8.9874 \times 10^{20} \text{ ergs}$$
$$= 8.9874 \times 10^{20} \times 10^{-7} \text{ Joules} = 8.9874 \times 10^{13} \text{ Joules}$$

Nuclear energies are generally expressed in million electronvolts (mega electronvolts) (MeV)

$$1 \text{ MeV} = 1.6022 \times 10^{-6} \text{ ergs, hence for}$$

$$1 \text{ g of matter } E = \frac{8.9874 \times 10^{20}}{1.6022 \times 10^{-6}} = 5.6094 \times 10^{26} \text{ MeV}$$

Atomic mass unit (a.m.u.) is another unit of mass and energy which is frequently used in nuclear science. 1 a.m.u. is equal to twelfth of the mass of the C^{12} atom. On this scale,

$$1 \text{ a.m.u.} = 1.6606 \times 10^{-24} \text{ g}$$
$$E = (1.6606 \times 10^{-24})(2.9979 \times 10^{10})^2 \text{ ergs} = 1.4924 \times 10^{-3} \text{ ergs}$$
$$= \frac{1.4924 \times 10^{-3}}{1.6022 \times 10^{-6}} = 931.14692 \text{ MeV} = 931.5 \text{ MeV}$$

Points to Remember

1. 1 standard a.m.u. = 1.6606×10^{-24} g = 1.6606×10^{-27} kg or 1 a.m.u. = 931.5 MeV and 1 eV = 1.6022×10^{-12} ergs
2. 10^{-7} ergs = 1 Joule

3. 1 MeV = 1.6022×10^{-13} J = 1.6022×10^{-6} ergs

4. $E_{(\text{in MeV})} = 931.5 \times \delta m$(mass in a.m.u.)

5. E(in ergs) = m(gram) × c^2(cm/sec)

6. 1 eV = 1.6022×10^{-19} Joule

7. $c = 2.9979 \times 10^{10}$ cm/sec = 2.9979×10^{8} m/sec

Example 2 *Masses of* ${}^{7}_{3}Li$, ${}^{6}_{3}Li$ *and* ${}^{1}_{0}n$ *are 7.016, 6.0151 and 1.0087 a.m.u. respectively. Calculate the binding energy of neutron in* ${}^{7}_{3}Li$ *in MeV.*

Solution ${}^{6}_{3}\text{Li} + {}^{1}_{0}\text{n} \rightarrow {}^{7}_{3}\text{Li}$

Mass of ${}^{6}_{3}\text{Li}$ = 6.0151 a.m.u. Mass of ${}^{1}_{0}n$ = 1.0087 a.m.u.

Total mass = 6.0151 + 1.0087 = 7.0238 a.m.u.

But mass of ${}^{7}_{3}\text{Li}$ = 7.016 a.m.u.

$$\Delta m = 7.0238 - 7.0160 = 0.0078 \text{ a.m.u.}$$

$$E = \Delta m \times 931.5 = 0.0078 \times 931.5 = 7.2657 \text{ MeV}$$

Example 3 *Calculate the mass defect and the binding energy of the helium nucleus having a mass of 4.0039 a.m.u. given that masses of proton and neutron are 1.00758 and 1.00893 a.m.u. respectively.*

Solution: Since the helium nucleus is formed from 2 neutrons and 2 protons,

$\therefore$ Δm or mass defect $= [2(1.00758) + 2(1.00893) - 4.0039]$

$= 0.02912$ a.m.u.

or $= (0.02912 \times 1.6606 \times 10^{-24})$ g

Binding energy $E = \Delta mc^2 = (0.02912 \times 1.6606 \times 10^{-24}) \times (2.9979 \times 10^{10})^2$

where 2.9979×10^{10} cm/s is velocity of light.

$$= 4.3460 \times 10^{-5} \text{ ergs}$$

$$1 \text{ MeV} = 1.6022 \times 10^{-6} \text{ ergs}$$

$\therefore$ $$E = \frac{4.3460 \times 10^{-5}}{1.6022 \times 10^{-6}} = 27.13 \text{ MeV}$$

Alternatively, binding energy can be calculated by multiplying the mass defect in a.m.u. by 931.5 to obtain E in MeV.

Binding energy per nucleon = 27.13/4 = 6.78 MeV

Example 4 *Calculate the binding energy per nucleon of* ${}^{16}_{8}O$.

Given mass of ${}^{16}_{8}O$ *= 15.9949 a.m.u.*

Mass of ${}^{1}_{1}H$ *=1.007825 a.m.u. Mass of* ${}^{1}_{0}n$ *=1.008665 a.m.u.*

Solution:

Mass of 1 proton + 1 electron – mass of $_1H$ atom – 1.007825 a.m.u. (Neglecting the mass of electron)

Mass of 8 protons + 8 electrons $= 8 \times 1.007825 = 8.0626$ a.m.u.

Mass of 8 neutrons $= 8 \times 1.008665 = 8.069320$ a.m.u.

Total mass of $8p + 8e + 8n = 8.06260 + 8.06932 = 16.13192$ a.m.u.

Actual mass of $O_8^{16} = 15.9949$ a.m.u.

$\Delta m = 16.13192 - 15.9949 = 0.13702$

Binding energy $E = \Delta m \times 931.5$ MeV

$= 0.13702 \times 931.5 = 127.63$ MeV

Binding energy per nucleon $= \dfrac{127.63}{16} = 7.977$

Example 5 *Calculate the binding energy of an a-particle. Express the result in MeV.*

Mass of proton = 1.0078 a.m.u.

Mass of neutron = 1.0089 a.m.u.

Mass of α-particle = 4.0084 a.m.u.

Solution: Mass of 2 protons and 2 neutrons

$= 2 \times 1.0078 + 2 \times 1.0089 = 4.0334$ a.m.u.

Mass of α-particle = 4.0084 a.m.u.

Loss of mass = 4.0334 − 4.0084 = 0.0250 a.m.u.

∴ Binding energy = 0.0250 × 931.5 = 23.288

4. Importance of Binding Energy Curve More important than the total binding energy is the energy per nucleon *E/A* which is plotted in Fig. 28.10 against mass number *A*. Binding energy per nucleon is known as ***mean binding energy.***

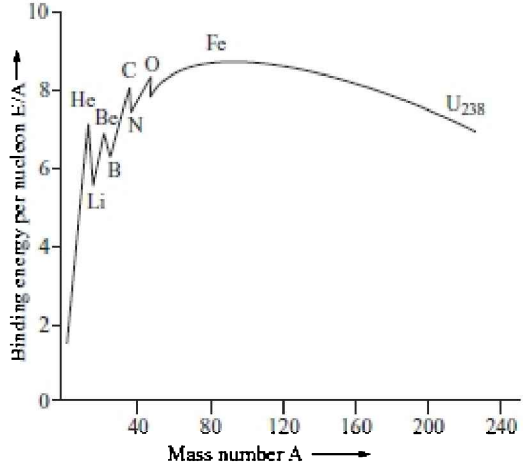


Fig. 28.10 *Variation of binding energy nucleon with mass number.*

Mean binding energy is helpful to compare the stability of nuclei of different elements. Except for fluctuation at the lower mass numbers, the binding energy increases with *A*, goes through a maximum at *A* = 60 and then decreases. Thus, nuclei of maximum stability have mass

numbers of about 60. The elements with low or high mass numbers become more stable by acquiring mass number of about 60. Because of the maximum in the binding energy per particle that occurs near mass number 60, the fission of a very heavy nucleus to a pair of nuclei of mass number approximately 60 is a process that releases energy. Similarly, the fusion of two of the lighter nuclei is also accompanied by release of energy.

5. Packing Fraction With the use of mass spectrograph, very precise determination of atomic masses becomes possible. Astron found that in most cases there was a slight deviation from the whole number for the mass of an isotope. The nearest integral number, called the mass number, is indeed the sum total of the numbers of neutrons and protons. The deviation from the whole number varies from nucleus to nucleus and Astron expressed it in terms of packing fraction which is defined as.

$$\text{Packing fraction} = \frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

The packing fraction thus indicates average mass gain or loss per nucleon for the isotope in question as compared with the condition existing in the O^{16} nucleus. Packing fractions are numerically of the order of magnitude of 10^{-4} and are customarily multiplied by 10^{14}.

A negative value of the packing fractions means the isotopic mass less than the nearest integer, i.e. nearest whole number. It means that some of the mass has been converted into energy in the formation of that particular nucleus. Such nuclei, therefore, would be stable. For example, in case of isotopes of chlorine, the isotopic mass is 34.980 whereas the mass number is 35. Hence,

$$\text{Packing fraction} = \frac{34.980 - 35}{35} \times 10^4 = -57$$

But a positive value of packing fraction shows that the resulting nucleus has a tendency towards instability. However, it is not strictly correct, particularly for those elements having small atomic masses. This is due to the fact that the masses of the protons and neutrons of which the nuclei are composed are shown as greater than unity. In general, the lower the packing fraction of an element, the greater is the stability of the nucleus.

When the packing fractions of different elements are plotted against their mass numbers, the packing fractions nearly fall on or are very close to the curve as shown in Fig. 28.11.

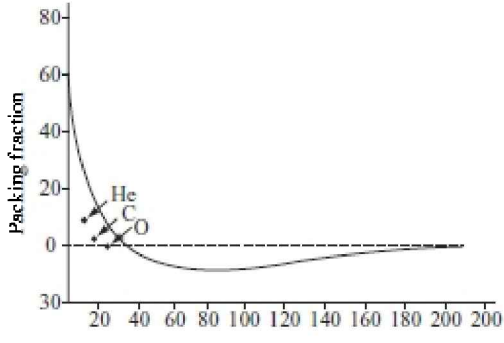


Fig. 28.11 *Plot of mass number vs. packing fraction*

Only He (4), carbon (12) and oxygen (16) show some departure from the general behaviour. It is seen that the transition elements between chromium and zinc have the lowest values of packing fractions, thereby indicating maximum stabilities of their nuclei. With elements of mass numbers more than 200, the packing fraction increases considerably and their nuclei, therefore, become more and more unstable. This agrees with the occurrence of spontaneous radioactive disintegration among such elements.

Henri Becquerel discovered that photographic plates wrapped in black paper that had been placed near uranium salts were fogged or blackened. He explained that the fogging was caused by radiations emanating from the uranium salts. Subsequently, it was shown that radiations are similar to *X*-rays, can ionise air, are emitted from the elements as well as their salts and are not affected by temperature or sources of uranium. This spontaneous emission of radiations by an element naturally without any external aid is called ***natural radioactivity.*** The elements which exhibit this behaviour are known as ***radioactive elements.***

28.3.1 Methods for Detection and Measurement of Radioactivity

The radioactivity of a substance can be detected and measured by the ionisation of gases caused by alpha and beta particles and also indirectly by gamma rays. Some methods commonly used are described below:

1. Wilson Cloud Chamber Method The apparatus consist of a chamber with a glass window and is closed by a movable piston (Fig. 28.12). It is filled with dust-free air and water vapour at saturation pressure. The piston is moved up to bring about cooling by sudden expansion. This causes condensation of water vapour in the form of extremely minute droplets. If alpha or beta particles from the radioactive source enter the cylinder at this stage through the window, the water droplets condense on them and the path can be photographed. This leads to the detection of alpha and beta particles.

