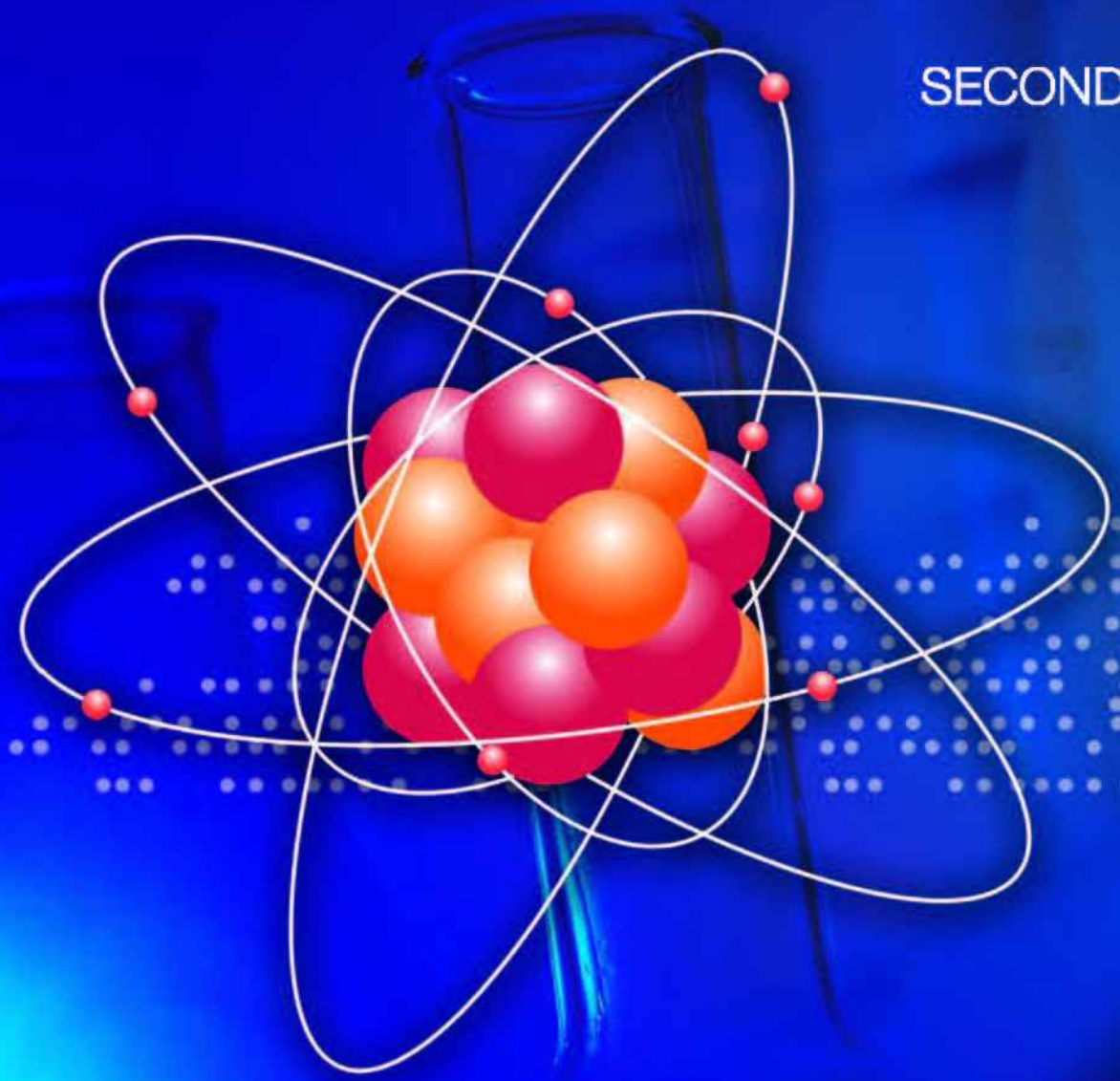
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Fundamentals of PHYSICAL CHEMISTRY

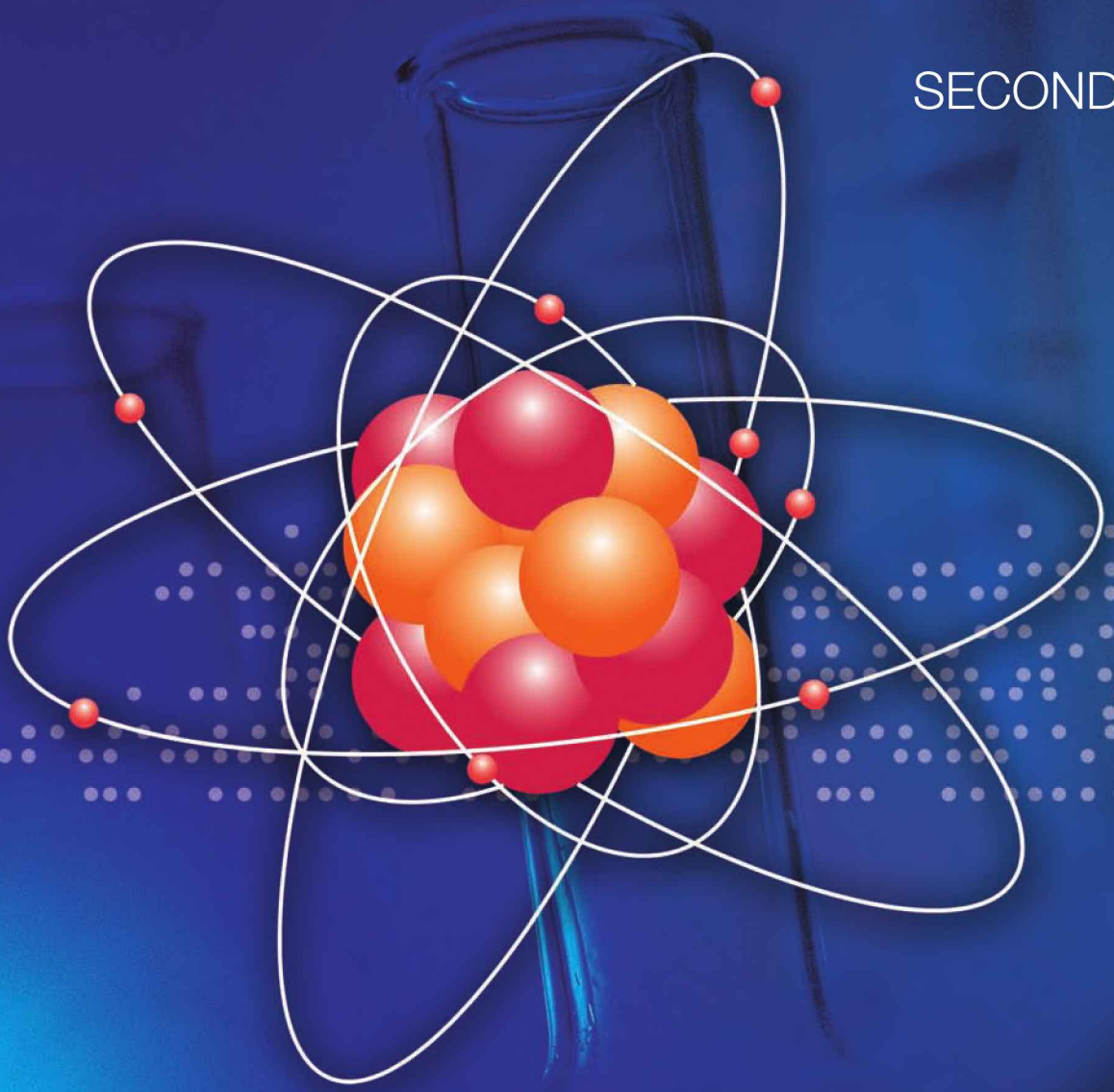
for Competitive Examinations

Ananya Ganguly

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SECOND EDITION



Fundamentals of PHYSICAL CHEMISTRY

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Fundamentals of
Physical Chemistry
for Competitive Examinations

Second Edition

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PEARSON

Chandigarh • Delhi • Chennai

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Preface to the Second Edition

The response to the first edition of the book and positive feedback from teachers and students has motivated me to work upon this revised and thoroughly pruned edition.

I hope that students will find this book useful. All the best!

Ananya Ganguly

Preface

In recent years, the question format of non-medical examinations like IIT-JEE and AIEEE has been restructured with greater emphasis on the theoretical and conceptual intricacies and the application of the underlying basic concepts and principles.

The poor performance of students in these examinations is partly due to non-availability of a comprehensive text book which lays adequate stress on the authentic logical theoretical concept building, numericals and related problems.

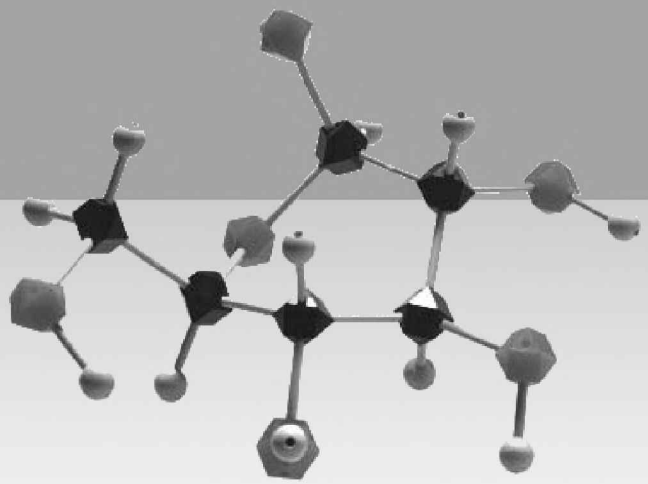
The present book grew out of my experience of classroom teaching through lectures, notes and assignments. Effort has been made to maintain lucid style and simplicity of expression. Apart from this, the book has numerous carefully selected examples and solved illustrations which include almost all the previous years' questions asked in IIT-JEE and AIEEE examinations.

Selected questions of different formats keeping in mind the recent pattern of examinations have been listed at the end of each chapter. Solutions to almost all advanced questions have been incorporated.

I would like to thank Showick Thorpe and Sanjay Sharma for their constant encouragement during the publication of this book. I extend my thanks to Nitkiran Bedi for her contribution in bringing out this book in record time. I am also thankful to the staff members of my academy for their sincere help.

I will appreciate comments, suggestions and criticism from the readers and will incorporate them in the subsequent editions.

Ananya Ganguly



CHAPTER 1

Atomic Structure

DALTON'S ATOMIC THEORY

Assuming that you have studied chemistry before, you would have met the idea that matter is made up of combinations of elements. You would also have learnt that each element has its own type of atom.

The first passable definition of an element was given by Robert Boyle (1627–1691). In his book, '*The Skeptical Chemist*', published in 1661, he proposed that the elements are,

> *... certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those perfectly mixed bodies are immediately compounded, and into which they are ultimately resolved.*

John Dalton (1766-1844) developed his atomic theory. In 1803, Dalton proposed that,

- Each element has its own unique type of atom.
- All atoms of an element are identical.
- The atoms of each individual element have the same size, and the same weight (the atomic weight).
- When elements combine together, the atoms of one element are not changed into those of another element.
- When elements combine together, their atoms join together in fixed proportions

Drawbacks

The researches done by various eminent scientists and the discovery of radioactivity have established beyond doubt that atom is not the smallest indivisible particle but has a complex structure of its own and is made up of still smaller particles like electrons, protons, neutrons etc. At present, 35 different subatomic particles are known but the three particles namely electrons, protons, and neutrons are regarded as the fundamental particles.

(i) It fails to explain why atoms of different kinds should differ in mass and valency etc.

(ii) The discovery of isotopes and isobars showed that atoms of same elements may have different masses (isotopes) and atoms of different kinds may have same atomic masses (isobars).

(iii) The discovery of various sub-atomic particles like X-rays, electrons, protons etc., during late 19th century lead to the idea that the atom was no longer an indivisible and smallest particle of the matter.

Models of Atoms

As it was experimentally well established that atom consisted of different particles, there have been attempts to present different models of atom.

Thomson's Model

The discovery that atoms contained electrons caused some consternation. Left to themselves, atoms were known to be electrically neutral; so the negative charge of the electrons had to be balanced by an equal amount of positive charge. The puzzle was to work out how the two types of charges were arranged. An initial guess made by Sir J. J. Thomson was that the electrons were embedded in a ball of positive charge (Figure 1.1). This model of the atom was given the rather unlikely name of the 'plum pudding' model. If you were to put an imaginary hand into an atom you might be lucky enough to pull out an electron; just like the nursery rhyme character Little Jack Horner, who was fortunate enough to put his hand into a pie and pull out a plum.

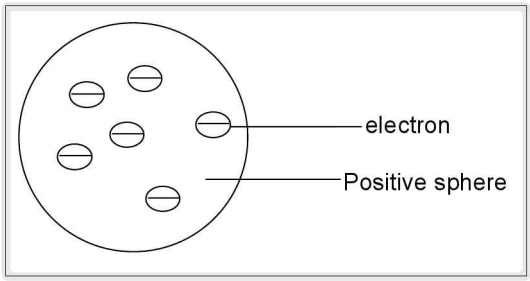


Fig. 1.1

Cathode Rays and Discovery of Electron

Gases are normally poor conductor of electricity at ordinary or high pressure. However, when a tube filled with a gas is evacuated to a pressure of 0.01 mm Hg or lower and an electric potential is applied across a pair of electrodes into the tube, discharge takes place between the electrodes during which a stream of rays moves from cathode to anode. William Crookes (1879) called these rays as cathode rays.

Discovery of electron

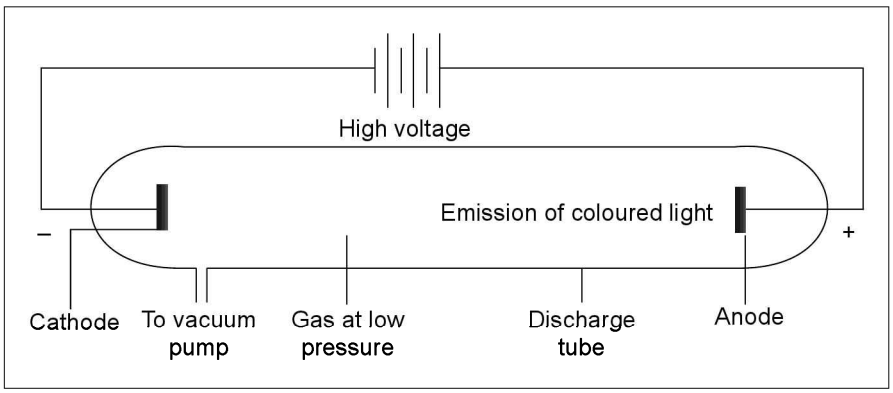


Fig. 1.2

Properties of cathode rays

1. Cathode rays travel in straight lines with a high speed approaching to that of light. Their linear propagation is shown by the fact that they caste shadows of the solid objects placed in their path.
2. They produce temperature rise in any object they strike.
3. They pass through thin films of metals but are stopped by thicker foils
4. Cathode rays can produce mechanical effect e.g., when allowed to fall on a small paddle wheel they cause rotation of wheel. This experiment shows that cathode rays consist of material particles.
5. The cathode rays can be deflected by electric and magnetic field. The direction of deflection is always such that these particles bear a negative charge.

6. Finally, no matter what the nature of the cathode or the gas in the discharge tube, the negatively charged particles are always the same as reflected by the same e/m ratio by J.J. Thomson.
   These particles constituting cathode rays have been named electron by J.J. Thomson. The fact that electrons are independent of the nature of source from which they come suggest that they are constituent of all elements.
   Thomson determined e/m ratio of electrons by applying electric and magnetic field

Method of experimental determination of e/m

$\frac{e}{m}$ of electron = 1.7588×10^{11} c/kg = 1.7588×10^{8} c/g

Determination of charge of electron

An American physicist R.A. Millikan determined charge on electron by oil drop experiment. Charge on electron = 1.6022×10^{-19} coulombs, from the data obtained from the above two experiments, mass of electron can be calculated.

$$m = \frac{e}{\frac{e}{m}} = 9.1 \times 10^{-28} g$$

Positive rays (anode rays) or canal rays

Since electrons an essential constituent of atom and since atom as a whole is electrically neutral, it follows that an equal magnitude of positive charge must be present in an atom. In 1886, Goldstein discovered that there are present in a discharge tube not only cathode rays composed of electrons moving towards anode but also positive rays moving in opposite direction. By perforating the cathode these positive rays can be made to pass through the hole. The properties of positive rays were investigated by J.J. Thomson.

Discovery of proton

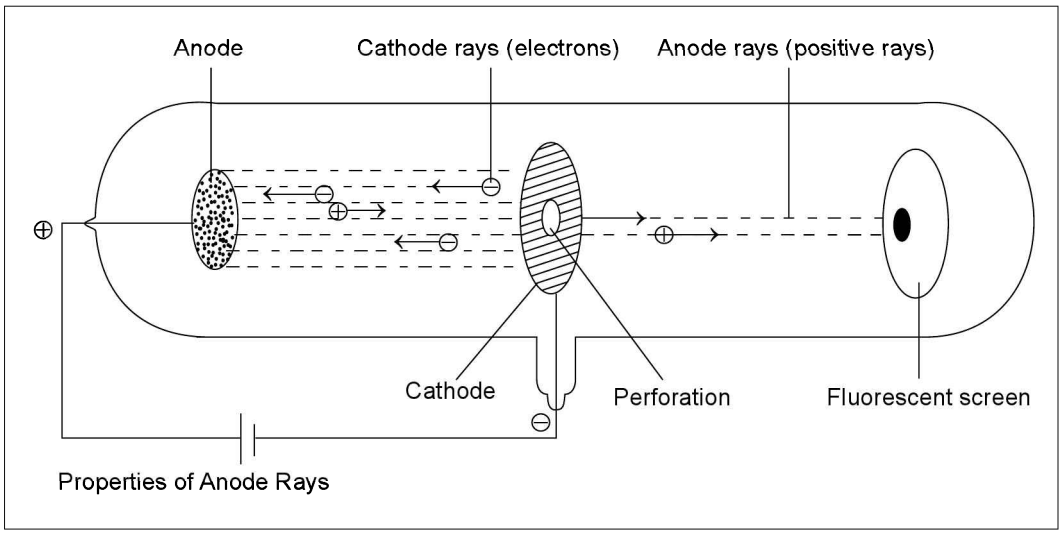


Fig. 1.3

(i) They are deflected in electric and magnetic field just as cathode rays but in the opposite direction showing that they consist of positively charged particles.