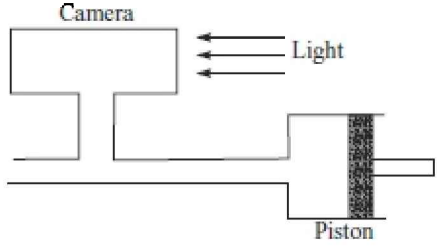


Fig. 28.12 *Wilson cloud chamber*

2. Scintillation Counter The high-energy particles are allowed to fall on a screen coated with zinc sulphide containing a trace of thallium. Each optical flash activates an electrically powered photoelectric cell and this arrangement can record radiations up to a million per second (Fig. 28.13).

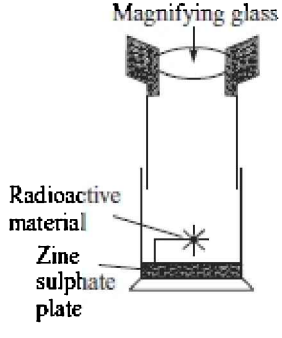


Fig. 28.13 *Scintillationcounter*

3. Geiger-Muller Counter The instrument consists of a copper cylinder closed with a thin quartz window at one end. The cylinder is fitted with a thin metal rod along its axis and insulated from the cylinder (Fig. 28.14). The cylinder is fitted with an ionisable gas such as oxygen or argon at a low pressure. A high potential of 1000 volts is applied between the rod (anode) and the other tube (cathode). When high-energy α and β-particles enter the metallic cylindrical tube through the quartz window, they produce enough ions to cause a pulse of a current to flow between the rod and the tube. The pulse can be amplified and recorded on a current meter.

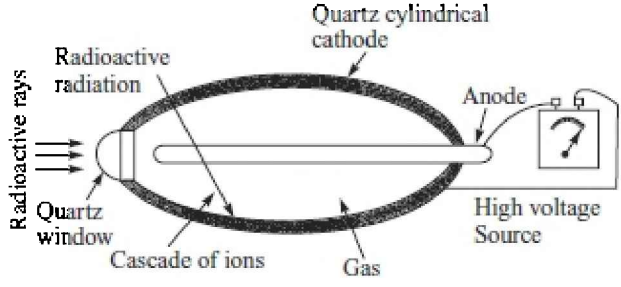


Fig. 28.14 *Geiger-Muller counter.*

4. Units of Radioactivity The standard unit of radioactivity is ***curie.***

A curie is a quantity of radioactive material decaying at the same rate as 1 g of radium (3.7×10^{10} disintegrations per second). Rutherford has been used as a unit for quite some time.

$$1 \text{ rutherford} = 10^6 \text{ dps (disintegrations per second)}$$

The SI unit of radioactivity is becquerel (after the name of the discoverer of radioactivity, Becquerel)

$$1 \text{ Bq} = 1 \text{ dps}$$

The relation between rutherford and becquerel units is

$$1 \text{ Rutherford} = 10^6 \text{ Bq}$$

Thus, the rutherford unit is a much bigger unit than the becquerel unit.



Fig. 28.15 *Marie Curie was a Polish and naturalised French physicist and chemist famous for pioneering research work on radioactivity. She discovered radium and polonium.*



Fig. 28.16 *Henri Becquerel was a French physicist, Nobel laureate along with Marie Curie and Pierre Curie (husband of Marie Curie) for which all the three won the 1903 Nobel Prize.*

28.3.2 Theory of Radioactive Disintegration

Various points of theory of disintegration are given below:

1. Radioactivity is the property of the nucleus of an atom.
2. Radioactivity elements possess unstable nucleus.
3. The unstable nuclei of radioactive elements undergo a process of disintegration.
4. During disintegration, the unstable nucleus of a radioactive atom gives α, or β-particles and a product which is the nucleus of another element. The new element formed as a result of the radioactive process is different in physical as well as chemical properties from its parent element. Thus, radium with atomic number 88 and mass number 226, which can be written as $^{226}_{88}Ra$, breaks to give an α-particle and the new element radon with atomic number 86 and mass number 222. The change can be written as
$$^{226}_{88}Ra \longrightarrow {}^{4}_{2}He + {}^{222}_{86}Rn$$
5. If the new element formed is unstable then it will also emit α-or β-particles with the production of another element. This succession of transformation will go on till a stable product is formed.
6. γ-rays are secondary effects of radioactive disintegration.

To understand the nature of products that will be formed, let us consider the following cases.

Case I If the *n/p* ratio for a nucleus lies above the stability belt, it means that it contains too many neutrons as compared to protons (high *n/p* ratio). In order to attain stability, this ratio must be lowered. It can be achieved by the emission of a β-particle in which one neutron will be changed to proton and the *n/p* ratio will come closer to the stability belt. For example,

$$^{1}_{0}n \longrightarrow {}^{1}_{1}P + {}^{0}_{-1}e + V \text{ (neutrino)}$$

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e + V \text{ (neutrino)}$$

In the above process, a β-particle is emitted by C^{14} and consequently, *n/p* ratio falls.

Case II If the *n/p* ratio for a nucleus lies below the stability belt, it means that it contains too many protons in comparison to neutrons (low *n/p* ratio). In order to come nearer to the stability

belt, this ratio must be increased. It can be achieved by the emission of a positron which converts a proton into a neutron.

$$^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}^{0}_{1}e + V^{-} \text{ (anti-neutrino)}$$

$$^{11}_{6}C \longrightarrow {}^{11}_{5}Be + {}^{0}_{1}e + V^{-} \text{ (anti-neutrino)}$$

In this process, a positron is emitted by C^{11} and hence, the ratio of *n/p* rises.

In cases where *n/p* ratio is low, the nuclear stability may be achieved in yet another way, viz. by the entry of an orbital electron into the nucleus. In this process, which is usually called an ***orbital electron capture or K-electron capture,*** a proton is converted into a neutron.

$$^{1}_{1}p + {}^{0}_{-1}e \rightarrow {}^{1}_{0}n$$

Here, the net change is the same as in a positron decay. This electron capture is not common but occurs in nuclei where the *n/p* ratio is low and the nucleus has insufficient energy for positron emission. Some typical examples are

$$^{7}_{4}Be + {}^{0}_{-1}e \longrightarrow {}^{7}_{3}Li$$

$$^{40}_{19}K + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}Ar$$

28.3.3 Rate of Radioactive Disintegration

Let the number of atoms of radioactive substance at the beginning = N_o

Number of atoms left after the time $t = N$

Rate of reaction (disintegration) $\propto N$

or $$\frac{dN}{dt} \propto N \quad \text{or} \quad \frac{dN}{dt} = \lambda N \qquad \ldots(28.1)$$

where λ = Disintegration constant

Equation (28.1) may be written as

$$\frac{dN}{N} = \lambda dt \qquad \ldots(28.2)$$

Integrating Eq. (28.2), we get

$$-\ln N = \lambda t + C \qquad \ldots(28.3)$$

where C is the constant of integration

when $t = 0$, $N = N_0$,

substituting in Eq. (28.3),

$$-\ln N_0 = C$$

Substituting the value of C in Eq. (28.3)

$$-\ln N = \lambda t - \ln N_0 \quad \text{or} \quad \lambda t = \ln N_0 - \ln N$$

or $$\lambda t = \ln \frac{N_0}{N} \quad \text{or} \quad \lambda = \frac{1}{t} \ln \frac{N_0}{N}$$

Converting natural log (ln) into log to the base 10, we get

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

This equation is called radioactive disintegration.

1. Half Life of a Radioactive Element Half-life of a radioactive element, represented by $t_{1/2}$ or $t_{0.5}$ is the time required for the disintegration of one half of the original amount.

At $t = t_{0.5}$, the disintegration equation can be written as

$$\lambda = \frac{2.303}{t_{0.5}} \log \frac{N}{N/2} \quad \text{or} \quad \lambda = \frac{2.303}{t_{0.5}} \log 2$$

or $$\lambda = \frac{2.303}{t_{0.5}} \times 0.3010 \quad \text{or} \quad \lambda = \frac{0.693}{t_{0.5}} \quad \text{or} \quad t_{0.5} = \frac{0.693}{\lambda}$$

2. Average Life of a Radioactive Element It will be found from the disintegration rate equation

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

that the whole of the radioactive material will never disintegrate theoretically. Thus, it is meaningless to talk about decay period.

Therefore, a term ***average life*** has been introduced. It is the reciprocal of disintegration constant.

$$\lambda = \frac{0.693}{t_{0.5}} \quad \text{or} \quad \frac{1}{\lambda} = \frac{t_{0.5}}{0.693}$$

or $$\text{Average life} \left(= \frac{1}{\lambda} \right) = \frac{t_{0.5}}{0.693} = 1.44\, t_{0.5}$$

3. K-electron Capture, Neutrino, Anti-neutrino

(a) K-electron Capture When an electron from the nearest orbital, i.e. *K*-shell orbital is absorbed by the nucleus to convert a proton into a neutron without emitting any particle, the process is known as an orbital electron capture. Since it is most usually a *K*-electron which is captured by the nucleus, the process is also known as *K*-electron capture. Usually, an electron from higher energy level L, M, N, etc., drops back to fill the vacancy in *K*-shell.

(b) Neutrino This elementary particle explains the conservation of angular momentum in β-decay and is postulated to balance the spin. It has zero charge and almost zero mass. It is represented as *V*.

(c) Anti-neutrino The existence of an anti-neutrino *(V)* was also postulated to balance the spin and to distinguish between β^- ($^0_{-1}e$) and β^+ ($^0_{+1}e$) decay. It was further suggested that neutrino *(V)* and anti-neutrino ($\bar{V}$) have relationship of the type existing between an electron and a positron.

Radioactive Equilibrium Consider a radioactive substance (A) (parent) which breaks down to give a second element B (daughter) which in turn disintegrates to give a third one C.

$$A \longrightarrow B \longrightarrow C$$

B is said to be in radioactive equilibrium with *A* when its decay is exactly compensated by its production from *A*. When the equilibrium is reached, the amount of *B* remains constant because it is being formed and disintegrated at the same rule. It is also called steady state. If K_1 and K_2 represent the disintegration constants of *A* and *B*; N_1 and N_2, are the number of atoms of radioactive elements (parent and daughter) present, then at equilibrium, the rate of formation of the daughter from its parent is equal to its own rate of disintegration

$$\left[\frac{dn}{dt}\right]_{\text{parent}} = \left[\frac{dn}{dt}\right]_{\text{daughter}}$$

$$K_1 N_1 = K_2 N_2$$

$$\frac{N_1}{N_2} = \frac{K_2}{K_1} = \frac{\lambda_1}{\lambda_2}$$

where λ_1 and λ_2 denote average life periods of parents and daughter element species

respectively.

Hence, at equilibrium, *A* and *B* are present in the ratio of their average life periods. They will also be present in the ratio of their half-life periods. This also implies that when radioactive elements are in equilibrium, the one with a high average life is present in greater amount than the other with shorter average life. Hence, at equilibrium, the following relations hold good:

(i) The number of atoms of each radioactive element present is inversely proportional to its decay constant.

(ii) It is directly proportional to its half life.

(iii) If the equilibrium mixture contains an element of an extremely long life and another of shorter measurable half-life, it is possible to calculate the former from the relative amount of both species present. For example, all uranium ores contain radium and uranium in the atomic ratio:

$$\frac{N_{Ra}}{N_U} = 3.48 \times 10^{-7}$$

From the above relation, it follows that

$$\frac{N_U}{t_{1/2}U} = \frac{N_{Ra}}{t_{1/2}Ra} \quad \text{or} \quad t_{1/2}U = \frac{N_U \times t_{1/2}Ra}{N_{Ra}}$$

Since $t_{1/2}$ Ra is 90 years,

$$t_{1/2}U = \frac{1}{3.48} \times 10^{-7} \times 1590 \text{ years} = 4.5 \times 10^{9} \text{ years}$$

28.4 | ARTIFICIAL DISINTEGRATION OR TRANSMUTATION OF ELEMENTS

Transmutation of elements means conversion of one element into another by artificial means. Nitrogen on bombardment with helium nuclei (α particles) gives oxygen as shown by the following equation:

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

In the process, protons are produced. In 1932, Chadwick identified a new particle obtained from the bombardment of beryllium by α-particles. It had a unit mass and no charge. It was named neutron $^{1}_{0}\text{n}$

$$^{9}_{4}\text{Be} + ^{4}_{2}\text{He} \longrightarrow ^{12}_{6}\text{C} + ^{1}_{0}\text{n}$$

α-particle (Neutrons)

This is how the neutron was discovered. Being a neutral particle, it can penetrate into the nuclei of even the heavier elements and has been successfully used for artificial transmutations. Accelerated proton ($^{1}_{1}\text{H}$), deuterons ($^{2}_{1}\text{H}$), i.e. heavy hydrogen, have also been used as projectiles for the rupture of the stable nuclei. Since α-particles carry double positive charge, they are not good projectiles for bombarding of atoms as they are repelled by the nucleus. An α-particle, proton or a deuteron, before it can be captured by a nucleus, must possess sufficient kinetic energy to overcome the repulsive force that develops as the +ve particle approaches the +ve nucleus. For this purpose, several instruments for accelerating these particles have been developed. One of the most effective apparatus invented by E O Lawrence is known as cyclotron which can impart energy up to 400 MeV (million electron volt). Synchrotron is a more powerful modern version.

A large number of transmutations have been carried out by means of alpha particle, protons, neutrons and deuterons. A few of these are given below in the form of equations. At the end of the reaction, two particles are given in the brackets. The first particle refers to the particles used for bombardment and the second particle refers to the new particle produced.

(a) Transmutation byAlpha Particles ($_2^4He$), α

(i) $^{12}_{6}C + ^{4}_{2}He \longrightarrow ^{15}_{8}O + ^{1}_{0}n$ (α, n-type)

(ii) $^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{14}Si + ^{1}_{1}H$ (α, p-type)

(b) Transmutation by Protons ($_1^1H$), p

(i) $^{27}_{13}Al + ^{1}_{1}H \longrightarrow ^{24}_{12}Mg + ^{4}_{2}He$ (p, α-type)

(ii) $^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{4}_{2}He + ^{4}_{2}He$ (p, α-type)

(iii) $^{11}_{5}B + ^{1}_{1}H \longrightarrow ^{11}_{6}C + ^{1}_{0}n$ (p, n-type)

(iv) $^{23}_{11}Na + ^{1}_{1}H \longrightarrow ^{23}_{12}Mg + ^{1}_{0}n$ (p, n-type)

(c) Transmutation by Deuterons ($_1^2H$), d

(i) $^{31}_{17}Cl + ^{2}_{1}H \longrightarrow ^{32}_{18}Ar + ^{1}_{0}n$ (d, n-type)

(ii) $^{31}_{15}P + ^{2}_{1}H \longrightarrow ^{32}_{15}P + ^{1}_{1}H$ (d, p-type)

(iii) $^{12}_{6}C + ^{2}_{1}H \longrightarrow ^{10}_{5}B + ^{4}_{2}He$ (d, α-type)

(d) Transmutation by Neutrons ($_0^1n$), n.

It is brought about by high-speed neutrons. It may result in the emission of a proton, an α-particle or another neutron.

(i) $^{16}_{8}O + ^{1}_{0}n \longrightarrow ^{13}_{6}C + ^{4}_{2}He$ (n, α-type)

(ii) $^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{11}_{5}B + ^{4}_{2}He$ (n, α-type)

(iii) $^{27}_{13}Al + ^{1}_{0}n \longrightarrow ^{27}_{12}Mg + ^{1}_{1}H$ (n, p-type)

(iv) $^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$ (n, p-type)

(v) $^{39}_{19}K + ^{1}_{0}n \longrightarrow ^{38}_{19}K + 2\,^{1}_{0}n$ (n, $2n$-type)

In some cases, only γ-radiation is emitted.

$^{23}_{11}Na + ^{1}_{0}n \rightarrow ^{24}_{11}Na + \gamma$-radiation (Energy)

Example 6 *Complete the following:*

(a) $^{30}_{15}P \longrightarrow ^{30}_{14}Si + \ldots$

(b) $^{37}_{17}Cl + \ldots \longrightarrow ^{38}_{18}Ar + ^{1}_{0}n$

(c) $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + \ldots$

(d) $^{27}_{13}Al + \ldots \longrightarrow ^{30}_{15}P + ^{1}_{0}n$

Solution:

(a) $^{30}_{15}P \longrightarrow ^{30}_{14}Si + ^{0}_{+1}e$

(b) $^{37}_{17}Cl + {}^{2}_{1}D \longrightarrow {}^{38}_{18}Ar + {}^{1}_{0}n$

Deuteron

(c) $^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$

(d) $^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}n$

α-particle

28.4.1 Artificial or Induced Radioactivity

Artificial, or induced, radioactivity is a phenomenon in which a new radioactive isotope of an element is formed by the artificial transmutation of a stable element. The artificial radioactive element behaves in the same fashion as the naturally occurring radioactive series. The radioactive substance produced in the first step disintegrates further to give a stable element. Many radioactive isotopes can be produced by the bombardment of stable isotopes by protons, a-particles and neutrons. Some examples are given below.

1. Induced Radioactivity by Bombardment with α-particles

$$^{24}_{12}Mg + {}^{4}_{2}He \longrightarrow {}^{27}_{14}Si + {}^{1}_{0}n$$

$$^{27}_{14}Si \longrightarrow {}^{27}_{13}Al + {}^{0}_{1}e$$

Stable Positron

2. Induced Radioactivity by Bombardment with Neutrons ($^{1}_{0}n$) Both high-speed and slow-speed neutrons are used for this purpose. Commonly, slow-speed neutrons are more effective in producing nuclear reactions than high-speed neutrons. Three types of nonfission reactions have been produced by neutrons:

(a) Radioactive Capture The (*n, r*) is the most common nuclear reaction and has been carried out for isotopes of all elements when slow-speed neutrons are bombarded on the target. For example,

$$^{40}_{18}Ar + {}^{1}_{0}n \longrightarrow {}^{41}_{18}Ar + \gamma$$

Slow Radioactive

$$^{41}_{18}Ar \longrightarrow {}^{41}_{19}K + {}^{0}_{-1}e$$

(b) Emission of Neutrons

$$^{39}_{19}K + {}^{1}_{0}n \longrightarrow {}^{38}_{19}K + 2\,{}^{1}_{0}n$$

$$^{38}_{19}K \longrightarrow {}^{38}_{18}Ar + {}^{0}_{+1}e$$

(c) Emission of Charged Particles These are favoured with large kinetic energy neutrons or highspeed or fast-moving neutrons.

$$^{35}_{17}Cl + {}^{1}_{0}n \longrightarrow {}^{35}_{16}S + {}^{1}_{1}H$$

Fast Radioactivity

$$^{35}_{16}S + \longrightarrow {}^{35}_{17}Cl + {}^{0}_{-1}e$$

3. Induced Radioactivity by Bombardment with Deuterons ($^{2}_{1}H$)or d

(a) $^{10}_{5}B + {}^{2}_{1}H \longrightarrow {}^{11}_{6}C + {}^{1}_{0}n$

Radioactive

$$^{11}_{6}C \longrightarrow {}^{11}_{5}B + {}^{0}_{1}e$$

(b) $^{12}_{6}C + {}^{2}_{1}H \longrightarrow {}^{13}_{7}N + {}^{1}_{0}n$

$^{13}_{7}N \longrightarrow {}^{13}_{6}C + {}^{0}_{1}e$

4. Induced Radioactivity by Bombardment with Protons ($^{1}_{1}H$)

$$^{7}_{3}Li + {}^{1}_{1}H \longrightarrow \underset{\text{Radioactive}}{^{7}_{4}Be} + {}^{1}_{0}n$$

$$^{7}_{4}Be \longrightarrow \underset{\text{Stable}}{^{7}_{3}Li} + \underset{\text{Positron}}{^{0}_{1}e}$$

Curie and Joliot explained that the nucleus formed in the artificial transmutation reaction is unstable, which exhibits radioactivity and then undergoes disintegration. This explanation was tested chemically by separating the target element from the product and it was found that the latter exhibited radioactivity

28.4.2 Types of Nuclear Reactions Depending Upon Transformation of Nucleus

On the basis of overall transformation, the various types of nuclear reactions may be classified as follows:

(a) Capture Reactions These reactions occur when the bombarding particle is absorbed by the target nucleus but no massive particle (α, *n*, *p*, etc.) other than the product nucleus is liberated. However, γ-radiation may be emitted. Slow neutron capture is a very common reaction and is known for many nuclei.

$$^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U + \gamma$$

A shorthand notation known as Bethe's reaction notation is used for the representation of the reaction as $^{238}_{92}U\ (n, \gamma)\ ^{239}_{92}U$.