(ii) The charge and mass of the particles constituting anode rays vary and depend upon the nature of gas contained in the discharge tube.

(iii) Positive rays are not emitted by anode but originate between the electrodes from the ionization of gas atoms. The mass of positively charged particle is virtually the same as that of the atoms from which they are derived. Wein (1898) determined the value of e/m for positive particles and found

that it was different for different gases. When hydrogen gas was taken in the discharge tube, the lightest positively charge particle was found. Its mass was nearly the same as that of H atom (1.673×10^{-24} g) and carried a positive charge exactly equal and opposite to that of an electron. This positively charged particle was named proton.

Discovery of neutron

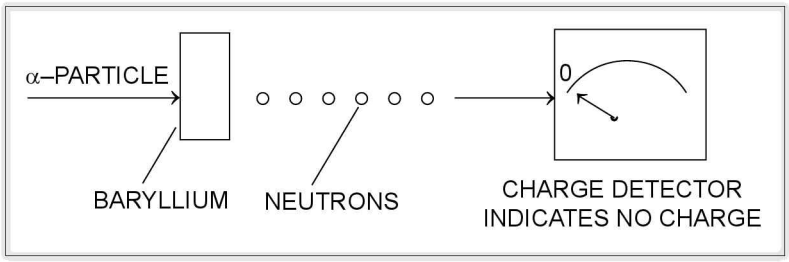
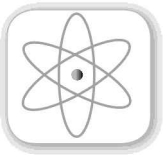


Fig. 1.4

Chadwick in 1932, performed some scattering experiment in which he bombarded some light elements like beryllium and boron with the fast moving α particles. He found that some new particles were emitted which carried no charge i.e., were neutral but had a mass equal to that of proton. This particle was termed neutron having no charge but mass equal to that of hydrogen atom or proton.

DISCOVERY OF NUCLEUS



α-particles emitted by radioactive substance were shown to be dipositive Helium ions (He^{++}) having a mass of 4 units and 2 units of positive charge.

In 1909, H. Geiger and E. Marsden published the results of a series of experiments that they had carried out at the University of Manchester under the direction of Ernest (later Lord) Rutherford.

One of the early discoveries was that some elements gave off alpha-particles (∝particles), that is, α-particles were helium ions, He^{2+}. Geiger and Marsden directed a stream of α-particles at thin metal foils Rutherford allowed a narrow beam of α-particles to fall on a very thin gold foil of thickness of the order of 0.0004 cm and determined the subsequent path of these particles with the help of a zinc sulphide fluorescent screen. The zinc sulphide screen gives off a visible flash of light when struck by an α particle, as ZnS has the remarkable property of converting kinetic energy of α particle into visible light. [For this experiment, Rutherford specifically used α particles because they are relatively heavy resulting in high momentum].

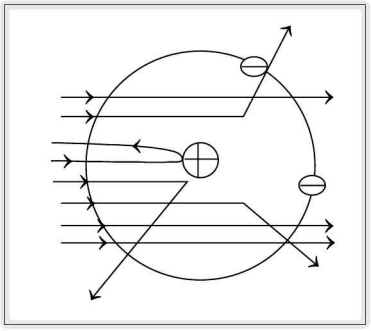


Fig. 1.5



Observation

(i) Majority of the α-particles pass straight through the gold strip with little or no deflection
(ii) Some α-particles are deflected from their path and diverge.
(iii) Very few α-particles are deflected backwards through angles greater than 90°.
(iv) Some were even scattered in the opposite direction at an angle of 180° [Rutherford was very much surprised by it and remarked that "It was as incredible as if you fired a 15 inch shell at a piece of tissue paper and it came back and hit you"]
(v) The number of alpha particles scattered through a given angle was proportional to the thickness of the foil, and the square of the nuclear charge and inversely proportional to the fourth power of the velocity of the alpha particle.

The numbers of α-particles scattered by a gold foil in Geiger and Marsden's experiments

Angle of deflection/degrees	*Percentage of α-particles deflected*
15	93
30	5
45	1
60	0.34
120	0.037
150	0.023

Conclusions

1. The fact that most of the α-particles passed straight through the metal foil indicates the most part of the atom is empty.
2. The fact that few α-particles are deflected at large angles indicates the presence of a heavy positively charge body i.e., for such large deflections to occur, α-particles must have come closer to or collided with a massive positively charged body.
3. The fact that one in 20,000 have deflected at 180° backwards indicates that volume occupied by this heavy positively charged body is very small in comparison to total volume of the atom.

Atomic Model

On the basis of the above observation, Rutherford proposed an atomic model as follows;

(i) All the protons (+ve charge) and the neutrons (neutral charge) i.e., nearly the total mass of an atom is present in a very small region at the centre of the atom. The atom's central core is called nucleus.
(ii) The size of the nucleus is very small in comparison to the size of the atom. Diameter of the nucleus is about 10^{-13}cm while the atom has a diameter of the order of 10^{-8} cm. So, the size of atom is 10^5 times more than that of nucleus.
(iii) Most of the space outside the nucleus is empty.
(iv) The electrons, equal in number to the net nuclear positive charge, revolve around the nucleus with fast speed in various circular orbits.
(v) The centrifugal force arising due to the fast speed of an electron balances the coulombic force of attraction of the nucleus and the electron remains stable in its path. Thus, according to him, atom consists of two parts (a) nucleus and (b) extra nuclear part.

The neutral charge particle, neutron was discovered by James Chadwick by bombarding boron or beryllium with α-particles.



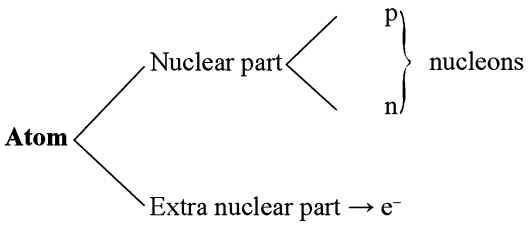
Worked-out Example

1. Rurtherford's experiment, which established the nuclear model of the atom, used a beam of **[IIT-JEE-2002]**

(a) β-particles, which impinged on a metal foil and got absorbed
(b) γ-rays, which impinged on a metal foil and ejected electrons
(c) helium atoms, which impinged on a metal foil and got scattered
(d) helium nuclei, which impinged on a metal foil and got scattered

Solution (d) Rutherford's experiment was actually α-particle scattering experiment, α-Particle is doubly positively charged helium ion i.e., He-nucleus.

Subatomic (fundamental) particle



	Electron	*Proton*	*Neutron*
Discoverer	J.J. Thomson (1897)	E. Goldstein (1911)	James Chadwick (1932)
Position	Moves around the nucleus	Constituent of nucleus	Constituent of nucleus
Symbol	e or e^-	P	n
Approximate relative mass	1/1836	1	1
Approximate relative charge	–1	+1	No charge
Mass in kg	9.109×10^{-31}	1.673×10^{-27}	1.675×10^{-27}
Mass in amu	5.485×10^{-4}	1.007	1.008
Actual charge	1.602×10^{-19}	1.602×10^{-19}	0

How these fundamental particles go to make the internal structure of the atom, is a fascinating story. The main landmarks in the evolution of atomic structure are:

1896	J.J. Thomson's discovery of the electron and the proton
1909	Rutherford's Nuclear Atom
1913	Mosley's determination of Atomic Number
1913	Bohr Atom
1921	Bohr-Bury Scheme of Electronic Arrangement
1932	Chadwick's discovery of the neutron.

The atomic mass unit (amu) is 1/12 of the mass of an individual atom of ${}_6C^{12}$, i.e., 1.660×10^{-27} kg.

The neutron and proton have approximately equal masses of 1 amu and the electron is about 1836 times lighter, its mass can sometimes be neglected as an approximation.

The electron and proton have equal, but opposite, electric charges while the neutron is not charged.

Quarks

A **quark** is an elementary particle and a fundamental constituent of matter. Quarks combine to form composite particles called hadrons, the most stable of which are protons and neutrons, the components of atomic nuclei. Due to a phenomenon known as *colour confinement*, quarks are never found in isolation; they can only be found within hadrons For this reason, much of what is known about quarks has been drawn from observations of the hadrons themselves.

There are six types of quarks, known as *flavours*: up, down, charm, strange, top, and bottom. Up and down quarks have the lowest masses of all quarks. The heavier quarks rapidly change into up and down quarks through a process of particle decay: the transformation from a higher mass state to a lower mass state. Because of this, up and down quarks are generally stable and the most common in the universe, whereas charm, strange, top, and bottom quarks can only be produced in high energy collisions (such as those involving cosmic rays and in particle accelerators).

Quarks have various intrinsic properties, including electric charge, color charge, spin, and mass. Quarks are the only elementary particles in the Standard Model of particle physics to experience all four

fundamental interactions, also known as *fundamental forces* (electromagnetism, gravitation, strong interaction, and weak interaction), as well as the only known particles whose electric charges are not integer multiples of the elementary charge. For every quark flavour there is a corresponding type of antiparticle, known as *antiquark*, that differs from the quark only in that some of its properties have equal magnitude but opposite sign.

The quark model was independently proposed by physicists Murray Gell-Mann and George Zweig in 1964. Quarks were introduced as parts of an ordering scheme for hadrons, and there was little evidence for their physical existence until 1968. All six flavours of quark have since been observed in accelerator experiments; the top quark, first observed at Fermilab in 1995, was the last to be discovered

Atomic terms

(a) Atomic Number (Z)

The atomic number of an element is the number of protons contained in the nucleus of the atom of that element.

(b) Nucleons

Protons and neutrons are present in a nucleus. These fundamental particles are collectively known as nucleons.

(c) Mass Number (A)

The total number of protons and neutrons i.e., the number of nucleons present in the nucleus is called the mass number of the element.

(d) Nuclides

Various species of atoms in general. A nuclide has specific value of atomic number and mass number.

IUPAC notation of an atom (nuclide)

Let X be the symbol of the element. Its atomic number be Z and mass number be A. Then the element can be represented as ${}_{Z}X^{A}$.

(e) Isotopes

Atoms of the element with same atomic number but different mass number example, ${}_{1}H^{1}$, ${}_{1}H^{2}$, ${}_{1}H^{3}$. There are three isotopes of hydrogen.

(f) Isobars

Atoms having the same mass number but different atomic numbers, example ${}_{15}P^{32}$ and ${}_{16}S^{32}$ are called isobars.

(g) Isotones

Atoms having the same number of neutrons but different number of protons or mass number, example ${}_{6}C^{14}$, ${}_{8}O^{16}$, ${}_{7}N^{15}$ are called isotones.

(h) Isoelectronic

Atoms, molecules or ions having same number of electrons are isoelectronic, example N_2,CO, CN^-.

(i) Nuclear isomers

Nuclear isomers (isomeric nuclei) are the atoms with the same atomic number and same mass number but with different radioactive properties.

Example of nuclear isomers is,

Uranium –X (half life 1.4 min) and

Uranium –Z (half life 6.7 hours)

The reason for nuclear isomerism is the different energy states of the two isomeric nuclei.

Other examples are:

${}_{30}Zn^{69}$	${}_{30}Zn^{69}$
($T_{1/2}$ = 13.8 hr)	($T_{1/2}$ = 57 min)
${}_{35}Br^{80}$	${}_{35}Br^{80}$
($T_{1/2}$ = 4.4 hour)	($T_{1/2}$ = 18 min)

(j) Isosters

Molecules having same number of atoms and also same number of electrons are called isosters.

Example

(i) N_2 and CO (ii) CO_2 and N_2O

(iii) HCl and F_2

(k) Atomic mass unit

Exactly equal to 1/12 of the mass of ${}_6C^{12}$ atom

1 amu = 1.66×10^{-27} kg

Worked-out Examples

2. The mass of a hydrogen atom is ..... kg. **[IIT-JEE-1982]**

Solution 1.66×10^{-27}

3. Isotopes of an element differ in the number of..... in their nuclei. **[IIT-JEE-1982]**

Solution neutrons

4. Elements of the same mass number but of different atomic numbers are known as..... **[IIT-JEE-1983]**

Solution isobars

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Distance of closest Approach/effective radius of nucleus

Let us consider an α particle approaching straight towards the nucleus of atomic number 'z'

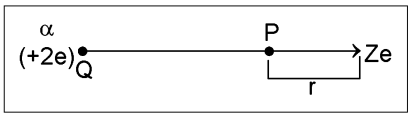


Fig. 1.6

As it moves closer to nucleus, the velocity will decrease due to repulsion between α particle and the nucleus (note that they are charged alike). As the α particle reaches the point 'P' its velocity becomes zero and particle will turn back on its own pattern. The distance of point 'P' from the nucleus is 'r'. This 'r' is know as the distance of closest approach or effective radius of nucleus.

As the α particles approaches towards the nucleus, the kinetic energy will decrease and potential energy will increase but total energy remains constant of any point of time.

Potential energy of α particle at point Q (in figure 1.6) = 0 (no interaction, far apart from nucleus

Kinetic energy of α particle at point Q (in figure 1.6) $= \frac{1}{2}mv^2$

m = mass of α particles

V → linear velocity of the alpha particle with which it is projected

At point 'Q' Total Energy = KE

Kinetic Energy A point 'P' = O

Potential Energy at point 'P' $= \frac{q_1 \times q_2}{r} K$

q_1 = charge on particles

q_2 = charge on nucleus

The difference between effective radius and radius of nucleus is very small.

$$P.E. = \frac{(2e)(Ze)}{r} K .$$

K = Permitivity constant

T.E = P.E

K.E. at Q = PE at P

$$\frac{1}{2} mv^2 = \frac{2Ze^2}{r} K$$

$$r = \frac{4Ze^2 K}{mv^2}$$

Higher the velocity of α particle, less will be effective radius. The α particle cannot approach the nucleus closer than r.

- Value of r will decrease with increase in velocity
- Value of r will increase with increase in Z.

When we change over from electrostatic units to SI units the interaction between two charged particles is given by:

$$F = k \frac{q_1 q_2}{r^2}$$

where ε_0 is a constant called the permittivity of vacuum i.e., free space. Permittivity of free space, ε_0, has a value

$8.854 \times 10^{-12}\ kg^{-1}\ m^{-3}\ s^4\ A^2$ (s = sec; A = ampere)

Then $r = 4K \frac{Ze^2}{mv^2}$

C.G.S. Unit	***S.I. Unit***
Z = atomic no. of metal (unitless) K = 1	Z = no unit
$e = 4.8 \times 10^{-10}$ e.s.u.	$K = 9 \times 10^9\ N\ m^2 C^{-2}$
m = mass of α particle = 4 a.m.u. $\times$ 4 $\times$ 10^{-10} e.s.u. or 4 a.m.u. $\times$ 1.66×10^{-24} g	$e = 1.6 \times 10^{-19}$ C
V = cm/s	m = 4 a.m.u. = 4 a.m.u. $\times$ 1.66×10^{-27} kg
r = cm	V = m/s
	r = m



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Worked-out Example

5. Calculate the effective radius of $_{29}Cu^{63}$ if α particle is projected on the nucleus with velocity 10^6 m/s. at mass = 63

Solution $r = \frac{4.Ze^2K}{mV^2}$

$$= \frac{4 \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9 \, Nm^2C^{-2} \times 29}{1 \times 1.66 \times 10^{-27} \times 10^{-6} \times 10^{-5}}$$

$= 4.025 \times 10^{-12}$ m

If Z is more than repulsion is more to +ve particle so effective radius will increase and if more velocity with which α particle is approaching then effective r will decrease because it will go nearer to the nucleolus.

From Rutherford's Atomic Model

Consider an electron of mass 'm' and charge 'e' revolving around a nucles of charge Ze (where, Z = atomic number and e is the charge of the proton) with a tangential velocity v. r is the radius of the orbit in which electron is revolving.

By Coulomb's Law, the electrostatic force of attraction between the moving electron and nucleus is

$$\text{Coulombic force} = \frac{KZe^2}{r^2}$$

$$K = \frac{1}{4\pi \in_o} \text{ (Where } \in_o \text{ is permittivity of free space)}$$

$K = 9 \times 10^9 \, Nm^2 \, C^{-2}$

In C.G.S. units, value of K = 1 dyne cm^2 $(esu)^{-2}$

The centrifugal force acting on the electron is $\frac{mv^2}{r}$.

Since the electrostatic force balance the centrifugal force, for the stable electron orbit.