(b) Particle-Particle Reactions In these reactions, along with the product nucleus, a massive particle, (*p*, *n*, α, etc.) is also produced. Such reactions are most common. Examples are

$$^{12}_{6}C\ (\alpha, n)\ ^{15}_{8}O,\ ^{27}_{13}Al\ (n, p) + {}^{27}_{12}Mg$$

(c) Fission Reactions These reactions take place when the target nucleus is of heavy mass. The product nucleus formed after bombarding breaks into two nearly equal parts and a large amount of energy along with several neutrons is liberated. Neutron-induced fission of $^{235}_{92}U$ and $^{239}_{94}Pu$ is quite important

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}K + 3\,{}^{1}_{0}n$$

(d) Spallation Reactions Spallation (meaning crumbling) reactions are very much similar to fission reactions but such reactions have a single residual nucleus as the end product and such reactions are not self-sustaining. As a result of the very high-energy projectiles, drastic nuclear reactions occur resulting in the formation of large numbers of light fragments. The light fragments corresponding to decrease in mass number up to 30 units and in charge up to 14 units along with the main product. Nuclear particles such as protons, neutrons, etc., are also emitted in large number.

An example of spallation reactions is bombardment of $^{238}_{92}U$ with α-particle of 400 MeV energy to produce Ra^{233} with the release of 6 protons and 13 neutrons.

$$^{238}_{92}U\ (\alpha, 6p, 13n)\ ^{223}_{88}Ra$$

(e) Fusion Reactions In these reactions, certain light nuclei may be fused together to produce heavier nuclei, under special circumstances. Tremendous amount of energy is liberated in this

process. An example is the fusion of hydrogen nuclei into helium:

$$_{1}^{1}H + {}_{1}^{1}H + 2\,{}_{0}^{1}n \longrightarrow {}_{2}^{4}He + \text{Energy}$$

28.4.3 Types of Nuclear Reactions on the Basis of Nature of Bombarding Particles

On the basis of nature of the bombarding particle, the various types of nuclear reactions may be classified as follows:

(a) Proton-induced Reactions In these reactions, the coulombic repulsions are less but the smaller mass of the protons renders it difficult to penetrate the nuclear energy barrier. The (*p*, α), (*p*, *n*), (*p*, *d*) and (*p*, γ) types of reactions are

$$_{7}^{14}N\ (p, \alpha)\ {}_{6}^{11}C;\ {}_{5}^{11}B\ (p, n),\ {}_{6}^{11}C;\ {}_{4}^{9}Be\ (p, d),\ {}_{4}^{8}Be;\ {}_{7}^{14}N\ (p, \gamma)\ {}_{8}^{15}O$$

(b) Deuteron-induced Reactions Deuterons are the most effective of the positively charged particles. On account of a comparatively large mass, the deuteron is inherently energetic. Further increase in energy may be done by cyclotron acceleration. *A* (*d*, *p*) reaction is similar to a simple (*n*, *V*) reaction. The deuteron is first broken up outside the target nucleus to proton and neutron. Then only the neutron brings about the reactions. The following three (*d*, α), (*d*, *n*) and (*d*, *p*) types of reactions are

$$_{8}^{16}O\,(d, \alpha)\ {}_{7}^{14}N;\ {}_{4}^{9}Be\,(d, n)\ {}_{5}^{10}B;\ {}_{11}^{23}Na\,(d, p)\,{}_{11}^{21}Na$$

(c) Alpha-induced Reactions In these reactions, there are large coulombic repulsions between the positively charged α-particles. α-particles are first accelerated sufficiently in a cyclotron or some other accelerating device. The two (α, *p*) and (α, *n*) common types of reactions are

$$_{7}^{14}N\,(\alpha, p)\ {}_{8}^{17}O;\ {}_{5}^{10}B\ (\alpha, n)\ {}_{7}^{13}N$$

(d) Neutron-induced Reactions Neutron, being a neutral particle, does not face any coulombic repulsion and, therefore, the neutron reactions depend only upon the energy of the bombarding particle. Generally, all the light as well as heavy elements interact with neutrons. On bombarding, lighter elements generally eject some particles such as α-particles or protons while heavier element generally capture them and form their own isotopes. The five (*n*, γ), (*n*, α), (*n*, *p*), (*n*, 2*n*) and (*n*, fission) types of reactions are:

$$_{92}^{238}U\ (n, \gamma)\ {}_{92}^{239}U,\ {}_{3}^{7}Li\ (n, \alpha)\ {}_{1}^{3}H,\ {}_{7}^{14}N\ (n, p)\ {}_{6}^{14}C,$$

$$_{92}^{238}U\ (n, 2n)\ {}_{92}^{237}U;\ {}_{92}^{235}U\ (n, \text{fission})\ \text{fission products.}$$

28.5 Q VALUE OF NUCLEAR REACTIONS

In all nuclear reactions, there is either an increase in the mass or decrease in the mass. This decrease or increase in mass Δm, called mass defect during the reactions, is converted into energy Q. This is measured in MeV (million electron volts). It means that the nuclear reactions, like chemical reactions, are always accompanied by a release or absorption of energy. This energy is expressed by adding the term Q to the right-hand side of the equation. For example, in the ordinary nuclear reactions studied by Rutherford in 1919,

$$_{2}^{4}He + {}_{7}^{14}N \longrightarrow {}_{8}^{17}O + {}_{1}^{1}H + Q\ (\text{energy})$$

The quantity Q is called the energy of the reaction, or more frequently just 'the Q of the reaction'. The Q can be positive or negative. Positive Q shows the energy is released and the reaction is said to be ***exoergic*** and negative Q shows energy absorption and the reaction is ***endoergic.***

There is an important difference between a chemical reaction and a nuclear reaction. In case

of chemical reactions, we always consider macroscopic amount of material undergoing reactions and consequently heats of reactions are usually given per mole or occasionally per gram of one of the reactants. In case of nuclear reactions, we usually consider single processes and the Q values are, therefore, given per nucleus transformed.

In the case of the above mentioned reaction Q can be calculated from the mass of the particles as follows:

Mass on the left-hand side:

$$^{4}_{2}\text{He} = 4.0026$$
$$^{14}_{7}\text{N} = 14.0031$$
$$18.0057 \text{ a.m.u.}$$

Mass on the right-hand side:

$$^{1}_{1}\text{H} = 1.0078$$
$$^{17}_{8}\text{O} = 16.991$$
$$= 18.0069 \text{ a.m.u.}$$

The RHS gives an increase of mass of 0.0012 a.m.u. Thus, an amount of energy equivalent to 0.0012 mass unit has to be supplied to make the reactions energetically possible.

Hence, $Q = -0.0012 \times 931.5 = -1.1178$ MeV [$\because$ 1 a.m.u. = 931.5 MeV]

This reaction is, therefore, endoergic as Q is –ve.

Example 7 *Calculate the Q-value for the reaction*

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{98}_{92}Mo + ^{136}_{54}Xe + 2^{1}_{0}n$$

The exact mosses of reactants and products are

$$^{235}_{92}U = 235.044 \text{ a.m.u.}; \; ^{1}_{0}n = 1.009 \text{ a.m.u.}$$
$$^{98}_{42}Mo = 97.905 \text{ a.m.u.}; \; ^{136}_{54}Xe = 135.917 \text{ a.m.u.}$$

Solution:

$$\Delta m = \text{Mass of products} - \text{Mass of reactants}$$
$$= [97.905 + 135.917 + 2.018] - [235.044 + 1.009] \text{ a.m.u.}$$
$$= -0.213 \text{ a.m.u.}$$

Thus, there is a decrease in mass equal to 0.213 a.m.u. Hence, energy will be released during the reaction. Hence, Q is positive.

$$\text{Energy released} = 0.213 \times 931.5 \text{ MeV}$$
$$= 198.41 \text{ MeV}$$

28.6 | NUCLEAR FISSION

The process of splitting up of a heavy nucleus into two, more or less, equal halves is called nuclear fission. This is accompanied by liberation of some neutrons and enormous energy.

Otto Hahn and Strassmann (1939) observed that when uranium was irradiated with neutrons, isotopes of intermediate mass number were obtained. They proved by analysis that one of the products of this nuclear reaction was $^{144}_{56}\text{Ba}$ Thus,

$$^{235}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{144}_{56}\text{Ba} + ^{92}_{36}\text{Kr}$$

These isotopes of Ba and Kr were radioactive and gave more stable isotopes by the release of more neutrons.

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n$$

When fission takes place, the nucleus breaks into two fragments of comparable sizes. The difference in the actual masses of product substances and the parent substances is converted into energy. Thus, in the following case,

$$^{235}_{92}U \quad + ^{1}_{0}n \longrightarrow ^{141}_{56}Ba + \quad ^{92}_{36}Kr \quad + 3\,^{1}_{0}n \quad + Q$$

235.0439 1.00886 140.9136 91.8976 3 × 1.00866

The total mass on the LHS is 236.04276 a.m.u. and on the RHS, it is 234.8371 a.m.u. Hence, there is a decrease of mass by 0.21566 a.m.u. Since 1 a.m.u. is equivalent to 931.5 MeV energy, an amount of 0.21566 × 931.5 or 200.88729 MeV of energy is produced. Thus, in the fission of one nucleus of ^{235}U, about 200 MeV energy is released. This is the Q value for this fission reaction. It may be understood that nuclear fission involves a net of loss of mass. This excess mass is transformed into energy according to the Einstein equation $E = mc^2$. The magnitude of energy is enormous. It has been calculated that the energy released by the fission of one kg of natural uranium is equal to that available from 20,000 kg of coal.

1. Chain Reactions It has been observed that the fission of ^{235}U is very rapid and releases a large amount of energy. In the reaction

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n$$

we see that three neutrons are produced as a result of fission of one ^{235}U nucleus. It may, however, be added that U-235 is known to split at least in 3° different ways. These three neutrons will cause further fission of three more ^{235}U nuclei producing nine neutrons as shown in Fig. 28.17. These nine neutrons will cause further fission of nine ^{235}U nuclei producing twenty-seven neutrons, and so on.

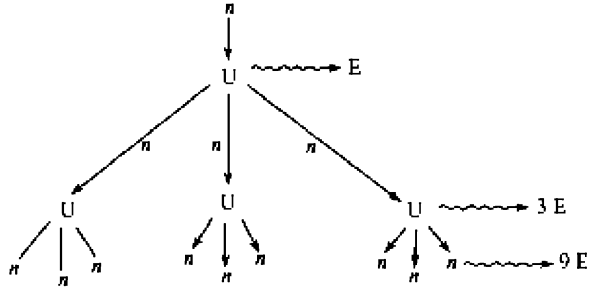


Fig. 28.17 *Fission of U^{235}*

This process is known as ***chain reaction*** or ***autocatalytic reaction.*** Absorption of neutron by nonfissionable material reduces the efficiency of chain reaction.

In order to ensure an efficient chain reaction, moderators are used. Moderators are substances which slow down the speeds of the fast neutrons obtained after fission very rapidly so that the chances of their capture (of neutron) by nonfissionable material becomes very small. Graphite and heavy water are used as moderators.

If E be the energy released per fission, the total energy liberated from the chain reactions goes on multiplying in each step and ultimately becomes enormous. This large amount of energy could be exploited for useful purposes.