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \quad \ldots (1)$$

$$(\text{or}) \; v^2 = \frac{KZe^2}{mr} \quad \ldots (2)$$

The total energy, (T.E.) of the electron is the sum of kinetic energy (K.E.) and potential energy (P.E.).
Kinetic energy of the electron = ½ mv^2

$$\text{Potential energy} = \frac{-KZe^2}{r}$$

P.E. α r (because of –ve sign)

$$\text{Total energy} = 1/2 \; mv^2 - \frac{KZe^2}{r} \quad \ldots (4)$$

From equation (1) we know that,

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

$$\therefore \quad \tfrac{1}{2} mv^2 = \frac{KZe^2}{2r} = \text{K.E. of electron}$$

$$\text{K.E.} \ \alpha \ \frac{1}{r} \ (\text{If r increase KE decreases})$$

Substituting this in equation (4),

$$\text{Total energy (E)} = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

As we move away from the nucleus the following changes are observed.

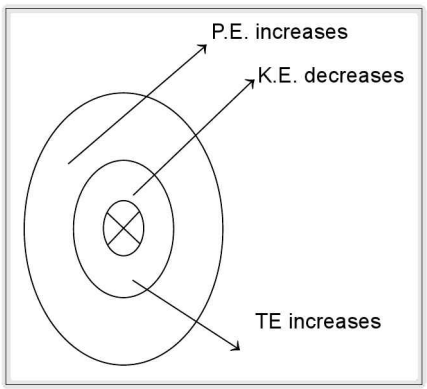


Fig. 1.7

The closer the e^- to the nucleus the greater the velocity.
As we move away from nucleus P.E. will increase but K.E. will decrease.

Total Energy = T.E. = P.E. + K.E.

$$= \left(-\frac{Ze^2K}{r} + \frac{Ze^2K}{2r}\right) \quad TE = -\frac{Ze^2k}{2r}$$

T.E. α r

$$\frac{PE}{KE} = -\frac{Ze^2K}{r} \times \frac{2r}{Ze^2k}$$

P.E. = –2K.E.

Magnitude of P.E. is twice the magnitude of kinetic energy.

TE = – K.E.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Defects of Rutherford's Atomic Model

Rutherford's theory was based on classical mechanics.

According to classical mechanics, any energy level is acceseble because energy levels are continuous. Hence, the radius 'r' can have any value) and Electromagnetic theory is based on classical mechanics.

IN A NUTSHELL

Electromagnetic radiation

Electromagnetic radiation in the form of self-propagating waves in a vacuum or in matter. It comprises electric and magnetic fiel components, which oscillate in phase perpendicular to each other and perpendicular to the direction of energy propagation. Electromagnetic radiation is classified into several types according to the frequency of its wave; these types include (in order of increasing frequency and decreasing wavelength): radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays. A small and somewhat variable window of frequencies is sensed by the eyes of various organisms; this is what is called the visible spectrum. The photon is the quantum of the electromagnetic interaction and the basic "unit" of light and all other forms of electromagnetic radiation and is also the force carrier for the electromagnetic force.

Electromagnetic theory

When a charged particle is accelerated, it creates a magnetic field around itself

Note that electron revolving in a circular orbit has angular acceleration and radiation is a form of energy.

1. **Position of electrons:** The exact positions of the electrons from the nucleus is not mentioned.
2. **Stability of the atom:** Neils Bohr pointed out that Rutherford's atom should be highly unstable. According to the law of electrodynamics, the electron should therefore, continuously emit radiation and lose energy. As a result of this, a moving electron will come closer and closer to the nucleus and after passing through a spiral path, it should ultimately fall into the nucleus with very high velocity.

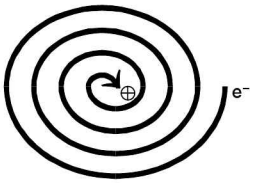


Fig. 1.8

It was calculated that the electron should fall into the nucleus in less than 10^{-8} sec. But it is known that electrons keep moving outside the nucleus.

To solve this problem, Neils Bohr proposed an improved form of Rutherford's atomic model.

Before going into the details of Neils Bohr model we would like to introduce you some important properties of wave.

Properties of wave

A wave is a sort of disturbance which originates from some vibrating source and travels outward as a continuous sequence of alternating crests and troughs. Every wave has five important characteristics, namely, wavelength (λ), frequency (ν), velocity (c), wave number ($\bar{\nu}$) and amplitude (a).

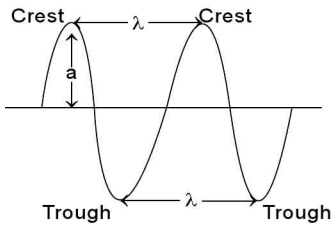


Fig. 1.9

Ordinary light rays, X-rays, γ-rays, etc., are called electromagnetic radiations because similar waves can be produced by moving a charged body in a magnetic field or a magnet in an electric field. These radiations have wave characteristics and do not require any medium for their propagation and all electromagnetic radiations travel with the velocity (e) of light, where $c = 3 \times 10^8\ ms^{-1}$.

(i) **Wave length (λ):** The distance between two neighbouring troughs or crests is known as wavelength. It is denoted by λ and is expressed in cm, m, nanometers (1nm = 10^{-9}m) or Angstrom (1Å = 10^{-10}m).

(ii) **Frequency (ν):** The frequency of a wave is the number of times a wave passes through a given point in a medium in one second. It is denoted by ν(nu) and is expressed in cycles per second (cps) or hertz (Hz) 1Hz = 1cps.

The frequency of a wave is inversely proportional to its wave length (λ)

$$\nu \propto \frac{1}{\lambda} \text{ or } \nu = \frac{c}{\lambda}$$

(iii) **Velocity:** The distance travelled by the wave in one second is called its velocity. It is denoted by c and is expressed in cm sec^{-1}.

$$c = \nu\lambda \text{ or } \lambda = \frac{c}{\nu}$$

(iv) **Wave number ($\bar{\nu}$):** It is defined as number of wavelengths per cm. It is denoted by $\bar{\nu}$ and is expressed in cm^{-1}.

$$\bar{\nu} = \frac{1}{\lambda} \text{ (or) } \bar{\nu} = \frac{\nu}{c}$$

(v) **Amplitude:** It is the height of the crest or depth of the trough of a wave and is denoted by a. It determines the intensity or brightness of the beam of light.

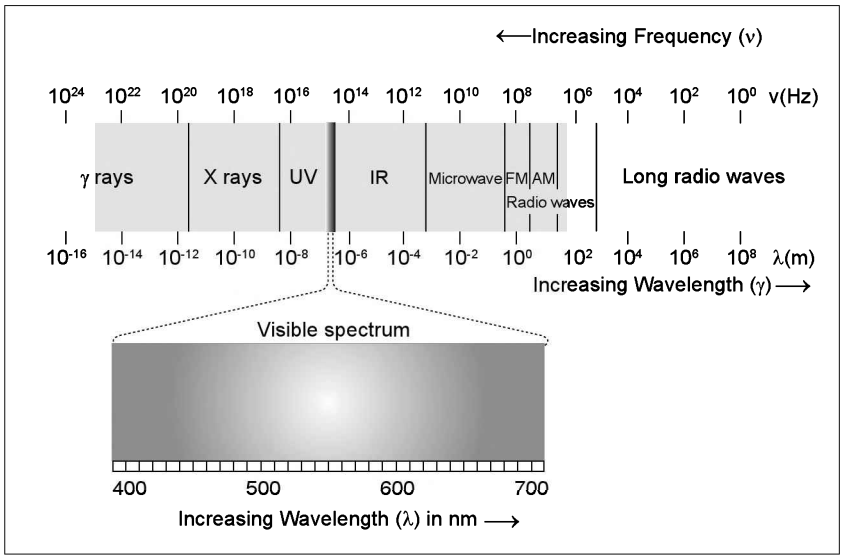


Fig. 1.10

Worked-out Examples

6. Gamma rays are electromagnetic radiations of wavelengths of 10^{-6} cm to 10^{-5} cm. (True or False) **[IIT-JEE-1983]**

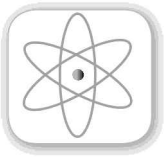
Solution False: Gamma rays are electromagnetic radiations of wavelengths 10^{-9} cm to 10^{-10} cm.

7. Which of the following does not characterize X-rays? **[IIT-JEE-1992]**

(a) The radiation can ionize gases.
(b) It causes ZnS to fluoresce
(c) Can be deflected by electric and magnetic fields
(d) Have wavelengths shorter than ultraviolet rays.

Solution (c) **X-rays:** Radiation can ionize gases and cannot get deflected by electric and magnetic fields, wavelength of these rays is 150 to 0.1 Å.

PLANCK'S QUANTUM THEORY



When a black body is heated, it emits thermal radiations of different wavelengths or frequency. To explain these radiations, Max Planck put forward a theory known as Planck's quantum theory. The main points of quantum theory are:

(i) Substances radiate or absorb energy discontinuously in the form of small packets or bundles of energy.

(ii) The smallest packet of energy is called ***quantum***. In case of light the quantum is known as ***photon.***
Photon → Smallest energy unit of all electromagnetic radiation. All the electromagnetic radiations will travel with same velocity to that of light (whether they are UV, IR, Radiowaves, X ways ray)

According to Quantum Mechanics,

Energy of 1 photon = E_{ph} = Quantum = $h\nu$ h = Plank's constant

$E_{ph} = \frac{h \times C}{\lambda}$ $h = 6.626 \times 10^{-34}$ J.S

C = velocity of light

$= 3 \times 10^8$ m/s (constant)

unit of $E_{ph} = \frac{Js \times ms^{-1}}{m} = J$

According to Quantum Mechanics, only one photon can be taken up at a time i.e., simultaneous absorption of more than 1 photon is not possible.

Hence, energy flow will be discrete (in packets) some specific amount will be absorbed at a time.

Storage of energy will also be discrete.

(iii) The energy of a quantum is directly proportional to the frequency of the radiation. $E \propto \nu$ (or) $E = h\nu$ were ν is the frequency of radiation and h is Planck's constant having the value 6.626×10^{-27} erg–sec or 6.626×10^{-34} J–sec.

(iv) A body can radiate or absorb energy in whole number multiples of a quantum $h\nu$, $2h\nu$, $3h\nu$…… $nh\nu$. where n is the positive integer.

Neils Bohr used this theory to explain the structure of atom.

The Quantum Theory of Radiation

When radiation strikes any surface of a body, part of the radiant energy is generally reflected, part is absorbed, and part is transmitted. The reason for the incomplete absorption is that ordinary bodies are as a rule imperfect absorbers of radiation. In contrast to these we have the *black body*, which by definition is the perfect absorber of energy and retains any radiant energy that strikes it.

Although, a blackened metallic surface or carbon black approximates fairly closely a black body, a hollow sphere, blackened on the inside and with a small opening, meets the denned condition much more satisfactorily. Any radiation that enters through the small opening is reflected repeatedly from the walls of the enclosure until all of the energy eventually becomes absorbed.

A black body is not only a perfect absorber of radiant energy, but also a perfect radiator. In fact, of all bodies heated to a given temperature, it is the black body which will radiate the maximum amount of energy possible for the given temperature. Furthermore, a black body is in thermal equilibrium with its surroundings and radiates in any given time per unit area the same amount of energy as it absorbs.

The total amount of energy E radiated by a black body per unit area and time is given by the *Stefan-Boltzmann fourth power law*, namely,

$$E = \sigma T^4$$

Where T is the absolute temperature, while σ is a universal constant equal to 5.6697×10^{-5} for energy is ergs, time in seconds, and area in square centimeters. This energy is not emitted with a single frequency, nor is it uniformly distributed along the spectrum. Lummer and Pringsheim showed that the energy emitted depends on the temperature and wave length in the manner indicated in Figure 1.11. For

each temperature there is a wavelength at which the energy radiated is maximum. Again, the position of this maximum shifts with increase in temperature toward lower wave lengths, and the maximum itself is the more pronounced the higher the temperature.

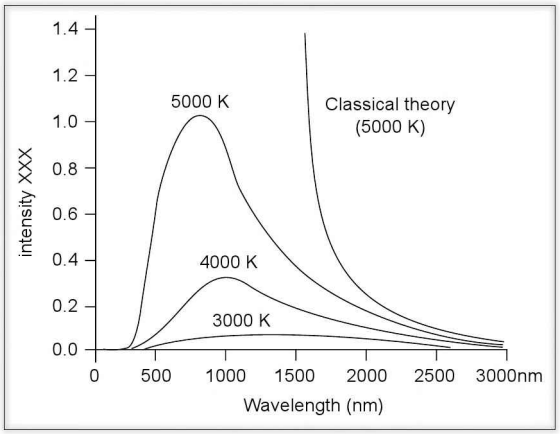


Fig. 1.11

Wien in 1896 and Lord Rayleigh in 1900 made attempts to account for this distribution of black body radiation on the basis of classical concepts of continuous emission of radiation.

Wien's Displacement Law

Wien's displacement law shows how the spectrum of black body radiation at any temperature is related to the spectrum at any other temperature. If we know the shape of spectrum at one temperature, we can calculate the shape at any other temperature.

A consequence of Wien's displacement law is that the wavelength at which the intensity of the radiation produced by a black body is at a maximum, λ_{max}, it is a function only of the temperature:

$$\lambda_{max} = \frac{b}{T}$$

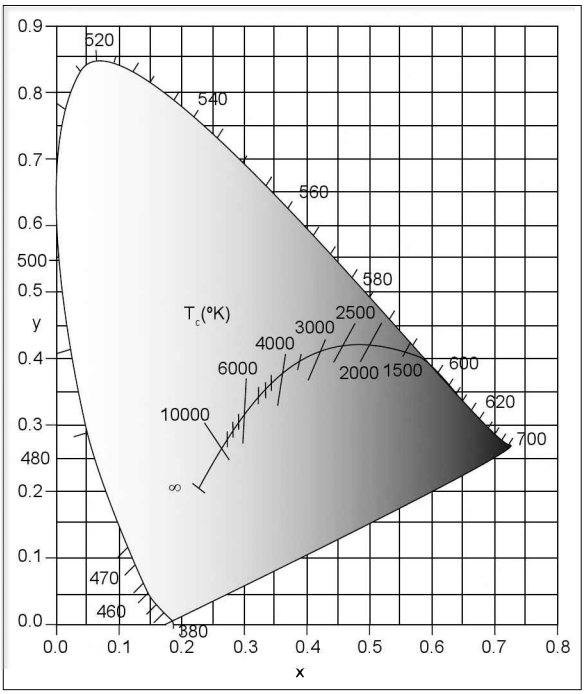


Fig. 1.12

Where the constant, b, known as Wien's displacement constant, is equal to $2.8977685(51) \times 10^{-3}$ m K.

Note that the peak intensity can be expressed in terms of intensity per unit wavelength or in terms of intensity per unit frequency. The form given in this section is in terms of intensity per unit wavelength, this form given in the Planck's Law section above was in terms of intensity per unit frequency. The wavelength at which the power per unit frequency is maximised is given by,

$$\lambda'_{max} = \frac{5.1 \times 10^{-3} \text{m.K}}{T}$$

The black-body radiation graph is also compared with the classical model of Rayleigh and Jeans.

The colour (chromaticity) of black-body radiation depends on the temperature of the black body; the locus of such colours, shown here in x, y space, is known as the Planckian locus.

Although, Wien's equation proved fairly satisfactory at low wave lengths and Rayleigh's at high ones, neither theory could account completely for the observed phenomena. This failure of classical theories of radiation led Max Planck in 1900 to discard these and to come forward with the bold hypothesis that *black bodies radiate energy not continuously, but discontinuously in energy packets called quanta*, given by the relation,

$$E = h\nu$$

E is the quantum of energy radiated, c is the frequency, and h, called *Planck's constant* is a universal constant equal to 6.6256×10^{-27} erg-sec. Planck considered the black body to consist of oscillators of molecular dimensions, each with a fundamental vibration frequency ν, and that each oscillator could emit energy either in the unit quantum $E = h\nu$, or in whole *number multiples n* thereof, $E = nh\nu$.

Planck's law of black-body radiation

Planck's law states that,

$$I(\nu, T)d\nu = \left(\frac{2h\nu^3}{c^2} \right) \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu$$

Where,

I(v, T) dv is the amount of energy per unit surface area per unit time per unit solid angle emitted in the frequency range between v and v + dv by a black body at temperature T;

h is the Planck constant;

c is the speed of light in a vacuum;

k is the Boltzmann constant;

ν is frequency of electromagnetic radiation; and

T is the temperature in kelvins.

Planck's success with the quantization of black body radiation led Albert Einstein in 1905 to a generalization of the quantum theory. Einstein postulated that *all radiant energy must be absorbed* or *emitted by a body in quanta whose magnitude depends on the frequency or multiples thereof.* Furthermore, Einstein argued that radiation is not only emitted or absorbed in quanta, but it is also propagated through space in these units, called *photons* of light. This theory ascribes to light a corpuscular character similar to that established for electricity and matter.

Einstein's theory of the corpuscular nature of all light has been amply substantiated by observations on electron omission produced by light, by the inverse photoelectric effect, i.e., the emission of radiation by electron bombardment, as in the generation X rays, by the Compton effect arising from collisions between photons and electrons, and other phenomena.

The Photoelectric Effect

J.J. Thomson identifies the particles

Thomson established that the ultraviolet light caused *electrons* to be emitted, the same particles found in cathode rays. His method was to enclose the metallic surface to be exposed to radiation in a vacuum tube,

in other words, to make it the cathode in a cathode ray tube. The new feature was that electrons were to be ejected from cathode by the radiation, rather than by the strong electric field used previousl .

By this time, there was a plausible picture of what was going on. Atoms in the cathode contained electrons, which were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually, some of them would be shaken loose, and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation. Increasing the intensity of radiation would shake the electrons were violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average. Increasing the frequency of the radiation would shake the electrons faster, so might cause the electrons to come out faster. For very dim light, it would take some time for an electrons to work up to a sufficient amplitude of vibration to shake loose

Lenard finds some surprises

In 1902, Lenard studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light, and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination. To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current. Lenard discovered that there was a well defined minimum voltage that stopped any electrons getting through, we'll call it V_{stop}. To his surprise, he found that V_{stop} did not depend at all on the intensity of the light Doubling the light intensity doubled the *number* of electrons emitted, but did not affect the *energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field

But Lenard did something else. With his very powerful arc lamp, there was sufficient intensity to separate out the colors and check the photoelectric effect using light of different colours. He found that the maximum energy of the ejected electrons *did* depend on the colour—the shorter wavelength, higher frequency light caused electrons to be ejected with more energy. This was, however, a fairly qualitative conclusion—the energy measurements were not very reproducible, because they were extremely sensitive to the condition of the surface, in particular its state of partial oxidation.

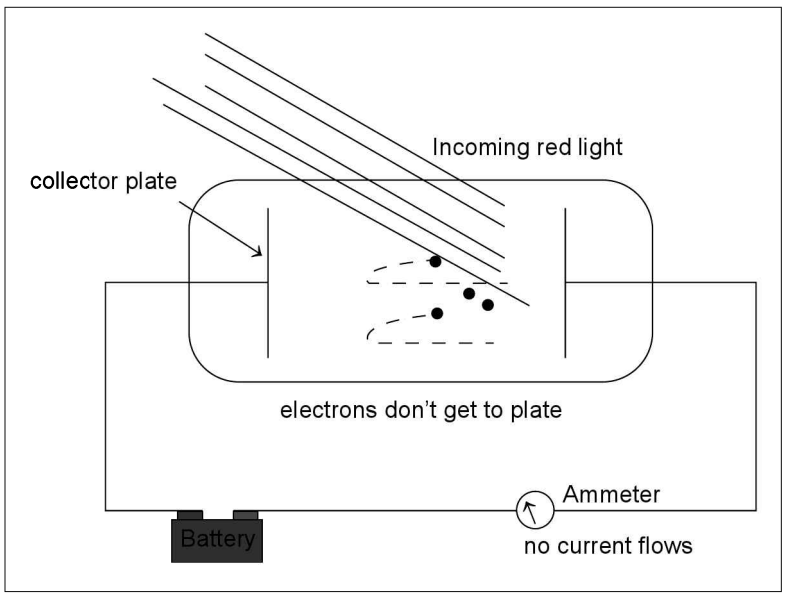


Fig. 1.13

Einstein Suggests an Explanation

In 1905, Einstein applied Planck's quantum theory of light to account for the extraordinary features of the photoelectric effect. He introduced a new concept that light shows dual nature. In phenomenon like reflection, refraction and diffraction it shows wave nature and in phenomenon like photoelectric effects, it shows particle nature. According to the particle nature, the energy of the light is carried in discrete units whose magnitude is proportional to the frequency of the light wave. These units were called as photons (or quanta).

According to Einstein, when a quantum of light (photon) strikes a metal surface, it imparts its energy to the electrons in the metal. In order for an electron to escape from the surface of the metal, it must overcomes the attractive force of the positive ions in the metal. So a part of the photon's energy is absorbed by the metal surface to release the electron, this is known as work function of the surface and is denoted by ϕ. The remaining part of the energy of the photon goes into the kinetic energy of the electron emitted. If E is the energy of the photon, KE is the kinetic energy of the electron and ϕ be the work function of the metal then we have;

$$\phi = hv_0 \text{ and } E_i = hv$$

$$\Rightarrow KE = E_i - \phi \quad \Rightarrow KE = hv - hv_0 = h(v - v_0)$$

Also, if m be the mass and v be the velocity of the electron ejected then $KE = \frac{1}{2} mv^2 = h(v - v_0)$.

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V_{stop}, the highest kinetic energy electrons must have had energy eV_{stop} on leaving the cathode. Thus,

$$eV_{stop} = h\upsilon - \varphi$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be h/e.

It is also clear that there is a minimum light frequency for a given metal, that for which the quantum of energy is equal to the work function. Light below that frequency, no matter how bright, will not cause photoemission.

Note: The electromagnetic radiation (or wave) now emerges as an entity which shows dual nature i.e., sometimes as Wave and sometimes as Particle (quantum aspect).



Worked-out Example

8. In a photoelectric experiment, the collector plate is at 2.0 V with respect to emitter plate made of copper (work function 4.5 eV). The emitter is illuminated by a source of mono-chromatic light of wavelength 200 nm. Find the minimum and maximum kinetic energy of photoelectrons reaching the collector.

Solution Since plate potentials 2 V, minimum K.E. will be 2 eV. For max. K.E. use the following relation:

Absorbed energy = Threshold energy + K.E.

$$h\frac{c}{\lambda} = 4.5 \times 1.6 \times 10^{-19} + \text{K.E.}$$

$$\frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{200 \times 10^{-9}} = 4.5 \times 1.6 \times 10^{-19} + \text{K.E.}$$

$$\text{K.E.} = 2.739 \times 10^{-19} \text{J} = 1.7 \text{ eV}$$

Max K.E. = 2eV + 1.7 eV = 3.7 eV.

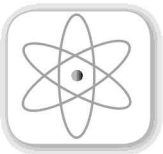
Millikan's Attempts to Disprove Einstein's Theory

If we accept Einstein's theory, then, this is a completely different way to measure Planck's constant. The American experimental physicist Robert Millikan, who did not accept Einstein's theory, which he saw as an attack on the wave theory of light, worked for ten years, until 1961, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory, measuring Planck's constant to within 0.5% by this method. One consolation was that he did get a Nobel prize for this series of experiments.

Bohr's Atomic Model

Bohr developed a model for hydrogen atom and hydrogen like one–electron species (hydrogenic species). He applied quantum theory in considering the energy of an electron bound to the nucleus.

BOHR'S THEORY



Bohr's theory is based on Quantum Mechanics.

Bohr's Postulates Based Upon Quantum Mechanics

Postulates means theory based asumptions which are not direct experimental results.
The postulates are based on three basic concepts:

1. Concept of stationary state
2. Quantization of angular momentum
3. Absorption and emission spectra

1. Concept of stationary state

Some specific orbits are only accessible to electron

When the electron revolves around the orbit, its total energy remains constant or stationary. No energy is emitted or absorbed as long as the electron revolves in the same orbit.

This is called stationary state of electron.

$$T.E = \frac{-Ze^2K}{2r}$$

Any value of 'r' is not accessible, only specific values are allowed

2. Quantization of angular momentum

Of the finite number of circular orbits around the nucleus, an electron can revolve only in those orbits whose angular momentum (mvr) is an integral multiple of factor $h/2\pi$.

$$mvr = \frac{nh}{2\pi}$$

Where, m = mass of the electron
v = velocity of the electron
n = orbit number in which electron is present
r = radius of the orbit

3. Absorption and emission spectra

Spectra is an impression on the photographic plate produced by the passage of radiation.

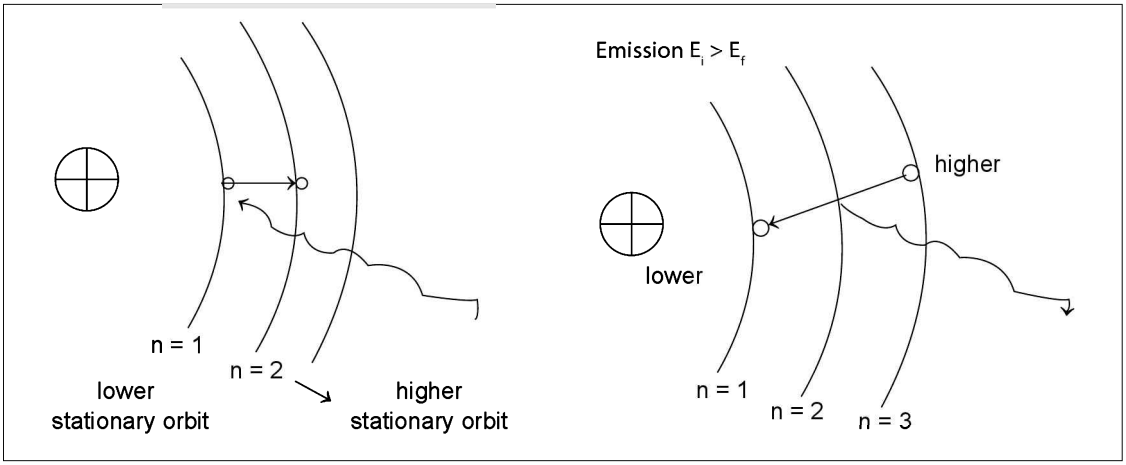


Fig. 1.14

When an electron makes a transition from lower stationary state to higher stationary state, it absorbs radiation (photon) which give rise to absorption spectra.

When an electron makes a transition from higher stationary state to lower stationary state it emits radiation (photon) that gives rise to emission spectra.

Only 1 photon can be absorbed or emitted during 1 electronic transition

$E_i \longrightarrow E_f$ $\quad E_1$ = Initial total energy of electron

$E_{ph} = \frac{hc}{\lambda}|E_f - E_i|$ $\quad E_f$ = final total ene gy of electron

After coming to a stationary state it does not emit any energy.

$$|\Delta E| = \frac{hc}{\lambda}$$

Ordinarily, an electron continues to move in a particular stationary state of orbit. Such a stable state of atom is called ground state. When energy is given to the electron it jumps to any higher energy level and is said to be in the excited state. When the electron jumps from higher to lower energy state the energy is radiated.

[Note: If the energy supplied to hydrogen atom is less than 13.6 eV, it will accept or absorb only those quanta which can take it to a certain higher energy level i.e., all those photons having energy less than or more than a particular energy level will not be absorbed by hydrogen atom. But if energy supplied to hydrogen atom is more than 13.6 eV then all photons are absorbed and excess energy appear as kinetic energy of emitted photo electron].

Radius and Energy Levels of Hydrogen Atom

Consider an electron of mass 'm' and charge 'e' revolving around a nucles of charge Ze (where, Z = atomic number and e is the charge of the proton) with a tangential velocity v. r is the radius of the orbit in which electron is revolving.

By Coulomb's Law, the electrostatic force of attraction between the moving electron and nucleus is

$$\text{Coulombic force} = \frac{KZe^2}{r^2}$$

$$K = \frac{1}{4\pi \in_o} \text{ (where, } \in_o \text{ is permittivity of free space)}$$

$$K = 9 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$$

In C.G.S. units, value of K = 1 dyne cm^2 $(esu)^{-2}$

The centrifugal force acting on the electron is $\frac{mv^2}{r}$

Since the electrostatic force balance the centrifugal force, for the stable electron orbit.

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \quad \ldots (1)$$

$$(\text{or}) \; v^2 = \frac{KZe^2}{mr} \quad \ldots (2)$$

According to Bohr's postulate of angular momentum quantization, we have

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\,\pi mr}$$

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \ldots (3)$$

Equating (2) and (3)

$$\frac{KZe^2}{mr} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

Solving for r, we get,

$$r = \frac{n^2h^2}{4\pi^2mKZe^2}$$

Hence $r_n \propto \frac{n^2}{Z}$

where n = 1, 2, 3-----∞

Hence only certain orbits whose radii are given by the above equation are available for the electron. The greater the value of n, i.e., farther the energy level from the nucleus the greater is the radius.

The radius of the smallest orbit (n = 1) for hydrogen atom (Z = 1) is r_o.

$$r_o = \frac{n^2h^2}{4\pi^2me^2K} = \frac{1^2 \times (6.626 \times 10^{-34})^2}{4 \times (3.14)^2 \times 9 \times 10^{-31} \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9}$$

$$= 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ Å}$$

Radius of nth orbit for an atom with atomic number Z is simply written as,

$$r_n = 0.529 \times \frac{n^2}{Z} \text{Å}$$

$$r_n = 0.529 \times \frac{n^2}{Z} \text{Å}$$

Hence, $r_n \propto \frac{n^2}{Z}$.

Note that radius decreases with the increasing number of protons in the nuleus. It is because the pull of nucleus towards the electron increases.



Worked-out Examples

9. Calculate radius of 3rd orbit of lithium ion.

Solution $r_n = \dfrac{0.529 n^2}{Z}$ Å

$$r_3 = \frac{0.529 \times (3)^2}{3} \text{ Å} = 1.587 \text{ Å}$$

10. For which of the following species, Bohr theory doesn't apply?

(a) H (b) He^+

(c) Li^{2+} (d) Na^+

Solution Bohr theory is not applicable to multi electron species

$\therefore$ (d)

11. If the radius of 2nd Bohr orbit of hydrogen atom is r_2. The radius of third Bohr orbit will be

(a) $\dfrac{4}{9} r_2$ (b) $4r_2$

(c) $\dfrac{9}{4} r_2$ (d) $9r_2$

Solution $r = \dfrac{n^2 h^2}{4\pi^2 m Z e^2}$

$$\therefore \quad \frac{r_2}{r_3} = \frac{2^2}{3^2}$$

$$\therefore \quad r_3 = \frac{9}{4} r_2 \qquad \therefore \varpi \quad \text{(c)}$$

12. The first use of quantum theory to explain the structure of atom was made by **[IIT-JEE-1997]**

(a) Heisenberg (b) Bohr

(c) Planck (d) Einstein

Solution (b) Bohr's theory was based upon some postulations of classical physics and some postulations of the newly proposed quantum theory of Planck.

13. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom? **[IIT-JEE-2004]**

(a) $He^+(n = 2)$ (b) $Li^{2+}(n = 2)$

(c) $Li^{2+}(n = 3)$ (d) $Be^{3+}(n = 2$

Solution (d) $r_n = 0.529 \dfrac{n^2}{Z}$ **Å**

For hydrogen, n = 1 and Z = 1; $\therefore \quad r_H = 0.529$

For Be^{3+}, n = 2 and Z = 4; $\therefore \quad r_{Be^{3+}} = \dfrac{0.529 \times 2^2}{4} = 0.529$

14. The light radiations with discrete quantities of energy are called..... . **[IIT-JEE-1993]**

Solution Photons

Calculation of Energy of an Electron

The total energy, E of the electron is the sum of kinetic energy and potential energy.

Kinetic energy of the electron = ½ mv^2

$$\text{Potential energy} = \frac{-KZe^2}{r}$$

$$\text{Total energy} = 1/2\ mv^2 - \frac{KZe^2}{r} \quad \ldots (4)$$

From equation (1) we know that,

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

$$\therefore \quad \tfrac{1}{2} mv^2 = \frac{KZe^2}{2r}$$

Substituting this in equation (4),

$$\text{Total energy (E)} = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

Substituting for r, gives us,

$$E = \frac{2\pi^2 mZ^2 e^4 K^2}{n^2 h^2}$$

Where n = 1, 2, 3……

This expression shows that only certain energies are allowed to the electron. Since this energy expression consist of so many fundamental constant, we are giving you the following simplified expressions

$$E = -21.8 \times 10^{-12} \times \frac{Z^2}{n^2} \text{ erg per atom}$$

$$= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2} \text{ J per atom} = -13.6 \times \frac{Z^2}{n^2} \text{ eV per atom}$$

($1eV = 3.83 \times 10^{-23}$ kcal

$1eV = 1.602 \times 10^{-12}$ erg

$1eV = 1.602 \times 10^{-19}$J)

$$E = -313.6 \times \frac{Z^2}{n^2} \text{ kcal/mole (1 cal = 4.18 J) (negative sign stands for attraction)}$$

The energies are negative since the energy of the electron in the atom is less than the energy of a free electron (i.e., the electron is at infinite distance from the nucleus) which is taken as zero. The lowest energy level of the atom corresponds to n=1, and as the quantum number increases, E becomes less negative.

When n = ∞, E = 0, which corresponds to an ionized atom i.e., the electron and nucleus are infinitely separated.

$H \longrightarrow H^+ + e^-$ (ionization).

$E = -13.6 \times \frac{Z^2}{n^2}$ eV per atom

Hence, E (total energy of electron) $\propto \frac{n^2}{Z^2}$

Note that T.E. = – K.E.

Hence, K.E. (kinetic energy of electron) $\propto \frac{Z^2}{n^2}$

&

P.E = –2 K.E.

Hence, E (Potential energy of electron) $\propto \frac{n^2}{Z^2}$

Ionization potential (I.P.)

It is the minimum amount of energy required to remove the most loosely bond electron (outermost electron, less attraction) completely from gaseous atom or ion in ground state.

Why Gaseous State?

$Na(s) \rightarrow Na^+(g) + e^-$

If the atoms make up solid state and energy is supplied, first the atom will be converted to gas. In the gaseous state electrons will be lost.