2. Plutonium Bomb Bombarding of ^{235}U with neutrons liberates a tremendous amount of energy. This raises the prospects of the utilisation of atomic energy as a source of power. But we are faced with a difficulty. Ordinary uranium consists of 99.28% of ^{238}U, 0.71% of ^{235}U and

about of 0.01% of ^{234}U. It is very difficult to isolate ^{235}U (fissionable material) from the above isotopic mixture. It was found that plutonium, which does not occur in nature but which can be prepared from the most abundant isotopes of ^{238}U, undergoes fission readily like ^{235}U. Plutonium can be prepared from ^{238}U by neutron bombardment as follows:

$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \text{ (Half life of 23 minutes)}$$

$$^{239}_{92}U \longrightarrow {}^{239}_{93}Np + {}^{0}_{-1}e \text{ (Half life of 2–3 days)}$$

$$^{239}_{93}Np \longrightarrow {}^{239}_{94}Pu + {}^{0}_{-1}e \text{ (Half life of } 2.4 \times 10^{4} \text{ years)}$$

The $^{238}_{92}U$ on capture of a neutron is converted into $^{239}_{92}U$ which is radioactive and changes over with emission of β-particle into the transuranic element $^{239}_{93}Np$. $^{239}_{93}Np$ is also radioactive and emits a β-particle to give plutonium of atomic number 94, i.e. $^{239}_{94}Pu$.

Plutonium, which is chemically different from uranium, can be separated easily. It has an additional advantage because its half-life period is very long, of the order of about 24,000 years. The problem of release of nuclear energy through nuclear fission was solved with the discovery of Pu. It is estimated that energy released by a gram of plutonium is equal to that of 30 tons of TNT. This forms the basis of the manufacture of atom bombs.

28.7 NUCLEAR FUSION

It is the process in which two or more light nuclei are made to combine to give a heavier nuclei. During this process also, some mass is lost and is converted into energy. Principle source of stellar energy, i.e. energy of the sun, is the nuclear energy released, during the fusion of hydrogen nuclei to form helium nuclei (4H → He) (See Fig. 28.18.)

$$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{1}e + \gamma$$

$$4\,{}^{1}_{1}H = 4 \times 1.00813 = 4.03252 \text{ a.m.u.}$$

$${}^{4}_{2}He = 4.00389 \text{ a.m.u.}$$

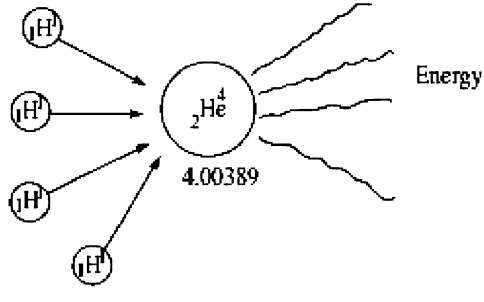


Fig. 28.18 *Principle of solar energy*

From four hydrogen atoms with atomic mass 4 × 1.00813 = 4.00389 a.m.u., an atom of helium is obtained with atomic mass 4.00389 a.m.u. The balance of mass (0.02863 a.m.u.) is converted into energy according to the relation.

Energy, equivalent to 0.02863 mass unit = 0.02863 × 931.5 MeV

= 26.6688 MeV

Weizacker and Bethe in 1939 showed that a closed carbon and nitrogen cycle is responsible for the origin of energy in stars including our sun, i.e. the stellar energy, as given below:

$$^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{13}_{7}N + \gamma$$

$$^{13}_{7}N \longrightarrow ^{13}_{6}C + ^{0}_{+1}e + \gamma$$

$$^{13}_{6}C + ^{1}_{1}H \longrightarrow ^{14}_{7}N + \gamma$$

$$^{14}_{7}N + ^{1}_{1}H \longrightarrow ^{15}_{8}O + \gamma$$

$$^{15}_{8}O \longrightarrow ^{15}_{7}N + ^{0}_{+1}e + \gamma$$

$$^{15}_{7}N + ^{1}_{1}H \longrightarrow ^{12}_{6}C + ^{4}_{2}He + \gamma$$

By cancellation,

$$4\,^{1}_{1}H \longrightarrow ^{4}_{2}He + 2\,^{0}_{+1}e + \text{energy}$$

The net reaction in the process is a closed chain comprising the fusion of four protons to give a helium nucleus, two positrons and release of vast amount of energy (26.6 MeV/cycle).

The process of nuclear fusion has a very high activation energy and takes place, therefore, at very high temperature, of the order of millions of degrees centigrade, ($> 10^6$ K) which only exists in the interior of the sun. It is for this reason that such processes are, therefore, called ***thermonuclear reactions.*** Once a fusion reaction is initiated, the process goes on since there are both H and He in the sun and the temperature in the interior is high enough to produce transmutation. This suggests that the process of producing the sun's energy may be due to the following cycles:

(i) $^{1}_{1}H + ^{1}_{1}H \longrightarrow ^{2}_{1}D + ^{0}_{+1}e + \text{energy}$

Positron

(ii) $^{1}_{1}H + ^{2}_{1}D \longrightarrow ^{3}_{2}He + \text{Energy}$

Isotope of helium

(iii) $^{3}_{2}He + ^{3}_{2}He \longrightarrow ^{4}_{2}He + 2\,^{1}_{1}H + \text{Energy}$

Helium

During the above cycle, the net effect is the conversion of four protons into the ***helium nucleus,*** for which the total energy change is 26.6 MeV.

Lighter Elements Generally Undergo Fusion while Heavier Elements show Nuclear Fission

Lighter elements have smaller values of *n/p*. They have a tendency to increase this *n/p* value. This can be achieved through fusion. For example,

$$4\,^{1}_{1}H \rightarrow ^{4}_{2}He + 2\,^{0}_{+1}e + \gamma$$

In helium, the *n/p* ratio is 1 whereas in hydrogen, there are no neutrons and the *n/p* value is zero. Heavier elements have a higher value of *n/p* and they have a tendency to reduce this value. They achieve it through fission in which a certain number of neutrons are ejected, thus lowering the *n/p* value of the products.

1. Hydrogen Bomb The manufacture of the hydrogen bomb is based upon the principle of nuclear fusion. The energy released in the process is about 1000 times that of an atomic bomb.

However, this reaction takes place at very high temperature, of the order of that prevailing in the interior of the sun. It is believed that in a hydrogen bomb, a mixture of heavy isotopes of hydrogen, i.e. deuterium or tritium, is enclosed in a space surrounding an ordinary atomic bomb. The transformation and possibilities are believed to be of the following four types. These are

(i) $_{1}^{2}H + {}_{1}^{2}H \rightarrow {}_{2}^{3}He + {}_{1}^{0}n + 3.25\ MeV$

(ii) $_{1}^{2}H + {}_{1}^{2}H \rightarrow {}_{1}^{3}H + {}_{1}^{1}H + 4.0\ MeV$

(iii) $_{1}^{3}H + {}_{1}^{2}H \rightarrow {}_{2}^{4}He + {}_{1}^{0}n + 17.6\ MeV$

(iv) $_{1}^{2}H + {}_{2}^{3}He \rightarrow {}_{2}^{4}He + {}_{1}^{1}H + 18\ MeV$

The reactions (iii) and (iv) are actually the reaction products of (i) and (ii) so that the overall conversion of six deuterons is as follows:

$$6\,{}_{1}^{2}H \longrightarrow 2\,{}_{2}^{4}He + 2\,{}_{0}^{1}n + 43\ MeV$$

For the fusion of 6 deuterons, as we see above, the total energy produced is 43 MeV. Thus, the energy produced per deuteron is 7.16 MeV. Therefore, for equal mass of material, much more energy is released in fusion than in fission.

In a hydrogen bomb, there is no limitation of the critical mass of fusible material; hence any amount of fusible material can be used. Thus, there is no limit for the explosive power of the hydrogen bomb.

In a hydrogen bomb, the fusion between deuterium nuclei and tritium nuclei is made to take place. The essential conditions for carrying out this fusion reactions are high temperature, of the order of millions of degrees and high pressure of the order of millions of atmospheres. These conditions can be attained by exploiting an atom bomb. Hence, for the preparation of a hydrogen bomb, a suitable quantity of a mixture of deuterium and tritium is combined with an atom bomb. The atom bomb first explodes and provides the essential conditions of temperature and pressure for the fusion reaction. The fusion reaction then starts and releases enormous amount of energy.

Thus, this hydrogen bomb is a fission fusion bomb.

2. Cobalt Bomb When the hydrogen bomb is encased in a sheath of cobalt, it is called a cobalt bomb. During explosion, the cobalt sheath is converted into a gigantic radioactive cloud producing lethal radiations. It destroys everything which is covered by it. Moreover, its effect is prolonged to a five-year span due to its long life period. Thus, the cobalt bomb is more dangerous than the hydrogen bomb.

28.8 APPLICATIONS OF RADIOACTIVITY

Important applications of radioactivity are described as under:

1. New Source of Energy Nuclear fusion has opened a new source of atomic energy at our disposal. The controlled fission chains reactions can be used to run various industries. Research is going on to achieve controlled fusion reactions which will give even more amount of energy.

2. Preparation of Luminiscent Paints If a radioactive substance like thorium is mixed with a fluorescent material like ZnS, it exhibits luminescence, so that it becomes visible in the dark. Such a mixture constitutes luminiscent paints. These are used to make the pointers and dials of watches visible during night.

3. Radiotherapy Radiations from Co^{60} sources have been used in treatment of cancer. Sometimes γ radiations from Au^{198} are also used.

4. Radioactive Dating This is the process of determining the age of a material. The age of the earth can be estimated by this method. We can distinguish ordinary lead and the lead obtained from radioactive material with the help of a mass spectrograph. Thus, we can find out the ratio of

Pb^{206} to that of uranium in the oldest mineral. Now, if we determine the overall rate of disintegration in the mineral then the age of the mineral can be obtained. It is assumed that the mineral originated a little later than the earth. The age of the earth calculated by this method comes out to be 2.3 billion years which is in close proximity with that obtained by other methods.

5. Measurement of Thickness of Material A source emitting β or γ-rays is placed on one side of the material whose thickness is to be measured and the detector on the other side. The force experienced by the radiation is a function of the thickness though which it is passed. Hence, from the measurement of force, the thickness of the absorbing material can be obtained.

6. Mutation Induced by Radiations If the plants and seeds are irradiated by a radioactive source, the rate of mutation is greatly increased and development of stains is achieved in a fraction of time taken otherwise.

7. Atomic Structure Revealed The famous experiment of scattering of α-particles by Rutherford was done by a radioactive material. This led to the concept of nucleus. The artificial disintegration of atoms increased our knowledge about the nature of the nucleus, i.e., presence of protons or neutrons in it. Moreover, many more fundamental particles like positron, mesons, etc., have been discovered as a result of work on radioactivity.

8. Discovery of New Elements and New Isotopes The discovery of transuranic elements has been achieved by artificial radioactivity. Moreover, radioactive isotopes of other stable elements have been discovered by the artificial transmutation of elements.