The atom or ion should be in gaseous state so that the energy for the phase transition can be excluded.

$$E_1 = \frac{-(13.6Z^2)}{n^2} \text{ eV} = (-13.6\ Z^2)\ \text{eV}$$

$$E_\infty = \frac{-13.6Z^2}{\infty} = 0$$

This shows that the electron is no longer attracted or repulsed because energy is zero when P.E. = 0

I.P. = (13.6 Z^2) eV

For unielectronic system only

When energy given = –ve

When energy taken = +ve

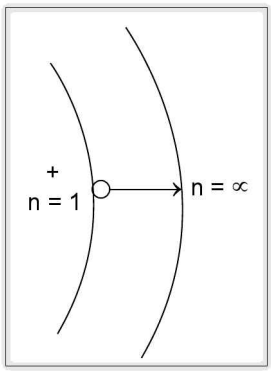


Fig. 1.15

Worked-out Example

15. Calculate ionization potential in volts of (a) He^+ and (b) Li^{2+}.

Solution $\text{I.E.} = \frac{13.6Z^2}{n^2} = \frac{13.6 \times Z^2}{1^2}$ [Z = 2 for He^+] = 13.6 × 4 = 54.4 eV

Similarly, for $Li^{2+} = \frac{13.6 \times 3^2}{1^2} = 13.6 \times 9 = 122.4$ eV

ATOMIC SPECTRA

Atoms give *discontinuous or line spectra.* The spectrum given by atoms consists of a series of bright lines or bands (a band is a group of spectral lines) separated from each other by a dark space. Each line in the spectrum corresponds to a specific wavelength

There are two types of atomic spectra:

(i) Atomic emission spectra (ii) Atomic absorption spectra

Atomic Emission Spectra

When a sample of atomic vapours is heated to a high temperature, the atoms in the vapour get energized and excited. These energized atoms then return to their stable ground state by emitting electromagnetic radiation of certain definite wavelengths (or frequencies). These emitted radiations produce a series of bright lines separated from each other by dark space. *A series of bright lines, separated from each other by dark spaces, produced by the excited atoms is called atomic emission spectrum.*

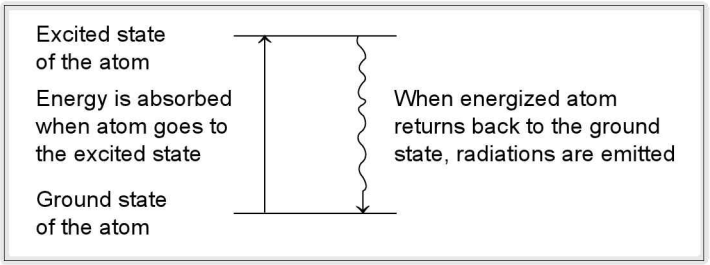


Fig. 1.16 The mechanism of the emission spectra

Each line in the emission spectrum corresponds to a specific wavelength. Therefore, each element gives a unique pattern of lines in the spectrum. No two elements give the same pattern of lines in their spectra.

In 1859, Robert Bunsen (1811-1899) and G. Kirchhoff (1824-1887) developed a spectroscope for studying emission spectra. A spectroscope consists of a prism for dispersing the light, and a telescope to observe the spectra. The spectroscope in which the telescope is replaced by a photographic film is called a **spectrograph.** The photograph of the spectrum is called a **spectrogram.** A typical spectroscope is shown in fig. 1.17.

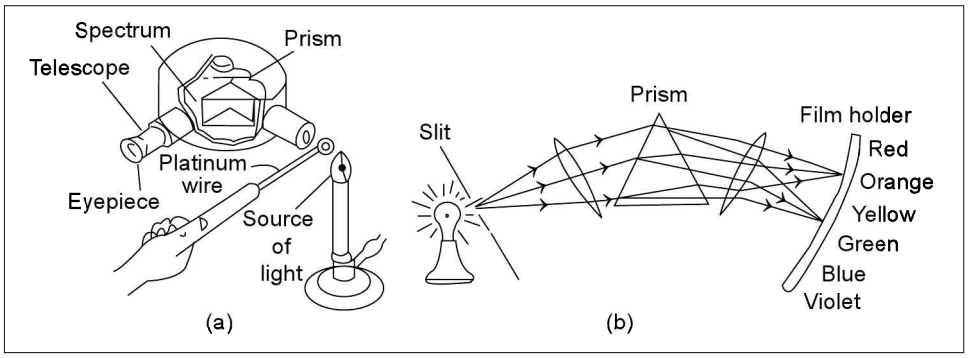


Fig. 1.17 (a) A simple prism spectroscope
(b) the principle of spectroscope for obtaining emission spectrum is illustrated

The emission spectra of hydrogen, helium and mercury are shown in fig. 1.18. It may be noted that each element gives its own characteristic pattern of lines in the spectrum.

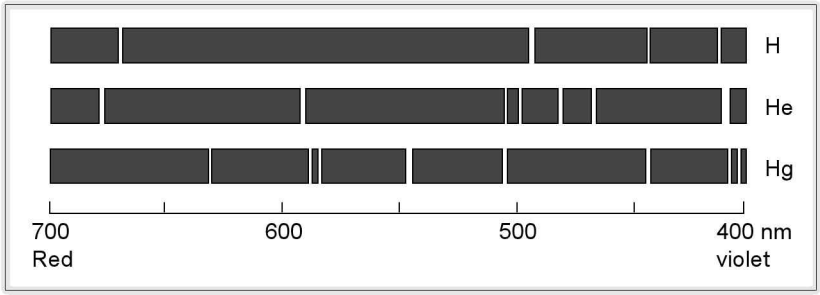


Fig. 1.18 Emission spectra of hydrogen, helium and mercury

Atomic Absorption Spectra

When a sample of atomic vapours is placed in the path of white light from an arc lamp, it absorbs the light of certain characteristic wavelengths and the light of other wavelengths get transmitted. This produces a series of dark lines on a white background (Fig. 1.19).

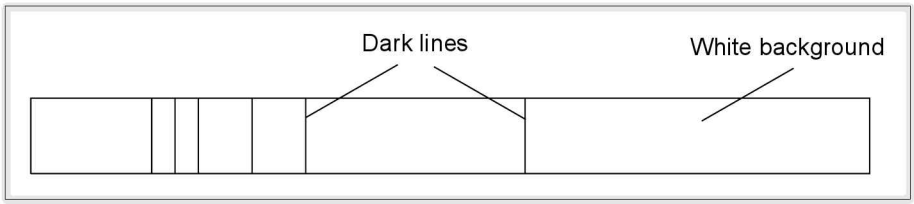


Fig. 1.19 A typical absorption spectrum

The dark lines in the absorption spectrum, and the bright lines in die emission spectrum of the same element appear at the same wavelengths. Fig. 1.20 shows the comparison of emission and absorption spectra of sodium vapours.

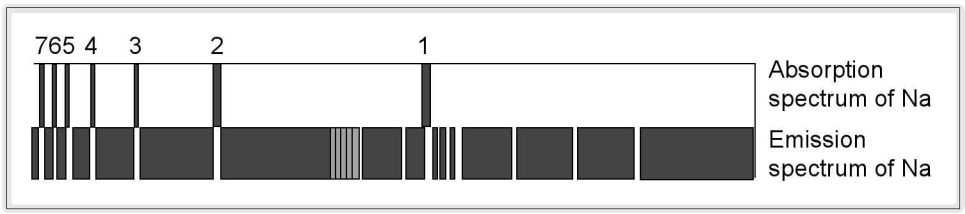


Fig. 1.20 Emission and absorption spectra of sodium vapour, *certain lines are too feeble to be seen in the spectrum

Usefulness of the Atomic Spectra

Each element gives a characteristic atomic spectra. No two elements give the same pattern of lines in their atomic spectra. Since, each element gives a definite pattern of lines at certain definite frequency (or wavelengths), hence the atomic spectra can be used in chemical analysis to identify, and estimate the elements present in any sample. The elements rubidium, and cesium were discovered this way. Other alkali metals like lithium, sodium and potassium are detected in the qualitative analysis by the flame test. These elements give flame of characteristic colours

Element :	Lithium	Sodium	Potassium
Colour of the flame	Red	Golden yellow	Purple (violet)

A simple experiment can be carried out at home by heating a copper vessel over a gas flame. A beautiful green flame, characteristic of copper compounds, will be observed

Atomic Spectrum of Hydrogen

Hydrogen atom has only one electron. The atomic spectrum of hydrogen is the simplest pattern of the spectral lines. Hydrogen spectrum has played an important role in the development of atomic structure.

The emission spectrum of hydrogen atom is obtained by passing electrical discharge through hydrogen gas at very low pressure. When an electric discharge is passed through hydrogen, the molecules of hydrogen break into atoms. These hydrogen atoms absorb energy from the electric spark and get energized. This energized state of atoms is called the *excited stale.* When the population of the atoms in the excited state increases, the excited atoms tend to return to the stable ground state by emitting light. Hydrogen atoms emit bluish light.

When the ray of this bluish light is passed through a prism (Fig. 1.21), a *discontinuous line spectrum* consisting of several sharp lines is obtained. Such a spectrum is called **line spectrum of hydrogen.**

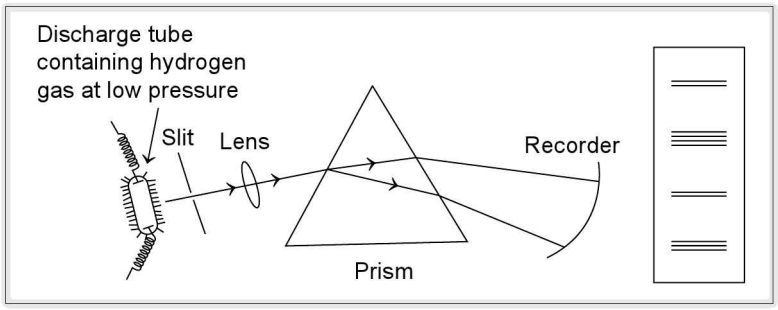


Fig. 1.21 An experimental set up for obtaining the emission spectra of hydrogen atoms

In 1884, Johann Balmer (1825-1898) examined the emission line spectrum in visible region, and found four sharp coloured lines in the spectrum. These were,

(i) a red line at $\lambda = 656.3$ nm
(ii) a blue-green line at $\lambda = 486.1$ nm
(iii) a blue line at $\lambda = 434.0$ nm
(iv) a violet line at $\lambda = 410.2$ nm

This series of lines is known as Balmer series. Balmer analysed these results and showed that, if the spectral lines of hydrogen spectrum are expressed in terms of inverse of wavelength (λ^{-1} or $\bar{\nu}$), then the visible lines of the hydrogen atom spectrum obey the formula,

$$\frac{1}{\lambda} = \bar{\nu}(\text{cm}^{-1}) = 109677\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

where n is an integer equal to or greater than 3, i.e., n = 3, 4, 5,...

Soon after, four other spectral series for hydrogen were discovered and were named after their discovers as the *Lyman series* (1906, 1916) in the ultraviolet, Paschen series (1908), Brackett series (1922) and P fund series (1924) in the infrared region.

Complete atomic spectrum of hydrogen in shown in fig. 1.2

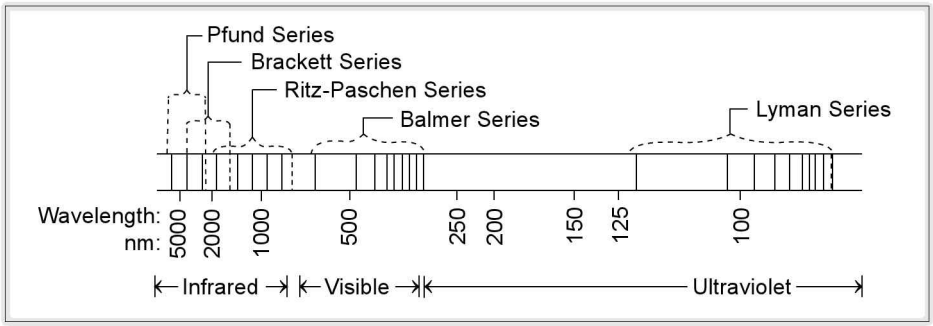


Fig. 1.22 Complete line spectrum of H-atom

To account for the presence of other spectral series, the Balmer equation was modified. The equation now used for describing the hydrogen spectrum is called the **Rydberg equation**. The Rydberg equation is,

$$\bar{\nu}(\text{cm}^{-1}) = \frac{1}{\lambda(\text{cm})} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where, R_H is called the **Rydberg constant.** For hydrogen, the value of Rydberg constant is 109678 cm^{-1}.

n_1 and n_2 are integers, and $n_2 > n_1$

The Rydberg equation also applies to the spectra of other elements, but with different values of the Rydberg constant (R_H).

Rydberg equation and Bohr Theory: The energy associated with the permitted orbits is given by,

$$E = -\frac{1}{2}\frac{e^2}{r} = -\frac{2\pi^2 me^4}{n^2h^2} = \frac{E_{(n=1)}}{n^2};\left[E_{(n=1)} = -\frac{2\pi^2 me^4}{1^2h^2}\right] \tag{7}$$

the energy being governed by the value of the quantum number n.

As n increases the energy becomes less negative and hence the system becomes less stable Also note that with increasing n, the radius, r, also increases. Thus increasing r also makes the orbit less stable.

The explanation of the Rydberg equation is now simple. The most stable orbit must be the one with the lowest energy (ground state). Equation (7) shows that the lowest energy state is the one with n = 1. States with n > 1 are the higher energy excited states. Provided the right amount of energy is supplied the electron may jump from n = 1 to another higher level. Conversely, energy will be released in the form of light of definite frequency when the excited electron returns to its ground state. Since energy and frequency of the emitted light are connected by Planck relation $E = h\upsilon$ it follows that $\upsilon = \frac{E}{h}$.

The energy corresponding to a particular line in the emission spectrum of hydrogen atom is the energy difference between an initial state I and a final state II, so that

$$E = E_{II} - E_I = -\frac{2\pi^2 me^4}{n_{II}^2h^2} - \left(-\frac{2\pi^2 me^4}{n_I^2h^2}\right) = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right) \tag{8}$$

Then υ corresponding to the energy E is given by:

$$E = \frac{E}{h} = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right) = R\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right) \tag{9}$$

where R is the Rydberg constant.

This relation tells us that as we go to higher and still higher orbits the energy gap between two immediate orbits continues to decrease.

Putting n = 1, n = 2, n = 3, etc., in equation (7), we get the energies of the different stationary states for the hydrogen electron. The transition energies can all be calculated from the above relation (9). Fortunately the experimental spectra of hydrogen atom also exhibited several series of lines (Fig. 1.23). Transitions to the ground state (n = 1) from n = 2, n = 3, n = 4, etc., excited states constitute the Lyman series in the ultraviolet region.

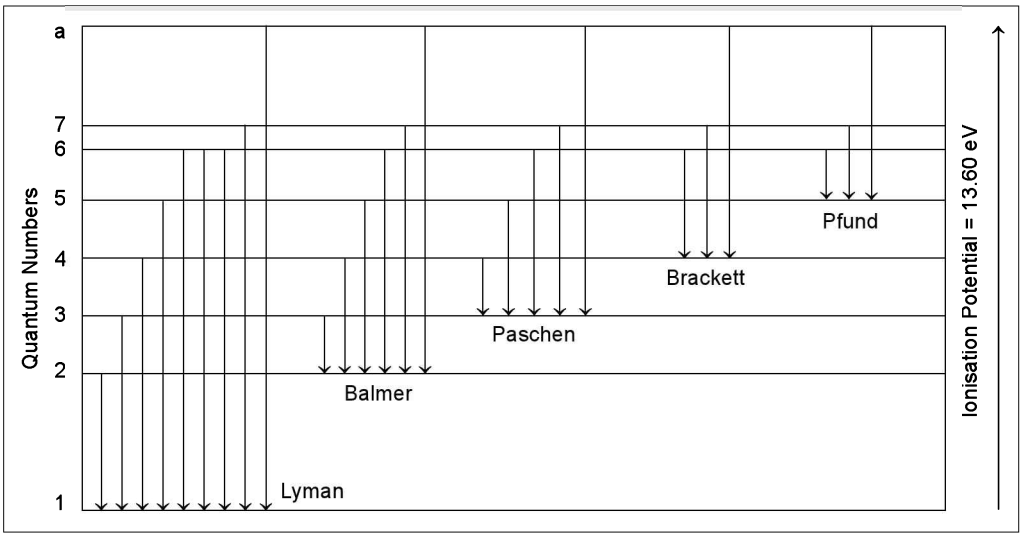


Fig. 1.23 Emission spectra of hydrogen atom

Transitions to the n = 2 level from the other excited levels (n > 2) constitute the Balmer series in the visible. Shifts of electrons from excited levels to the n = 3 level give the Paschen series in the infrared. The energy corresponding to the transition from n = ∞ to n = 1 obviously gives the ionisation potential (Chapter 4) of the hydrogen atom:

Ionisation potential of the hydrogen atom

$$= E_H = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{1^2} - 0\right) = 2.179 \times 10^{-11} \text{ erg}$$

$$= 2.179 \times 10^{-11} \times 6.2419 \times 10^{11} \text{ eV} = 13.60 \text{ eV} = 21.79 \times 10^{-19} \text{ J}$$

Note that $-E_H = E_{(n=1)}$ = energy of the ground state. The energies of the excited states are:

for $n = 2; -13.6/2^2 = -3.4$ eV

$n = 3; -13.6/3^2 = -1.51$ eV etc.

Using the value of 9.108×10^{-28} g for the mass of the electron, the Bohr theory predicts the following value of the Rydberg constant:

$$R = \frac{2\pi^2 me^4}{h^3} = \frac{2(3.1416)^2(9.108 \times 10^{-28}\text{g})(4.8 \times 10^{-10}\text{esu})^4}{(6.627 \times 10^{27}\text{erg} - \text{sec})^3}$$

It is a common practice to evaluate R in terms of wave number $\bar{\upsilon}$ instead of in frequency. As mentioned earlier (section 1.2.1) wave number and frequency are connected:

$$\lambda\upsilon = c; \upsilon = \frac{c}{\lambda} = c\bar{\upsilon} \text{ so that } \bar{\upsilon} = \frac{\upsilon}{c}$$

Where c is the velocity of light. Recall that frequency, υ, indicates the number of waves passing a given per second and is expressed as cycles per second. Wave number, $\bar{\upsilon}$, on the other hand, stands for the number of waves contained in unit length i.e., per centimetre (cm^{-1}) or per meter (m^{-1}).

$$\text{Thus, } R = \frac{3.2898 \times 10^{15}\text{cycle / sec}}{2.9979 \times 10^{10}\text{cm / sec}} = 109{,}737 \text{ cm}^{-1} = 109{,}73700 \text{ m}^{-1}$$

The experimental value of R is 109,677 cm^{-1} (109,67700 m^{-1}) showing a remarkable agreement between experiment and Bohr's theory.



Worked-out Examples

16. In a hydrogen atom, if energy of an electron in ground state is –13.6 eV, then that in the 2nd excited state is: **[AIEEE-2002]**

(a) –1.51 eV (b) –3.4 eV (c) –6.04 eV (d) –13.6 eV

Solution (a) 2nd excited state means third energy level.

$$E_3 = \frac{E_1}{3^2} = -\frac{13.6}{9} = -1.51\text{eV}$$

17. The wavelength of the radiations emitted, when in a hydrogen atom electron falls form infinity to stationary state is: ($R_H = 1.097 \times 10^7$ m^{-1}) **[AIEEE-2004]**

(a) 9.1×10^{-8} nm (b) 192 nm

(c) 406 nm (d) 91 nm

Solution (d) $\frac{1}{\lambda} = R_H\left[\frac{1}{\infty} - \frac{1}{1^2}\right]$ $\therefore \lambda = \frac{1}{R_H} = \frac{1}{1.097 \times 10^7}\text{m}$

$= 9.1 \times 10^{-8}$ m $= 91 \times 10^{-9}$ m = 91 nm

18. The ionization enthalpy of hydrogen atom is 1.312×10^6 J mol^{-1}. The energy required to excite the electron in the atom from $n_1 = 1$ to $n_2 = 2$ is **[AIEEE-2008]**

(a) 8.51×10^5 J mol^{-1} (b) 6.56×10^5 J mol^{-1}

(c) 7.56×10^5 J mol^{-1} (d) 9.84×10^5 J mol^{-1}

Solution (d) (ΔE), The energy required to excite an electron in an atom of hydrogen from n = 1 to n = 2 is given by the following relation (difference in energy E_2 and E_1)

$$E_2 = \frac{-1.312 \times 10^6 \times (1)^2}{(2)^2} = -3.28 \times 10^5 \text{ J mol}^{-1}$$

$$E_2 = -1.312 \times 10^6 \text{ J mol}^{-1}$$

$$\therefore \quad \Delta E = E_2 - E_1 = [-3.28 \times 10^5] - [-1.312 \times 10^6] \text{ J mol}^{-1}$$

$$= (-3.28 \times 10^5 + 1.312 \times 10^6) \text{ J mol}^{-1}$$

$$= 9.84 \times 10^5 \text{ J mol}^{-1}$$

19. The energy of an electron in the first Bohr orbit of H atom is –13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are) **[IIT-JEE-1998]**

(a) –3.4e V (b) –4.2e V

(c) –6.8e V (d) +6.8e V

Solution (a) The energy of an electron on Bohr orbits of hydrogen atoms is given by the expression

$$E_n = - \text{Constant}/n^2$$

Where n takes only integral values. For the first Bohr orbit, n = 1 and it is given that $E_1 = -13.6$ eV;

Hence, $E_n = 13.6 \text{ eV}/n^2$ of the given values of energy, only–3.4 eV can be obtained by substituting; n =2 in the above expression.

Quantum Number

With increasing value of quantum number, the energy different between two successive energy levels decreases.

$$E_{2\to1} > E_{5\to6}$$

At very high value of quantum number, there is hardly any energy gap between successive energy levels hence e.l are continuous. Hence, quantum mechanics corresponds to classical mechanics at a very high value of quantum number.

Lowest energy or frequency in Lyman series = $2 \to 1$

This equation is known as "Ritz equation".

where R_H is Rydberg's constant

$R_H = 1.09678 \times 10^7 \text{ m}^{-1} = 109678 \text{ cm}^{-1}$

Note that the value of 'R' that we would get from $R_H = \frac{2\pi^2 mZ^2e^4}{h^3c} = 1.09728 \text{m}^{-1}$

But the experimental value ($R_H = 1.09678 \times 10^7 \text{ m}^{-1} = 109678 \text{ cm}^{-1}$)

of Rydberg is taken

$\frac{1}{\lambda} = \bar{\upsilon}$ = wave number i.e., number of wavelength per cm decreases, because the difference of energy between two consecutive energy levels or orbits decreases.

(b) As electron enters to infinite orbit, E_n becomes zero. It indicates the electron is free from the nuclear force of electron.

20. In Bohr series of line of hydrogen spectrum, third line from the red end corresponds to which one of the following inner orbit jumps of electron for Bohr orbit in atom of hydrogen?

[AIEEE-2003]

(a) $4 \rightarrow 1$ (b) $2 \rightarrow 5$

(c) $3 \rightarrow 2$ (d) $5 \rightarrow 2$

Solution (d) The emission is in visible (VIBGYOR) region. The Balmer series i.e., either (c) or (d). In (c) there is only one emission. The third line will be in the jump from 5 to 2.

Intensity of Spectral Lines

Within each series the intensity of spectral line decreases as the frequency increases (or the wavelength decreases), that is, as n_H increases. The observed intensity of a transition from $n_H \rightarrow n_L$ depends on the population of the energy level with energy E_{n_H}. The population of a state decreases as n increases. Thus there are more hydrogen atoms with n = 3 than there are with n = 4 and so the intensity of the first Balmer line ($n_H = 3 \rightarrow n_L = 2$) is greater than the intensity of the second Balmer line ($n_H = 4 \rightarrow n_L = 2$)

When an electron jumps from any higher energy level to the ground state in H-atom, the number of spectral lines obtained is given by $\frac{n(n-1)}{2}$.

Hydrogen atom in its ground state is excited by means of monochromatic radiations of wavelength 970.6 A°. How many lines are possible in the resulting emission spectrum? How many of these lines are in the visible region of the spectrum? Calculate the longest wavelength amongst them. The ionization energy for hydrogen atom is 13.6 eV. ($h = 6.63 \times 10^{-34}$ Js)

$\lambda = 970.6\ \text{Å} = 970.6 \times 10^{-10}\ \text{m}$

$$E = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\times3.0\times10^{8}}{970.6\times10^{-10}} = 2.049\times10^{-18}\ \text{J}$$

$$= \frac{2.049\times10^{-18}}{1.6\times10^{-19}} = 12.81\ \text{eV}$$

Energy of an electron in n^{th} orbit of Hydrogen atom is

$$E = \frac{-13.6}{n^2}\ \text{eV}$$

In ground state, n = 1

$\therefore \quad E_1 = -13.6\ \text{eV}$

Total energy of electron after absorbing 12.81 eV energy corresponding to given wavelength

$E_2 = -13.6 + 12.81 = -0.79\ \text{eV}$

This value corresponds to n = 4

$$n^2 = \frac{-13.6}{-0.79} = 17.21$$

$$n = 4$$

This means that the electron is excited ton = 4 state

Total number of lines obtained $= \frac{n(n-1)}{2} = \frac{4\times(4-1)}{2} = 6$

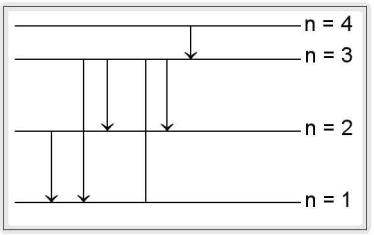


Fig. 1.24

Out of the six lines, only two are as the visible region of the spectrum (n = 4 to n = 2 n = 3 to n = 2)

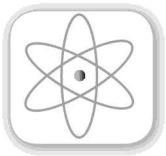
The longest wavelength is emitted corresponding to minimum energy, when transitin occurs from n = 4 to n = 3.

$$\Delta E = 13.6\left[\frac{1}{3^2} - \frac{1}{4^2}\right] = 13.6 \times \frac{7}{44} = 0.66\,eV$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^{8}}{0.66 \times 1.6 \times 10^{-19}}$$

$$\lambda = 1.88 \times 10^{-6}\,m$$

MERITS OF BOHR'S THEORY

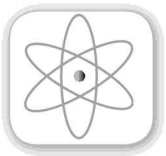


(i) The experimental value of radii and energies in hydrogen atom are in good agreement with that calculated on the basis of Bohr's theory.

(ii) Bohr's concept of stationary state of electron explains the emission and absorption spectra of hydrogen like atoms.

(iii) The experimental values of the spectral lines of the hydrogen spectrum are in close agreement with that calculated by Bohr's theory.

LIMITATIONS OF BOHR'S THEORY



(i) It does not explain the spectra of atoms having more than one electron.

(ii) Bohr's atomic model failed to account for the effect of magnetic field (Zeeman effect) or electric field (Stark effect) on the spectra of atoms or ions. It was observed that when the source of a spectrum is placed in a strong magnetic or electric field, each spectral line further splits into a number of lines. This observation could not be explained on the basis of Bohr's model.

(iii) De Broglie suggested that electrons like light have dual character. It has particle and wave character. Bohr treated the electron only as particle.

(iv) Another objection to Bohr's theory came from ***Heisenberg's Uncertainty Principle***. According to this principle, ***"It is impossible to determine simultaneously the exact position and momentum of a small moving particle like an electron"***. The postulate of Bohr, that electrons revolve in a well defined orbits around the nucleus with well defined velocities is thus not tenable.

Refinements to the Bohr Theory

It has been assumed that the nucleus remains stationary except for retaining on its own axis. This would be true if the mass of the nucleus were infinite, but the ratio of the mass of an electron to the mass of the hydrogen nucleus is 1/1836. The nucleus actually oscillates slightly about the centre of gravity, and to allow for this the mass of the electron m is replaced by the reduced mass μ in equation.

$$\mu = \frac{mM}{m + M}$$

Where M is the mass of the nucleus. The inclusion of the mass of the nucleus explain why different isotopes of an element produce lines in the spectrum at slightly different wavenumbers.

The orbits are sometimes denoted by the letter K, L, M, N... counting outwards from the nucleus, and they are also numbered 1, 2, 3, 4... This number is called the principal quantum number, which is given the symbol n. It is therefore possible to define which circular orbit is under consideration by specifying the principal quantum number.

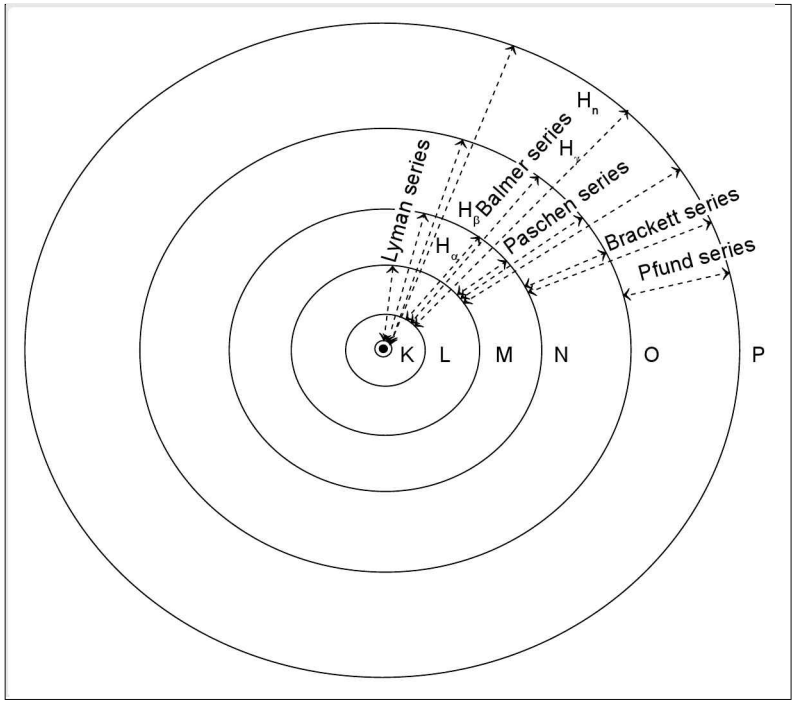


Fig. 1.25 Bohr orbits of hydrogen and the various series of spectral lines.

When an electron moves from one orbit to another it should give a single sharp line in the spectrum, corresponding precisely to the energy difference between the initial and final orbits. If the hydrogen spectrum is observed with a high resolution spectrometer it is found that some of the lines revel 'fine structure'. This means that a line is really composed of several lines together. Sommerfeld explained this splitting of lines by assuming that some of the orbits were elliptical, and that they precessed in space round the nucleus. For the orbit closest to the nucleus, the principal quantum number n = 1, and there is a circular orbit. For the rest orbit, the principal quantum number n = 2, and both circular and elliptical orbits are possible. To define an elliptical orbit, a second quantum number k is needed. The shape of the ellipse is defined by the ratio of the lengths of the major and minor axes.

$$\frac{\text{major axis}}{\text{min or axis}} = \frac{n}{k}$$

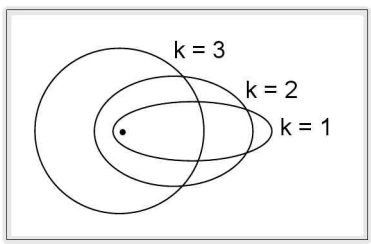


Fig. 1.26 Bohr-Sommerfield orbits when n = 3

Thus, k is called the azimuthal or subsidiary quantum number, and may have values from 1, 2…n. Thus for n = 2, n/k may have the values 2/2 (circular orbit) and 2/1 (elliptical orbit). For the principal quantum number $n = 3$ n/k may have values 3/3 (circular), 3/2 (ellipse) and 3/1 (narrower ellipse).

The presence of these extra orbits, which have slightly different energies from each other, accounts for the extra lines in the spectrum revealed under high resolution. The original quantum number k has now been replaced by a new quantum number l. where $l = k - 1$. Thus for

$n = 1$ $l = 0$
$n = 2$ $l = 0$ or 1
$n = 3$ $l = 0$ or 1 or 2
$n = 4$ $l = 0$ or 1 or 2 or 3

this explained why some of the spectral lines are split into two, three, four or more lines. In addition some spectral lines are split still further into two lines (a doublet). This is explained by assuming that an electron spin on its axis in either a clockwise or an anticlockwise direction. Energy is quantized, and the value of the spin angular momentum was first considered to be m_s . h2/π. where m_s is the spin quantum number with values of $\pm\frac{1}{2}$ (Quantum mechanics has since shown the exact expression to be $s(s + 1).h/2\pi$, where s is either the spin quantum number or the resultant of several spins.)

Zeeman showed that if atoms were placed in a strong magnetic field additional lines appeared on the spectrum. This is because elliptical orbits can only lake up certain orientations with respect to the external field, rather than precessing freely. Each of these orientations is associated with a fourth quantum number m which can have values of l, $(l - 1)$, …0…$(-l + 1)$, $-l$.

Thus, a single line in the normal spectrum will appear as $(2l + 1)$ lines if a magnetic field is applied.

Thus, in order to explain the spectrum of the hydrogen atom, four quantum numbers are needed. The spectra of other atoms may be explained in a similar manner.

Dual Character (Particle and Wave Character of Matter and Radiation)

In case of light, some phenomenon like diffraction and interference can be explained on the basis of its wave character. However, the certain other phenomenon such as black body radiation and photoelectric effect can be explained only on the basis of its particle nature. Thus, light is said to have a dual character. Such studies on light were made by Einstein in 1905.

Louis de Broglie, in 1924 extended the idea of photons to material particles such as electron and he proposed that matter also has a dual character—as wave and as particle.

Derivation of de Broglie Equation

The wavelength of the wave associated with any material particle was calculated by analogy with photon.

In case of photon, if it is assumed to have wave character, its energy is given by,

$E = h\nu$----------(i) (According to the Planck's quantum theory)

Where ν is the frequency of the wave and 'h' is Planck's constant

If the photon is supposed to have particle character, its energy is given by,

$E = mc^2$----------(ii) (According to Einstein's equation)

where 'm' is the mass of photon, 'c' is the velocity of light.

By equating (i) and (ii)

$h\nu = mc^2$

But $\nu = c/\lambda$

$$h\frac{c}{\lambda} = mc^2$$

(or) $\lambda = h/mc$

The above equation is applicable to material particle if the mass and velocity of photon is replaced by the mass and velocity of material particle. Thus for any material particle like electron,

$$\lambda = h/m\upsilon \quad (\text{or}) \ \lambda = \frac{h}{p}$$

where, $m\upsilon = p$ is the momentum of the particle. Consider an electron with de Broglie wavelength "λ" is accelerated by the potential difference "V" with its velocity υ, then the kinetic energy of the electron will be given by relation

$$KE = \frac{1}{2}m\upsilon^2 = eV$$

$$\therefore \quad \upsilon = \sqrt{\frac{2eV}{m}}$$

$$\text{or,} \quad \upsilon = \sqrt{\frac{2KE}{m}}$$

$$\therefore \quad \text{Linear momentum} = P = m\upsilon = m \times \sqrt{\frac{2eV}{m}}$$

$$= \sqrt{2 \times meV}$$

$$= 2m \times \text{K.E.}$$

$$\because \quad \lambda = \frac{h}{m\upsilon} = \frac{h}{\sqrt{2m \times KE}} = \frac{h}{\sqrt{2m \times eV}}$$

$$\lambda = \sqrt{\frac{150}{V}} = \frac{12.24}{\sqrt{V}} \text{ Å}$$

If λ is known, then potential difference in volt can be calculated and vice versa.