9. Sterilization Antibodies are sterilised by radiations from radioactive substances. Partial sterilization of food is also done for its preservation.

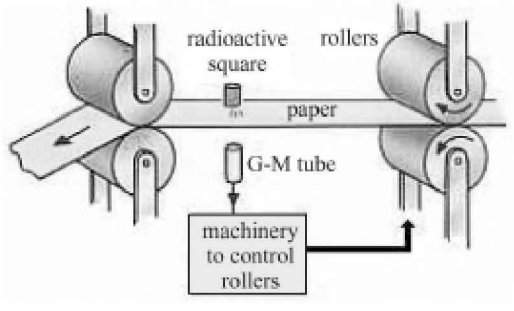


Fig. 28.19 *Thickness control In paper mills, thickness of the paper is controlled by measuring how much β-radiation passes through the paper to GM counter. The counter controls the pressure of the rollers to give the correct thickness.*



Fig. 28.20 *Sterilising γ-rays are used to kill bacteria, mould and insects in food. This process prolongs the shelf life of the food Gamma rays are also used to sterilise hospital equipment.*

10. Determination of Avogadro Number The γ-rays from radioactive material have been used to determine Avogadro number. The value comes out to be 6.02×10^{32} from this method and agrees well with those found by other methods.

11. Preparation of Nuclear Batteries Radioactive energy is converted into electrical energy in these batteries. Two electrodes are used in an evacuated chamber. One of the electrodes *A* is the cathode with β-emitter. The flow of β-particles inside the chamber results in the passage of current in the external circuit connected with these electrodes.

12. Tracer Applications In these applications, the radioactive isotopes are used as a label to study the behaviour of some materials. These are the most important applications of radioactive isotopes in various branches of applied science.

13. Measurement of the Level of Liquids A radioactive source is placed on the surface of liquid in a closed container. The detector outside the vessel will detect the level of the radioactive source, which will be the level of liquid inside the container. This technique is used to know the level of oil in refineries.

28.9 | TRACER AND TRACER TECHNIQUE

The majority of elements occur as a mixture of isotopes, the proportion of which remains constant throughout the course of physical, chemical and biological changes. Some of these isotopes are radioactive. The radioactive isotopes of a given element behave chemically in the same way as nonradioactive isotopes. Hence, if a radioactive isotope is added to its nonradioactive variety, the mixture will behave in the same way chemically. Since radioactive isotopes can always be detected easily, they may be used as indicators or tracers in various fields. The process in which a radioactive isotope is mixed with its nonradioactive variety and the activity of radioactive isotopes is noted after physical, chemical or biological changes, is called ***radioactive tracing*** or ***tracer technique.*** The success of radioactive tracing lies in the selection of a suitable nucleide.

28.10 | APPLICATIONS OF TRACER (RADIO ISOTOPES) TECHNIQUE

Various applications of tracer techniques are discussed as under:

1. In Quantitative Analysis Isotopic dilution analysis is applied for the determination of the amount of substance which is present in a concentration that cannot be measured by physical or chemical methods. The substance under investigation is mixed in a known ratio with its active form and the mixture is introduced into the system. Any change in the ratio will be due to the dilution caused by the substance originally present in the system. Knowing the change in the ratio and by measuring the activity, the amount of the substance can be determined.

2. Exchange Phenomena The study of several exchange reactions using tracers has given valuable information regarding reactivity, chemical bond types, effect of solvent on properties and structure of ions and compounds. It was thought that when a salt is in contact with its saturated solution, there is continuous exchange of molecules between the liquid and the salt along boundary surface. This has been verified by a tracer technique. Crystals of activated lead chloride were placed in a saturated solution of inactive lead chloride. The saturated solution after some time was found to be radioactive. It has been shown by a tracer technique that the two

sulphur atoms of thiosulphate are not equivalent. Inactive sulphite is converted into thiosulphate by treating with radio-sulphur. On adding dilute acid to the product, the sulphurous acid that is regenerated is found to be inactive.

$$Na_2SO_3 + S^* \longrightarrow Na_2SS^*O_3$$

$$Na_2SS^*O_3 + 2HCl \longrightarrow 2NaCl + H_2SO_3 + S^*$$

3. Radiometric Titrations Radioactive tracers may also be used to determine the end points of a titrations where the reaction product is either insoluble or extractable. For example, if Ag is to be estimated with standard HCl solution, Ag^{110} tracer is added. The specific activity of the solution is determined after each addition of the known volume of HCl solution. As the titration proceeds, Ag is removed from the solution as AgCl precipitates so that the specific activity of the solution is lowered. A plot of activity versus volume of HCl gives a line, the extrapolation to zero activity gives the end point of titration.

4. Reaction Mechanism Radioactive isotopes find wide applications in the study of the mechanism of reactions. The oxidation of chlorite to perchlorate by hyprochlorous acid labelled with ^{33}Cl is found to proceed thus:

$$2HCl^*O + NaClO_2 \longrightarrow NaClO_4 + 2HCl^*$$

The study of the reduction of chlorate to chloride using Cl^{33} as tracer shows that the reaction proceeds in the following steps.

$$ClO_3^- \longrightarrow ClO_2^- \longrightarrow ClO^- \longrightarrow Cl^-$$

Radiocarbon, ^{14}C, is extensively used in the study of the mechanism of organic reactions. There are a number of reactions in which carbon atoms or groups of carbon atoms migrate from one part of the molecule to another. By labelling the migrating groups with radio-carbon at suitable position, it is possible to understand the course of the reactions.

5. Applications in Medicine In medical science, the radioactive tracing is mainly used to locate disorder in the human body and to cure diseases. ^{131}I is used to study the functioning of thyroid glands, and to locate brain tumours. ^{58}Co has been used in the study of function of vitamin B_{12} in the body. ^{24}Na is used to find out whether the blood of a patient is reaching the wound or not. Similarly, ^{32}P is used to find out whether phosphorus is being absorbed by the bones of a patient with a bone fracture. Apart from this, radium and radio-cobalt are used to cure cancer.

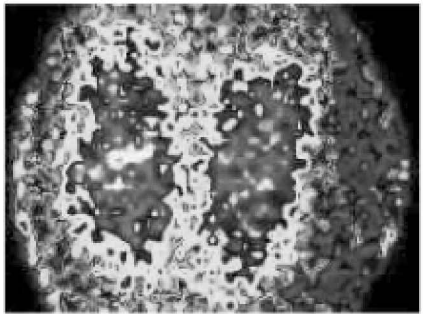


Fig. 28.21 Radioactive Tracers *Radioisotopes can be used for checking a blocked kidney. A small amount of I-123 is injected into the patient. After 5 minutes, two Geiger-Muller counters are placed over the kidneys.*



Fig. 28.22 *γ-rays can kill living cells. Therefore, theyare used to kill cancer cells. This is called radiotherapy. It works because cancer cells cannot repair themselves after damage by γ-rays while healthy cells can. Not all cancers can be treated easily by radiations. For example, it is easier to aim γ-rays at breast tumour. Lungs are easily damaged by γ-rays. Therefore, lungs are not subjected to this treatment.*

6. Applications in Industry Using tracer technique, the movement of mud and sand in rivers, and harbours has been investigated. ^{131}I has been used to trace the direction and velocity of underground water. ^{24}Na can be used to locate leaks in underground water pipes. Cracks are inspected by putting them in radioactive salt baths and then finding out with Gieger-Muller counter whether any penetration has taken place in the metal.

An important application of the tracer technique is that one pipeline can be used for the transportation of several kinds of petroleum products with little mixing at the interface of liquids. A radioactive material is added between the products at the source end of the pipeline. A Gieger counter at the receiving end placed outside the pipe promptly indicates the arrival of the new product.

7. Applications in Biology A number of biological processes, both in plants and animals, have been studied using the tracer techniques. The mechanism of photosynthesis in plants was established using tracer technique. A small amount of C^*O_2 was introduced with ordinary CO_2 in the plant. It was found that the oxygen which is evolved comes from the water molecules. Accordingby, the reaction for photosynthesis can be written as

$$6CO_2^* + 12H_2O \rightarrow C_6H_{12}O_6^* + 6H_2O^* + 6O_2$$

8. Diffusion The process of diffusion has been studied by tracer method. The rate of diffusion of lead has been determined by mixing radio-lead with ordinary lead and allowing the mixture to diffuse into inactive lead. It is found that at 473 K, diffusion of lead is about ten times slower than that of tin in lead.

9. Solubility Solubility of sparingly soluble salts can be determined accurately by this method. For example, solubility of lead chromate can be determined as follows.

A known mass of radioactive lead is mixed with a weighed amount of inactive lead, and the mixture is converted into lead chromate and a saturated solution of the salt in water is prepared. A known volume of the solution is evaporated to dryness and by determining the radioactivity of the residue, the concentration of lead chromate in water is calculated.

10. Discovery of New Compounds The possibility of preparing hydrides of bismuth and lead was established by tracer method. When magnesium filings coated with radio-bismuth are treated with dilute acid, the gas evolved is found to be radioactive. This gas cannot be pure hydrogen, since the acid, which is a source of hydrogen, is inactive. Therefore, it is inferred that the gas is bismuth hydride which contains radio bismuth.

$$3Mg + 6HCl \longrightarrow 3MgCl_2 + 6H$$

$$2Bi + 6H \longrightarrow 2Bi^*H_3 \ (^* = \text{Radioactive})$$

Detection of this hydride would have been almost impossible otherwise.

11. Completion of Precipitation Lead salt containing a known amount of radioactive lead is precipitated from the solution. In order to test for complete precipitation, the amount of activity remaining in solution is determined after evaporating it to dryness. This measurement will give the amount of lead which has not been precipitated.

12. Application in Agriculture In recent years, tremendous amount of work has been done to study rates and mechanisms of absorption of essential elements by the plants from various compounds. These have resulted in the improvement of crops and essential use of fertilizers. ^{32}P has extensively been used in such studies. Tritium (^3_1H) has been used as a tracer to measure the rate of movement and distribution of water absorbed by roots of plants. ^{14}C, labelled CO_2, has been used in the investigation of respiration by plants.

13. Radiocarbon Dating It is based on the radioactivity of ^{14}C isotope and hence, known as radiocarbon dating. The isotope is radioactive with a half-life period of 5568 years. The ^{14}C isotopes are continually being produced in the upper atmosphere where it combines with oxygen to form $C^{14}O_2$. Generally, $C^{14}O_2$ mixes with the nonradioactive CO_2 in the atmosphere and is absorbed by plants during photosynthesis. Animals, by eating plants and secreting waste products, continually have an intake and output of ^{14}C. But as soon as a plant or animal dies, its ^{14}C intake terminates. The ^{14}C present in the dead species then undergoes radioactive decay. It follows that any material which is constructed from plants or animals will have ^{14}C incorporated in them. The amount of ^{14}C present leads to determination of the age of the materials.