[Distinction between the wave-particle nature of a photon and the particle-wave nature of a sub atomic particle]

Photon	**Sub Atomic Particle**
1. Energy $= h\nu$	Energy $= \frac{1}{2}m\nu^2$
2. Wavelength $= \frac{c}{\nu}$	Wavelength $= \frac{h}{m\nu}$

*[**Note:** We should never interchange any of the above]*



Worked-out Examples

21. Which of the following relates to photons both as wave motion and as a stream of particles? **[IIT-JEE-1992]**

(a) Inference
(b) $E = mc^2$
(c) Diffraction
(d) $E = h\nu$

Solution (d) As packet of energy equal to $h\nu$; as wave having frequency ν.

22. K.E. of a subatomic particle is 6.626×10^{-19} J. Calculate its frequency.

Solution $\text{K.E.} = \frac{1}{2} mv^2$

$$= \frac{1}{2} (mv)\, V = \frac{1}{2} pV$$

$$= \frac{1}{2} \frac{h}{\lambda} \times \lambda \times \nu$$

$$= \frac{1}{2} \mathbf{h\nu} \quad \textbf{(NOT} \quad \mathbf{E = h\nu)}$$

$$6.626 \times 10^{-19}\ \text{J} = \frac{1}{2} \times (6.626 \times 10^{-34}\ \text{Js}) \times \nu$$

$$\nu = \frac{6.626 \times 10^{-19} \times 2}{6.626 \times 10^{-34}}\ \text{s}^{-1} \text{ or Hz} = 2 \times 10^{15}\ \text{Hz}$$

23. Calculate the wavelength (in nanometer) associated with a proton moving at 1.0×10^3 ms^{-1} (Mass of proton = 1.67×10^{-27} kg and h = 6.63×10^{-34} Js). **[AIEEE-2009]**

(a) 0.032 nm (b) 0.40 nm (c) 2.5 nm (d) 14.0 nm

Solution (b) $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 10^3} \equiv 0.40\,\text{nm}$

The mass of an object can change when it is moving with a velocity that is comparable with velocity of light. This is quantitatively explained in Einstein's relativity equation.

Einstein's Relativity-equation is as follows

$$m = \frac{m_c}{\sqrt{1-(v^2/c^2)}}$$ where m = mass of object moving with velocity v

m_c = mass of object at rest

c = velocity of light (3×10^8 m/s)

Case I In normal condition, the velocity of any particle is quite negligible as compared to the velocity of light.

$$V << C$$

$$\frac{V}{C} << 1$$

$$\left(\frac{V}{C}\right)^2 <<< 1$$

$$1-\left(\frac{V}{C}\right)^2 \approx 1$$

$m = m_0$ when $1 - \left(\frac{V}{C}\right)^2 \approx 1$ in equation of Einstein

$\mathbf{m_o}$ is constant but m is variable

The mass of the moving object increases slightly with increasing velocity of object.

Rest mass of photon

$$m = \frac{m_o}{\sqrt{1-\left(\frac{V}{C}\right)^2}} \quad \text{But for photon, } V = C$$

$$\Rightarrow \frac{m_o}{m} = \sqrt{1-(1)^2} = 0 \text{ for photon}$$

This situation can be explained as follows

Case I $m_o \rightarrow$ finit

$\Rightarrow m \rightarrow$ infinite $E = mc^2$ $\Rightarrow$ The energy of photon will be infinite. This is not practically feasible.

Case II $m_o = o$

$\Rightarrow m \rightarrow$ finit

so energy of photon will be finite. This is an acceptable conclusion.

So, the rest mass of photon is considered to be zero or photon cannot remain at rest.

Worked-out Example

24. An electron is moving with a kinetic energy of 4.55×10^{-25} J. What will be de Broglie wavelength for this electron?

(a) 5.28×10^{-7} m (b) 7.28×10^{-7} m (c) 2×10^{-10} m (d) 3×10^{-5} m

Solution $KE = \frac{1}{2} mv^2 = 4.55 \times 10^{-25}$

$$V^2 = \frac{2 \times 4.55 \times 10^{-25}}{9.1 \times 10^{-31}} = 1 \times 10^6 \qquad V = 10^3 \text{ m/s}$$

De Broglie wave length $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3} = 7.28 \times 10^{-7}$ m

$\therefore$ (b)

Derivation of Angular Momentum from de Broglie Equation

According to Bohr's model, the electron revolves around the nucleus in circular orbits. According to de Broglie concept, the electron is not only a particle but has a wave character also.

THE WAVE THEORY OF THE ELECTRON

To answer the question of why the energy of the electron in the hydrogen atom should be quantized, a French graduate student, Louis de Broglie, suggested in 1924 that electrons have wave properties as well as particle properties. De Broglie reasoned that the electron in the hydrogen atom is "fastened" in the space around the nucleus by the attraction of the positive charge on the nucleus. He argued that the electron's wave behavior should be that of a standing wave. The water waves and electromagnetic waves we have talked about are all traveling waves.

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

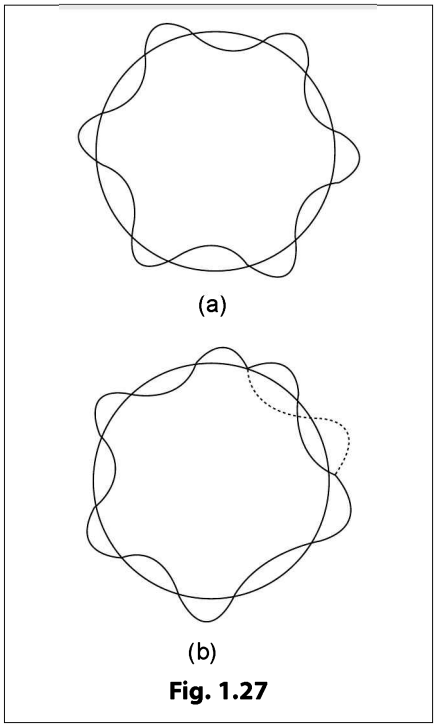


Fig. 1.27

If the wave is completely in phase, the circumference of the orbit must be equal to an integral multiple of wave length (λ)

Therefore, $2\pi r = n\lambda$

Where 'n' is an integer and 'r' is the radius of the orbit

But, $\lambda = h/mv$

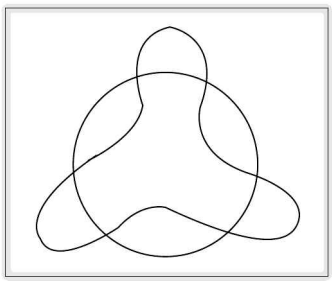


Fig. 1.28

$\therefore \quad 2\pi r = nh/mv$

(or) $mvr = n\,h/2\pi$

which is Bohr's postulate of angular momentum, where 'n' is the principal quantum number.

"Thus, the number of waves an electron makes in a particular Bohr orbit in one complete revolution is equal to the principal quantum number of the orbit".

Alternatively

$$\text{Number of waves 'n'} = \frac{2\pi r}{\lambda} = \frac{2\pi r}{h/mv} = \frac{2\pi mvr}{h}$$

where v and r are the velocity of electron and radius of that particular Bohr orbit in which number of waves are to be calculated, respectively.



Worked-out Examples

25. The electron is revolving around the nucleus in a circular orbit. How many revolutions it can make in one second?

Solution Let the velocity of electron be v m/sec. The distance it has to travel for one revolution $2\pi r$, (i.e., the circumference of the circle).

Thus, the number of revolutions per second is = $\frac{v}{2\pi r}$

Common unit of energy is electron volt which is amount of energy given when an electron is accelerated by a potential of exactly 1 volt. This energy equals the product of voltage and charge. Since in SI units coulombs × volts = Joules, 1 eV numerically equals the electronic charge except that joule replaces coulombs.

26. Number of waves made by a Bohr electron in one complete revolution in 3rd orbit is

(a) 2 (b) 3 (c) 4 (d) 1

Solution Circumference of 3rd orbit = $2\pi r_3$

According to Bohr, angular momentum of electron in 3rd orbit is

$$mvr_3 = 3\frac{h}{2\pi}$$

or $$\frac{h}{mv} = \frac{2\pi r_3}{3}$$

By de Broglie equation,

$$\lambda = \frac{h}{mv}$$

$$\therefore \quad \lambda = \frac{2\pi r_3}{3}$$

$$\therefore \quad 2\pi r_3 = 3\lambda$$

i.e., circumference of 3rd orbit is three times the wavelength of electron or number of waves made by Bohr electron in one complete revolution in 3rd orbit is three.

$\therefore$ (b) is the correct answer.

27. According to Bohr's theory, the angular momentum of an electron in 5th orbit is:

[AIEEE-2006]

(a) $25\frac{h}{\pi}$ (b) $\frac{h}{\pi}$ (c) $10\frac{h}{\pi}$ (d) $2.5\frac{h}{\pi}$

Solution (d) Angular momentum = $\frac{nh}{2\pi} = \frac{5h}{2\pi} = \frac{2.5h}{\pi}$

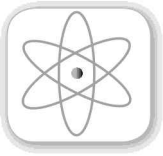
28. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order

(a) 10^{-10} m (b) 10^{-20} m

(c) 10^{-30} m (d) 10^{-40} m **[IIT-JEE-2001]**

Solution (a) $\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\times3600}{200\times10^{-3}\times5} = 2.38\times10^{-10}$ m

HEISENBERG'S UNCERTAINTY PRINCIPLE



From de Broglie's equation, it is very clear that the particle nature of matter is characterised by the term momentum (p) and the wave nature by wavelength (λ). These two terms are inversely related to each other i.e., particle nature is inversely related to wave nature i.e., if p is large, then λ is small and vice versa. The macroscopic particle having larger value of P, λ will be very small to be determined experimentally. For a macroscopic particle, the wave nature will be completely ignored and therefore, it has only die corpuscular or particle nature. The motion of such particle is governed by classical Newtonian mechanics. At any instant, the precise value of its position and momentum can be calculated from Newton's law and can also be determined experimentally. Thereby, the motion of the particle can be described by a well defined path or trajectory. Since Bohr assumes an electron as material particle, therefore, it will have well defined trajectory because it will obey Newtonian classical mechanics. So, according to Bohr's theory the precise value of the position and the momentum of an electron can be determined simultaneously.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

However, this is not true for the atomic or subatomic particles which have significant wave nature besides particle nature. According to de Broglie, electron has significant wave nature besides particle nature. So, whether the position and the momentum of the subatomic particles (i.e., electrons, protons etc.) can be determined simultaneously with great accuracy was answered on theoretical reasoning by Heisenberg's Uncertainty principle. According to this principle, *"it is not possible to measure the precise values of both the position and the momentum along the same axis simultaneously for subatomic particles such as electron, proton etc.*

If Δx be the uncertainty in measurement is position and Δp be the uncertainty in momentum, then from Heisenberg's Uncertainty principle, its relationship is as under:

$$\Delta p.\ \Delta x \geq \frac{h}{4\pi}$$

0 or, $$m\Delta\upsilon.\ \Delta x \geq \frac{h}{4\pi}$$

or, $$\Delta\upsilon.\ \Delta x \geq \frac{h}{4\pi m}$$

$(\because \Delta p = m\Delta\upsilon)$

Where, $\Delta\upsilon$ = uncertainty in velocity.

If the position be the more accurate i.e., Δx be less, then Δp will be more i.e., the momentum will be more inaccurate or, more uncertain and vice versa. It means if one is more accurate, then another will be less accurate.

For another conjugate pair of variables,

$$\Delta E.\Delta t \geq \frac{h}{4\pi}$$ (for energy and time)

$$\Delta\phi.\Delta\theta \geq \frac{h}{4\pi}$$ (for angular motion)

Explanation of Heisenberg's uncertainty principle

Consider a photon of light strikes on a particle and the particle is of reasonable size, its position and velocity will not be altered by that the light photons. So, the precise value of position and momentum for macroscopic particle can be measured simultaneously. But this cannot be so when the particle is very such as like electron. *It suffers a change in its velocity and path, when a photon of light strikes to the pinpoint position of electron and reflected photon is seen in microscope in order to observe it and the reflected photon of light is seen in the aperture of the microscope.*

(a) By using the microscope of small aperture, the value of momentum (p) will be more precise, i.e., less uncertainty in momentum, but more uncertainty in position.
(b) On the other hand, with the radiation of high frequency such as γ-radiation, decreases the uncertainty in position (x), but increases the uncertainty in the momentum.

The Heisenberg uncertainty principle

It is impossible to determine the exact position and momentum of a subatomic paticle simultaneously with precision.

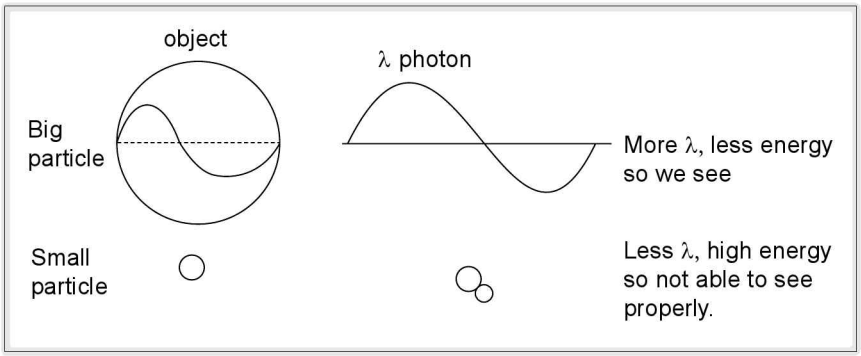


Fig. 1.29

Δx = error or uncertainty in the measurement of position of subatomic particle.
Δx ∝ λ wavelength of photon used to visualize particle.

More the λ more is the error.

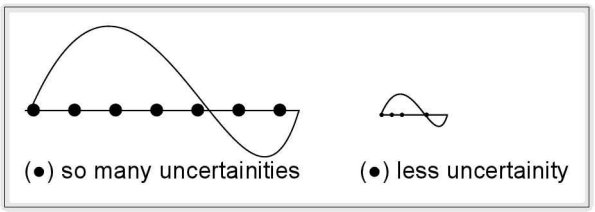


Fig.1.30

When the photon strikes the particle it changes the momentum of the particle. The greater the energy of the stricking photon, the more is the change in moventum of particle.

Δp = uncertainity in measurement of momentum = Δ (mv) = m × ΔV

$$\Delta p \propto \frac{hc}{\lambda}$$

$$\Delta p \propto \frac{1}{\lambda} \qquad hc = \text{constant}$$

$$\Delta p\, \Delta x \qquad \propto \frac{1}{\lambda} \times \lambda$$

$$\Delta p\, \Delta x \geq \frac{h}{4\pi}$$

The greater than sign is included for human error.

If Δp is high, Δx is small (because product has to be constant, when position is precise, accurate, momentum is not).

If Δx is greater, Δp is smaller(hence momentum can be determined accurately but position cannot be)

We see objects by noting their interaction with visible light. The object must be at least as large as the

wavelength of the light. Electromagnetic radiation of an extremely short wavelength would be needed to locate an object as small as an electron. Photons of radiation having a short wavelength and a high frequency have a great deal of energy. When a photon of high-energy radiation strikes an electron, the collision causes the direction of motion and the speed of the electron to change. The attempt to locate the electron changes the velocity of the electron.

Photons with longer wavelengths are less energetic and would have a smaller effect on the electron's velocity. However, because of their longer wavelength, these photons would not show the position of the electron very precisely. According to the German physicist Werner Heisenberg, the uncertainty in the position of an object times the uncertainty in the velocity of the object is equal to or greater than h/4πm,

$$\Delta x \cdot \Delta \upsilon \geq \frac{h}{4\pi m}$$

In the above equation, Δx is the uncertainty in position of the particle and Δv, the uncertainty in its velocity; h is Planck's constant, 6.626×10^{-34} kg.m²/s, and m is the mass of the particle in kg.

Smaller the mass of an object, the greater the product of the uncertainty of its position and velocity. The uncertainty in measuring position and velocity is very important for objects as small as an electron. The uncertainty in measuring position and velocity is not significant for objects of ordinary size. Police officers have no difficulty measuring both the position and the velocity of speeding cars. The world of submicroscopic particles like the electron is very different from the ordinary macroscopic world of our everyday life.

Uncertainty in measuring the position and velocity of a submicroscopic particle is different from ordinary uncertainty in measurements. Ordinary uncertainty in measurements can be reduced by using more precise and more accurate instruments; uncertainty in measuring the position and velocity of a submicroscopic particle is unavoidable. An exact description of the path of an electron in an atom like the orbits in Bohr's model is impossible and attempts to patch up Bohr's theory are useless. Looking at an electron as a wave, it is not surprising that we are uncertain about its position.

Schrodinger was 39 years old when he published his wave equation, his first important work. Most scientists are much younger than this when they begin making major contributions.



Worked-out Examples

29. If the uncertainity in the measurement of position and uncertainty is measurement of momentum are equal for an electron, calculate uncertainty in measurement of velocity.

Solution $\Delta p \quad \Delta x \geq \frac{h}{4\pi}$

$\Delta p = \Delta x$

$\Delta p \times \Delta x \geq \frac{h}{4\pi} \qquad \Delta^2 \geq \frac{h}{4\pi}$

$\Delta (mv)^2 \geq \frac{h}{4\pi}$

$\Delta mv \geq \sqrt{\frac{h}{4\pi}} \qquad \Delta v \geq \sqrt{\frac{h}{\pi}} \times \frac{1}{2m}$

30. Uncertainty in position of a minute particle of mass 25 g in space is 10^{-5} m. The uncertainty in its velocity (in ms^{-1}) is: **[AIEEE-2002]**

(a) 2.1×10^{-34} (b) 0.5×10^{-34}

(c) 2.1×10^{-28} (d) 0.5×10^{-23}

Solution (c) $\Delta_H = \dfrac{h}{4\pi m.\Delta x} = \dfrac{6.626\times10^{-34}}{4\times3.14\times25\times10^{-3}\times10^{-5}} = 2.1 \times 10^{-18}$ m sec^{-1}

31. The uncertainty principle and the concept of wave nature of matter were proposed by..... and ..... respectively. (Heisenberg, Schrodinger, Maxwell, de Broglie) **[IIT-JEE-1988]**

Solution Heisenberg, de Broglie.