Animals and plants have a known proportion of carbon-14 in their tissues. When they die, they stop taking carbon in and the amount of carbon-14 goes down at a known rate (C-14 has a half-life of 5700 years). The age of ancient organic materials can be found by measuring the amount of C-14 that is left



Fig. 28.23 *Radioactive dating*

28.11 | DESIGN OF A NUCLEAR REACTOR

Nuclear reactor is a device to produce the nuclear energy in a controlled way to be used for

peaceful purposes. It works on the same principle as the atomic bomb but under controlled conditions. All the neutrons produced are not allowed to carry out chain reaction.

The essential parts of a reactor (Fig. 28.17) are the following:

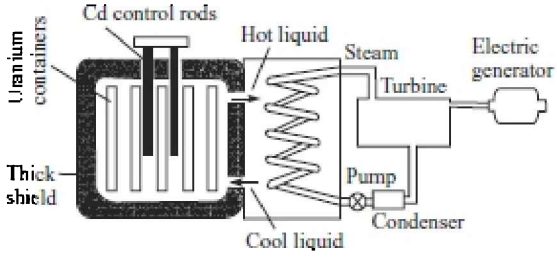


Fig. 28.24 *A diagrammatic view of a nuclear reactor*

1. Core It consists of rods of fissionable material such as ^{235}U or ^{239} Pu.

Conversion of ^{235}U into plutonium is effected in a nuclear reactor. Uranium is purified from other elements but not separated into isotopes. The uranium rods are 'canned' in aluminium cylinders to protect them against corrosion by water that may be used as a cooling agent.

2. Moderator A reactor using graphite bricks as moderator consists of cubic blocks of graphite provided with slots into which are inserted metallic rods of natural uranium canned in aluminium cylinders, some ^{235}U atoms undergo fission with production of fast neutrons. Since slow neutrons are captured by ^{238}U, neutrons are slowed down by collisions with graphite which acts as a moderator. ^{238}U absorbs slow neutrons forming plutonium. The rods are removed from time to time and plutonium is separated by chemical processes.

In some reactions, heavy hydrogen in the form of heavy water, is used as a moderator instead of graphite, for example, in the atom pile at Mumbai plant. If graphite is used as a moderator, the reactor is usually called an atomic pile and if heavy water is used as moderator, the reactor is called a swimmingpool-type reactor. In the swimming-pool-type reactor, the moderator is heavy water in a tank in which the uranium rods are suspended.

3. Control Rods The rate of the reaction may be controlled by varying the amount of uranium inserted in the pile or the reactor and also by the insertion of rods of cadmium or of boron steel which absorb neutrons. If the temperature of the reactors appears to be going higher than regarded safe for the reactor, control rods of cadmium or of boron steel are pushed into the pile. Cadmium is a very good absorbent of neutrons. Absorption of neutrons breaks up the chain processes and the nuclear fissions can thus be kept under control and can even be stopped.

4. Coolant The heat generated in the reactor is removed constantly from it by circulating in it a liquid which is known as coolant. Usually, a low melting alloy of sodium and potassium metals is employed. The alloy takes heat to the heat exchanger for raising steam. Steam generates electricity.

5. Protective Screen Since neutrons have a very damaging influence on human beings and other living organisms, protective walls are needed around the reactor. They may be of lead glass or of special concrete about 3 metres thick.

Applying Chemistry to Life

Nuclear energy: a boon or curse?

It depends on how we use it. Barbaric killing of humans using nuclear bombs puts us in shame. At the same time, it can fulfil our energy needs. A few grams of fissile material per day is enough to cater to the energy needs of a medium town.



Fig. 28.25 Bombing of Hiroshima and Nagasaki

On August 6, 1945, a US plane dropped a uranium atom bomb on Hiroshima, Japan. 60000-70000 people were killed or reported missing and, 1,40,000 were injured. Three days later, another bomb was dropped on Nagasaki again causing a huge loss of life.



Fig. 28.26 Kudankulam Nuclear Plant, India

Nuclear power corporation of India is setting up two 1000 MW Russian reactors at Kudankulam in Tiruneveli district

28.12 | SODDYS GROUP-DISPLACEMENT LAW

The atomic number of an element is decreased by two units and atomic mass is decreased by four units when it emits an α-particle

$$ {}^{b}_{a}\mathrm{M} \xrightarrow{-\alpha\text{-particle}} {}^{b-4}_{a-2}\mathrm{M}' $$

where the metal M has the atomic number a and mass number b.

The element is shifted two positions to the left in the periodic table as a result of α-emission And the atomic number of an element is increased by one unit while the mass number remains unchanged when it emits a β-particle.

$$^{b}_{a}M \xrightarrow{-\beta \text{ particle}} {}^{b}_{a+1}M'$$

The position of the element is shifted one position to the right as a result of β-emission.

Example 8 The final product of ^{238}U is ^{206}Pb. A sample of pitchblende contains 0.0453 g of ^{206}Pb for every gram of ^{238}U present in it. Supposing that the mineral pitchblende formed at the time of formation of the earth did not contain any ^{206}Pb, calculate the age of the earth. (Half-life period of $^{238}U = 4.5 \times 10^9$ years)

Solution: Amount of ^{238}U present now, i.e. $(a - x) = 1$ g

Amount of ^{238}U originally present (a) = Amount of ^{238}U now present + Amount of ^{238}U changed into

0.0453 g of ^{206}Pb

$$= 1 + \frac{238}{206} \times 0.0453 = 1.05234 \text{ g}$$

Suppose t is the time in which 1.05234 g of ^{238}U changed into 1 g of ^{238}U

Using the equation, $$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

But $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9} = 1.54 \times 10^{-10} \text{ years}^{-1}$$

Substituting the values,

$$t = \frac{2.303}{1.54 \times 10^{-10}} = \log \frac{1.05234}{1}$$

$$= 3.29 \times 10^8 \text{ years}$$

Example 9 *Half-life of ^{232}Th is 1.4 × 10 years and that of its daughter element ^{228}Ra is 7 years. What is the mass of ^{228}Ra in equilibrium with 1 g of ^{232}Th?*

Solution: For two radioactive species in equilibrium,

$$\lambda_A N_A = \lambda_B N_B$$

or $$\lambda_{Th} N_{Th} = \lambda_{Ra} N_{Ra}$$

λ_{Th} and N_{Th} stand for disintegration constant and concentration of Th. λ_{Ra} and N_{Ra} are corresponding values for Ra.

or $$\frac{0.693}{t_{0.5}(\text{Th})} 1 \text{ g} = \frac{0.693}{t_{0.5}(\text{Ra})} \times N_{Ra}$$

or $$\frac{0.693}{1.4 \times 10^{10}} = \frac{0.693}{7} \times N_{Ra} \quad \text{or} \quad N_{Ra} = \frac{7}{1.4 \times 10^{10}} = 5 \times 10^{-10} \text{ g}$$

Example 10 *Complete the following reactions.*

(a) $^{27}_{13}Al + {}^{4}_{2}He \longrightarrow \ldots + {}^{1}_{0}n$

(b) $^{14}_{7}N + \ldots \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$

(b) F^{18} is found to undergo 90% radioactive decay in 356 minutes. Calculate its half life.

Solution:

(a) (i) $^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}n$

(ii) $^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$

(b) Apply the relation

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

After the time 356 minutes, 90% matter has decayed or 10% matter has been left. Substituting the values for t and N,

$$\lambda = \frac{2.303}{356} \log \frac{N_0}{0.1N_0} \quad \text{or} \quad \lambda = \frac{2.303}{356} \log 10$$

or $$\lambda = \frac{2.303}{356}$$

Half-life is related to disintegration constant as

$$t_{0.5} = \frac{0.693}{\lambda} \quad \text{or} \quad \frac{0.693}{2.303} \times 356 \quad \text{or} \quad t_{0.5} = 107 \text{ minutes}$$

Example 11

(a) Calculate the disintegration constant and average life of α radioactive element if its half-life is 30 days.

(b) Complete the following artificial nuclear reactions:

(i) $^{9}_{4}Be + {}^{1}_{1}H \longrightarrow \ldots + {}^{4}_{2}He$

(ii) $^{27}_{13}Al + {}^{1}_{0}n \longrightarrow \ldots + {}^{1}_{1}H$

(iii) $^{10}_{5}B\,(\alpha, \rho) \longrightarrow \ldots + \ldots$

Solution: Relation between average life and half-life is

Average life = $1.44 \times t_{0.5}$

or, Average life = $1.44 \times 30 = 43.2$ days

Relation between disintegration constant and half-life is

$$\lambda = \frac{0.693}{t_{0.5}} \quad \text{or} \quad \lambda = \frac{0.693}{30} = 0.2231 \text{ days}^{-1}$$

(b)

(i) $^{9}_{4}Be + {}^{1}_{1}H \longrightarrow {}^{6}_{3}Li + {}^{4}_{2}He$

(ii) $^{27}_{13}Al + {}^{1}_{0}n \longrightarrow {}^{27}_{12}Mg + {}^{1}_{1}H$

(iii) $^{10}_{5}B + {}^{4}_{2}He \longrightarrow {}^{13}_{6}C + {}^{1}_{1}H$

Example 12 *A piece of wood from an archaeological source shows a C-14 activity which is 60% of the activity found today. Calculate the age of the sample ($t_{1/2}$ for $^{14}_{6}C$ = 5770 years)*

Solution:

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.20 \times 10^{-4} \text{ years}$$

Let the age of the wood be t years. The activity of the sample is found to be 60% of the activity of a fresh sample.

$$\lambda_t = \frac{2.303}{t} \log \frac{N_0}{N_t} \qquad \text{(i)}$$

Also $$\frac{N_t}{N_0} = \frac{60}{100}$$

where N_0 and N_t are the activities of the material in the beginning and after time t respectively.

or $$\frac{N_0}{N_t} = \frac{100}{60} = 1.6666$$

Substituting the values in Eq. (i), $1.20 \times 10^{-4} = \frac{2.303}{t} \log 1.6666$

or $$\log 1.666 = \frac{1.2 \times 10^{-4} \times t}{2.303} \quad \text{or} \quad 0.2218 = \frac{1.2 \times 10^{-4} \times t}{2.303}$$

or $$t = \frac{2.303 \times 0.2218}{1.2 \times 10^{-4}} = 4256.7 \text{ years.}$$

SUMMARY

1. Particles having the same atomic number but different atomic masses are called *isotopes*, while those having different atomic numbers but same atomic mass are called *isobars*. Particles having equal number of neutrons are called *isotones*.
2. *Methods* which are used for the separation of isotopes are gaseous diffusion, thermal diffusion, electromagnetic method, fractional distillation, electrolytic method, chemical exchange method and centrifugal method.
3. According to *meson theory*, π-mesons act as a glue binding the protons and neutrons together in a nucleus.
4. Nuclei of radioactive elements lie *above* and *below* the belt of stability.
5. According to *liquid drop model*, the nucleus is like a droplet of incompressible and homogeneous liquid and all nuclei have same density.
6. As per *shell model*, each nucleon moves independently in an average potential generated by the remaining nucleus.
7. Nuclei with 2, 8, 20, 28, 50, 82 and 126 neutrons or protons are particularly stable. These numbers are called *magic numbers*.
8. Energy required to break up a nucleus into its individual nucleons is called *binding energy*.
9. Einstein mass energy relation is $E = mc^2$
10. Radioactivity can be detected and measured by (a) Wilson cloud chamber method, (b) Geiger-Muller method, and (c) Scintillation method.
11. Radioactive disintegration follows first-order kinetics
12. When an electron from the nearest orbit, i.e. K-orbit, is absorbed by the nucleus to convert a proton into neutron, this process is known as *K- electron capture*
13. Transmutation of element by conversion of one element into another by artificial means is called *artificial disintegration*.
14. *Artificial* or *induced radioactivity* is a phenomenon in which a new radioactive isotope of an element is formed by artificial transmutation of a stable element.

15. The process of splitting up of a heavy nucleus into two, more or less, equal halves is called *nuclear fission.*

16. The process in which two or more light nuclei are made to combine to give a heavier nuclei is called *nuclear fusion.*

17. The process in which a radioactive isotope is mixed with its nonradioactive variety and the activity of the radioactive isotope is noted after physical, chemical or biological changes, is called *radioactive tracing* or *tracer technique.*

KEY RELATIONS

1. Packing fraction = $\frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$

2. $\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$

3. Average life $\left(\frac{1}{\lambda}\right) = 1.44\, t_{0.5}$

4. $\frac{N_1}{N_2} = \frac{K_2}{K_1} = \frac{\lambda_1}{\lambda_2}$

EXERCISES

Based on Different University Papers

Multiple-Choice Questions

1. Isotopes are atom having the
   (a) same atomic number but different atomic masses
   (b) different atomic numbers but same atomic mass
   (c) same atomic number and atomic mass
   (d) different atomic numbers and atomic masses
2. The stable end product in the uranium series ($^{238}_{92}U$) is
   (a) $^{205}_{82}Pb$
   (b) $^{206}_{82}Pb$
   (c) $^{207}_{82}Pb$
   (d) $^{208}_{82}Pb$
3. $^{30}_{14}Si$, $^{31}_{15}P$ and $^{32}_{16}S$ are
   (a) isotopes
   (b) isobars
   (c) isotones

(d) none of these

4. Magic numbers as applied to stability of atom are
   (a) 1, 7, 19, 27
   (b) 3, 9, 21, 29
   (c) 10, 20, 30, 40
   (d) 2, 8, 20, 28
5. Which of the following is not a method of detection and measurement of radioactivity?
   (a) Slater method
   (b) Wilson cloud chamber method
   (c) Geiger-Muller counter
   (d) Scintillation method
6. The reaction ${}_1^1H + {}_1^1H + 2\,{}_0^1n \longrightarrow {}_2^4He$ + Energy is an example if
   (a) capture reaction
   (b) spallation reaction
   (c) fusion reaction
   (d) fission reaction
7. When an atom emits an α-particle, for the new atom formed,
   (a) the atomic number is decreased by one unit and the atomic mass is increased by one unit
   (b) the atomic number is decreased by one unit and the atomic mass is decreased by two units
   (c) the atomic number is decreased by two units and atomic mass is increased by four units
   (d) the atomic number is decreased by two units and atomic mass is decreased by four units

Answers

1. (a)
2. (b)
3. (c)
4. (d)
5. (a)
6. (c)
7. (d)

SHORT-ANSWER QUESTIONS

1. Give the parent atom and stable end product in uranium, actinium and thorium series.
2. Draw the electronic configurations of isobars of argon.

3. Which of the quantities—atomic number, mass number and neutrons are same and which are different for isotopes, isobars and isotones?
4. Describe the gaseous diffusion method for the separation of isotopes with the help of a labelled diagram.
5. Give the symbol, charge and mass for the following particles: position, neutrino, photon.
6. How does meson theory explain the stability of the nucleus?
7. What is meant by zone of stability? Indicate with the help of a diagram.
8. Give the main points of liquid drop model to explain stability of the nucleus
9. Write notes on the following: (a) Binding energy (b) Mass defect
10. Describe Wilson cloud chamber method for the detection and measurement of radioactivity
11. Write notes on the following:
    (a) Half-life of a radioactive substance
    (b) Average life
12. Give one example of each type of the reaction given below.

$(n, \alpha\text{-type}), (n - p - \text{type})(n, 2n - \text{type})$

GENERAL QUESTIONS

1. What are isotopes? How do we represent them? Represent the isotopes of oxygen and carbon
2. Write detailed notes on the following:
    (a) Isotopes
    (b) Isobars
    (c) Isotones
3. Discuss any two methods for the separation of isotopes of a substance.
4. Compare and contrast liquid drop model and shell model to explain stability of the nucleus.
5. What is Einstein mass-energy relation? Convent 1 g of matter energy in MeV units.
6. (a) What is the importance of binding energy curve?
    (b) What is packing fraction? What is its significance?
7. Discuss the theory of radioactive disintegration with suitable examples.
8. Derive an equation for the rate of radioactive disintegration. How are the half life and average life related?
9. Give one example of each of the following types of reactions.

α, n type, α, p type, p, α type, p, n type and n, $2n$ type

10. Write notes on the following:
    (a) Capture reactions
    (b) Particle-particle reactions
    (c) Spallation reactions
11. What is meant by Q-value of a nuclear reaction? How is it calculated?
12. Write notes on

(a) Hydrogen bomb

(b) Cobalt bomb

13. Discuss any four applications of radioactivity.

14. What is tracer technique? What are its applications?

15. Write short notes on

(a) Radioactive series

(b) Nuclear fission

(c) Tracer technique

(d) Geiger-Muller counter

16. $^{210}_{84}Po$ decays to give alpha particles and $^{206}_{82}Pb$ with a half life of 138.4 days. If 1.0 g ^{210}Po is placed in a sealed tube, how much helium will accumulate in 69.2 days? Express the answer in cm^3 at STP.

[Ans. 31.248 cm^3]

17. (a) Define radioactive constant and derive the relation between decay constant and number of particles left at time *t*.

(b) Half-life period of thorium is 24.5 minutes. How much thorium would be left after 30 minutes if the initial amount of thorium is one gram? **[Ans.** (b) 0.429 g]

18. A sample of ^{238}U (half-life = 4.5×10^9 years) ore is found to contain 23.8 g of ^{238}U, and 20.6 g of ^{206}Pb. Calculate the age of the ore. **[Ans.** 4.50×10^9 years]

19. Calculate the time required for a radioactive sample to lose one-third of the atoms of its parent isotope. The half-life is 33 min. **[Ans.** 19.31 min]

20. The mass number and atomic number of a radioactive element actinium are 227 and 89 respectively. Calculate the number of α and β particles emitted if the mass number and atomic number of the new element lead are 207 and 82 respectively. **[Ans.** 5 α and 3 β]

21. A piece of wood recovered in excavation has 30% as much $^{14}_{6}C$ as a fresh wood today. Calculate the age of the excavated piece assuming half-life period of $^{14}_{6}C$ as 5700 years. **[Ans.** 9908 years]

22. What do you mean by tracer technique? Write different applications of tracer techniques.

23. (a) What is group displacement law in radioactivity? What is binding energy and how is it related to mass number of the nucleus?

(b) A radioactive isotope has half-life of 20 days. What is the amount of isotope left over after 40 days if the initial amount is 5 g? **[Ans.** (b) 1.25 g]

24. Calculate the number of α and β particles emitted in the conversion of thorium $^{232}_{90}Th$, to Lead, $^{206}_{82}Pb$.

[Ans. 6 α and 4 β]

25. The half-life of cobalt-60 is 5.26 years. Calculate the percentage activity after eight years.

[Ans. 34.87%]

26. An old wooden article shows 2.0 counts per minute per gram. A fresh sample of wood shows

15.2 counts per minute per gram. Calculate the age of the wooden article. ($t_{1/2}$ of ^{14}C = 5760 years).

[**Ans.** 1686.6 years]

27. Calculate the age of a tooth in which ^{14}C activity is 20% of the activity found at the present time ($t1/2$ for ^{14}C = 5580 years) **[Ans.** 12961.4 years]

28. The activity of a radioactive sample falls to 85% of the initial value in four years. What is the half-life of the sample? Calculate the time by which activity will fall by 85%.

[Ans. 17.05 years; 46.735 years]

29. (a) Write a note on nuclear fission and nuclear fusion.

    (b) What are nuclear reactions? How are they classified? Explain with examples.

30. Write notes on

    (a) Nuclear fusion

    (b) Nuclear binding energy

    (c) Tracers and their applications

31. (a) Give the details of the application of ^{14}C isotope in carbon dating. How is the age of an old wooden sample determined?

    (b) The rate of disintegration of an old wooden sample was found to be 25% as compared to a fresh identical sample. Find out the age of the old sample (Half life of C^{14} = 5760 years).

[Ans.(b) 11525 years]

32. (a) Calculate the (a) Mass defect, (ii) binding energy per nucleon of $^{12}_{6}C$ (Given ^{12}C = 12.0038 amu; H^1 = 1.0081 amu; n^1 = 1.0089 amu)

    (b) What is artificial radioactivity? Give two examples.

33. (a) What is group-displacement law of radioactivity? How does it throw light on the idea of radioactive isotopes?

    (b) The half-life of a radioactive isotope is 47.2 seconds. Calculate N/N_0 left after one hour.

[Ans. (b) 1.12×10^{-23}]

34. Write short notes on

    (a) Mass defect

    (b) Packing fraction

    (c) Nuclear fission

    (d) Half-life period

35. (a) Discuss the stability of the nucleus under the following heads:

        (i) Binding energy per nucleon

        (ii) Neutron-proton ratio and odd-even rule

    (b) What is the difference between fission and fusion reactions?

    (c) How do two isotopes of elements differ in the number of nucleons?

36. Explain:

    (a) Radioactive dating

(b) Average life

(c) Radioactive equilibria

37. Write short notes on

(a) Carbon dating

(b) Nuclear reaction

38. (a) What is group-displacement law? Explain with examples.

(b) How does discovery of isotopes help in explaining fractional atomic weight of elements? Mention some applications of radioactivity.

39. Define binding energy of a nucleus. Explain with the help of binding energy curve, the stability of the nuclei.

40. (a) How many α and β-particles are emitted for the transformation

$$^{232}_{90}Th \longrightarrow {}^{208}_{82}Pb$$

(b) What is a nuclide? Mention different kinds of nuclides with suitable examples.

(c) What is a nuclear reactor? Describe its main parts briefly.

41. Give the postulates of theory of radioactive emissions.

42. Derive an expression for the disintegration constant of a radioactive element and show that decay of the element is exponential.

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