32. Uncertainty in the position of an electron (mass 9.1×10^{-31} kg) moving with a velocity 300 ms^{-1}, accurate upto 0.001% will be: **[AIEEE-2006]**

(a) 19.2×10^{-2} m (b) 5.76×10^{-2} m

(c) 1.92×10^{-2} m (d) 3.84×10^{-2} m

Solution (c) $\Delta x = \dfrac{h}{4\pi m\Delta u} = \dfrac{6.626\times10^{-34}\times100}{4\times3.14\times9.1\times10^{-31}\times0.001\times300} = 1.93 \times 10^{-2}$ m

33. In an atom, an electron is moving with a speed of 600m/s with an accuracy of 0.005% Certainity with which the position of the electron can be located is ($h = 6.6 \times 10^{-34}$ kg m^2s^{-1}, mass of electron, $e_m = 9.1 \times 10^{-31}$ kg) **[AIEEE-2009)**

(a) 1.52×10^{-4} m (b) 5.10×10^{-3} m

(c) 1.92×10^{-3} m (d) 3.84×10^{-3} m

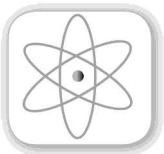
Solution (c) $\Delta x.m\ \Delta v = \dfrac{h}{4\pi}$

$$\Delta x = \frac{h}{4\pi\ m\Delta v}$$

$$\Delta v = 600\times\frac{0.005}{100} = 0.03\ ms^{-1}$$

$$\Rightarrow \Delta x = \frac{6.625\times10^{-34}}{4\times3.14\times9.1\times10^{-31}\times0.03} = 1.92\times10^{-3} m$$

QUANTUM NUMBERS AND ATOMIC ORBITALS



Each electron in an atom is described by four different quantum numbers, three of which (n, *l*, m) specify the wave function that gives the probability of finding the electron at various points in space. A wave function for an electron in an atom is called an atomic orbital. An atomic orbital is pictured qualitatively by describing the region of space where there is high probability of finding the electrons

Quantum numbers may be defined as a set of four numbers with the help of which we can get complete information about all the electrons in an atom i.e., location, energy, the type of orbital occupied, shape and orientation of that orbital etc.



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Principle Quantum Number

It tells us about the shell in which the electron resides and is denoted by the letter 'n'. It can have any positive value 1, 2, 3 and so on. It gives the following information:

(i) It gives the average distance of the electron from the nucleus.
(ii) It determines the energy of the electron in hydrogen atom and hydrogen like species.
(iii) The maximum number of electrons present in any principal shell is given by $2n^2$ where n is the number of principal shell.

Shell	K	L	M	N
Principal quantum number (n)	1	2	3	4
Maximum number of electrons	2	8	18	32

Azimuthal or Angular Momentum Quantum Number (l)

This represents the number of subshells persent in the main shell and is denoted by *l*. It can have any integral value ranging from 0 to n-1. This quantum number gives the following information:

(i) The number of sub-shells present in the main shell.
(ii) The shape of the subshells.
(iii) The orbital angular momentum of the electron in any subshell.

As *l* is responsible for the ellipticity of the orbits, *l* values describe the shapes of the electron orbits.

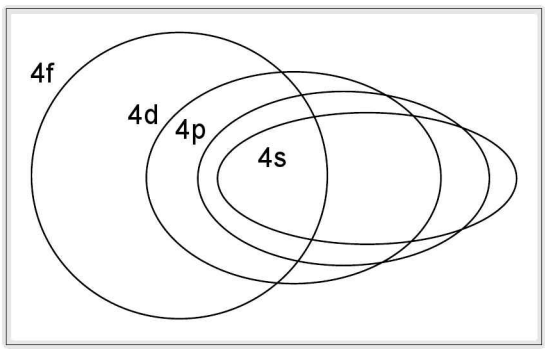


Fig. 1.31

A pictorial representation of the Bohr-Sommerfeld orbits for n = 4 is shown in figure. The smaller the value of k for a given n the greater is the eccentricity of the ellipse. Electrons with *l* = 0, 1, 2, 3 are called s, p, d, f electrons and the corresponding levels are called s, p, d, f sublevels or subshells. When *l* = 0 angular momentum is zero and we have the most eccentric elliptic orbits. The s electrons are closest to the nucleus, are held more firmly and are of lower energy than electrons with higher *l* values.

When *l* = (n – 1) the orbits become circular. Therefore, orbits with increasing values of *l* are also orbits of increasing energy. It should be pointed out at this stage that the shapes of the orbits rather the orbitals (which are the most probable regions for the electrons to stay) which chemists work with are those derived from the wave mechanical treatment of the atom.

Zeeman had noticed that line spectra became more complicated on application of a magnetic field. This could be explained by further elaborating the azimuthal quantum number. It was necessary to postulate that the angular momentum of the electron in the direction of the magnetic field was given by $m_l\, h/2\pi$ where m_l is an additional quantum number designated as magnetic quantum number.

Since the line spectra were split further in a magnetic field it was concluded that the magnetic quantum number can assume only certain permitted values. These are given by,

$$m_l = +l, (l-1).....0.....-(l-1), -l,$$

a total of $2l + 1$ values. If the orbital angular momentum is represented by a vector l(where $l = \sqrt{l(l+1)}\frac{h}{2\pi}$, l being the azimuthal quantum number).

Magnetic quantum number (m)

An electron due to its angular motion around the nucleus generates an electric field. This electric field is expected to produce a magnetic field. Under the influence of external magnetic field, the electrons of a sub-shell can orient themselves in certain preferred regions of space around the nucleus orbitals. The magnetic quantum number determines the number of preferred orientations of the electron present in a sub-shell. The number of allowed orientations depend on the value of l. m can assume all integral values between $-l$ to $+l$ including zero. Thus m can be +1, 0, –1 for t, = 1 and for $l = 2$, m will have five values i.e., +2, +1, 0, –1, –2. The orbital angular momentum of an electron is given, according to quantum mechanics, not as l (h/2π) but as:

$$mvr = \sqrt{l(l+1)}\frac{h}{2\pi}$$

then the vector can assume $2l + 1$ orientations in a magnetic field (figure). The components of l in different orientations along the direction of the applied magnetic field represents the different m_l values ($m_l = l \cos\theta$). For $l = 2$ we have five different orientations possible for the orbital in a magnetic field since m_l can have values +2, +1, 0, –1 and –2. These five orientations of the orbit are shown in Figure. The direction of the vector is the direction to which the forefinger points while the tumb describes a progressing right handed screw motion, the motion being that of the moving body. Note when the plane of rotation of the electron is perpendicular to the field direction, the length of the component of the vector l along the field direction is equal to $l(\theta = 0)$. Thus, m_l values indicate the tilts of the orbits with respect to the field direction. Positive m_l values indicate components of l along the field direction and negative values stand for components opposite to the field direction

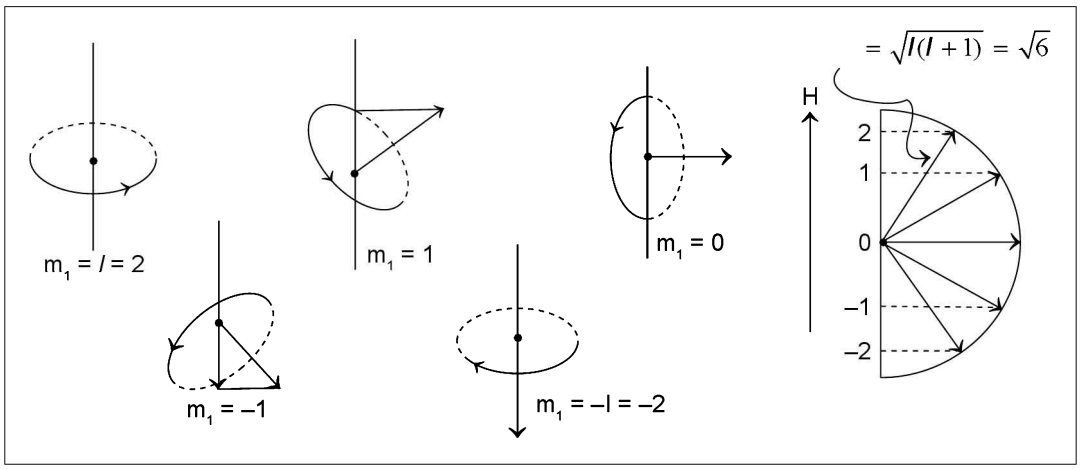


Fig. 1.32

Spin quantum number (s)

Besides the three quantum numbers n, l and m_l and fourth quantum number, namely spin quantum number, was necessary to completely describe an electron in a particular shell. The electron itself can be regarded as a small magnet. A beam of hydrogen atoms can be spit into two beams by a strong magnetic field. This indicates that there are two kinds of hydrogen atoms which can be differentiated on the basis of their

behaviour in a magnetic field. It has been postulated that each electron spins around its axis like a top and thereby behaves like a small magnet. A spinning electron can have only two possibilities. The electron can either spin clockwise or counter-clockwise (Figure). The two directions of spin are represented by arrows pointing either up or down (↑or ↓). This fourth quantum number, s, $(= \frac{1}{2})$ is independent of the other three quantum numbers n, l or m_l 's' can have two possible m_s values $+\frac{1}{2}$ or $-\frac{1}{2}$ depending on the direction of rotation of the electron about its axis. This spin angular momentum is given by: $\sqrt{s(s+1)}\frac{h}{2\pi}$

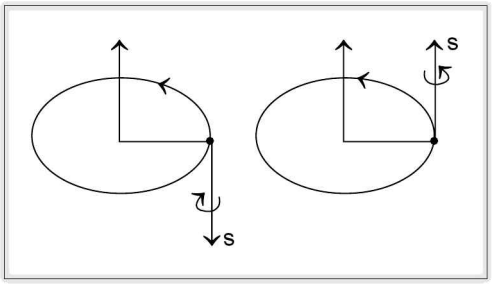


Fig. 1.33

With these four quantum numbers it is possible to proceed with the building up of the electronic structure in multielectron systems. But we will defer that till we describe the currently followed probability model of the electron.



Worked-out Examples

35. In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic field **[AIEEE-2005]**

(i) n = 1, l = 0, m = 0 (ii) n = 2, l = 0, m = 0

(iii) n = 2, l = 1, m = 1 (iv) n = 3, l = 1, m = 1

(v) n = 3, l = 2, m = 0

(a) (i) and (ii) (b) (ii) and (iii) (c) (iii) and (iv) (d) (iv) and (v)

Solution (d) Orbitals having (n + l) same possess same energy in the absence of magnetic field

36. Match the entries is Column-I with the correctly related quantum number(s) is Column-II. Indicate your answer by darkening the appropriate bubbles in the 4 × 4 matrix given in the ORS. **[IIT-2008]**

Column-I	Column-II
(a) Orbital angular momentum of the electron in hydrogen in a hydrogen-like atomic orbital	(p) Principal quantum number
(b) A hydrogen-like one-electron wave function obeying Pauli principle	(q) Azimuthal quantum number
(c) Shape, size and orientation of hydrogen like atomic orbitals	(r) Magentic quantum number
(d) Probability density of electron at the nucleus in hydrogen-like atom	(s) Electron spin quantum number

Solution (a): (q); (b): (s); (c): (p.q.r); (d): (p.q)

Shapes and size of orbitals

An orbital is the region of space around the nucleus within which the probability of finding an electron of given energy is maximum (90–95%). The shape of this region (electron cloud) gives the shape of the orbital. It is basically determined by the azimuthal quantum number *l*, while the orientation of orbital depends on the magnetic quantum number (m). Let us now see the shapes of orbitals in the various sub-shells.

s-orbitals: These orbitals are spherical and symmetrical about the nucleus. The probability of finding the electron is maximum near the nucleus and keeps on decreasing as the distance from the nucleus increases. There is vacant space between two successive s–orbitals known as radial node. But there is no radial node for 1s orbital since it is starting from the nucleus.

The size of the orbital depends upon the value of principal quantum number(n). Greater the value of n, larger is the size of the orbital. Therefore, 2s-orbital is larger than 1s orbital but both of them are non-directional and spherically symmetrical in shape.

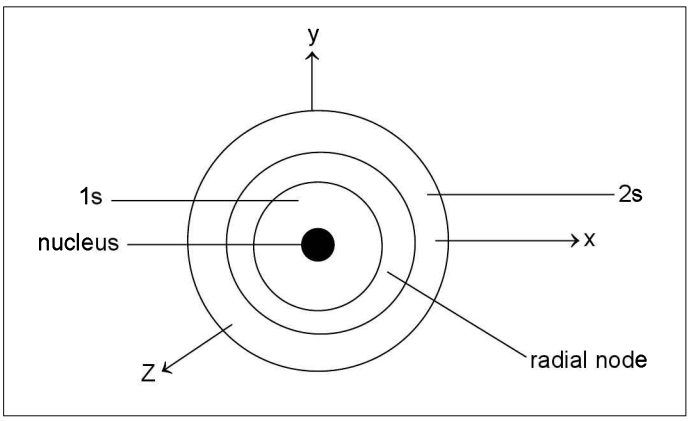


Fig. 1.34

p-orbitals (l =1): The probability of finding the p-electron is maximum in two lobes on the opposite sides of the nucleus. This gives rise to a dumb–bell shape for the p–orbital. For p-orbital $l = 1$. Hence, m = –1, 0, +1. Thus, p–orbital has three different orientations. These are designated as p_x, p_y and p_z depending upon whether the density of electron is maximum along the xy and z axis respectively. As they are not spherically symmetrical, they have directional character. The two lobes of p–orbitals are separated by a nodal plane, where the probability of finding electron is zero

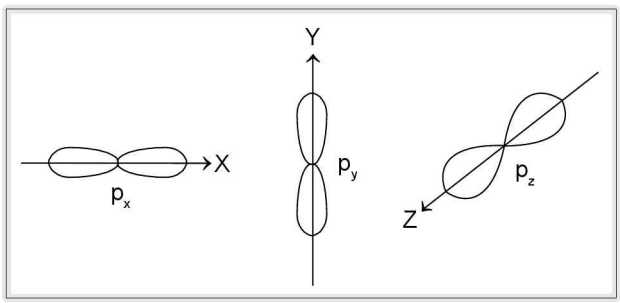


Fig. 1.35

The three p-orbitals belonging to a particular energy shell have equal energies and are called ***degenerate orbitals***.

d—orbitals (l = 2): For d-orbitals, $l = 2$. Hence, m = –2, –1, 0, +1, +2. Thus, there are 5 d-orbitals. They have relatively complex geometry. Out of the five orbitals, the three (d_{xy}, d_{yz},d_{zx}) project in between the axis and the other two d_{z^2} and $d_{x^2-y^2}$ lie along the axis.

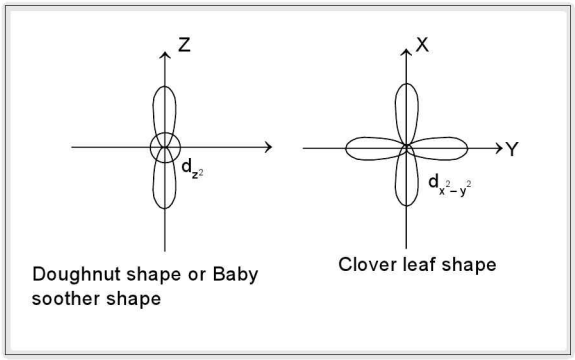


Fig. 1.36 (a)

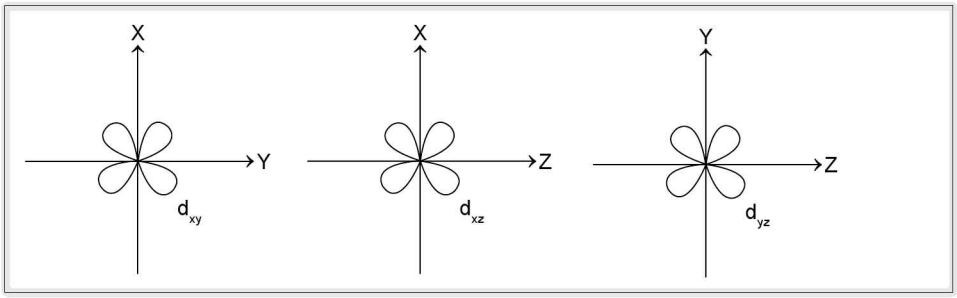


Fig. 1.36 (b)

Rules for filling of electrons in various orbitals

The atom is built up by filling electrons in various orbitals according to the following rules

Aufbau Principle: This principle states that the electrons are added one by one to the various orbitals in order of their increasing energy starting with the orbital of lowest energy. The increasing order of energy of various orbital is

1s,2s,2p,3s,3p,4s,3d,4p,5s,4d,5p,6s,4f,5d,6p,5f,6d,7p……

How to remember such a big sequence? To make it simple we are giving you the method to write the increasing order of the orbitals. Starting from the top, the direction of the arrows gives the order of filling of orbitals.

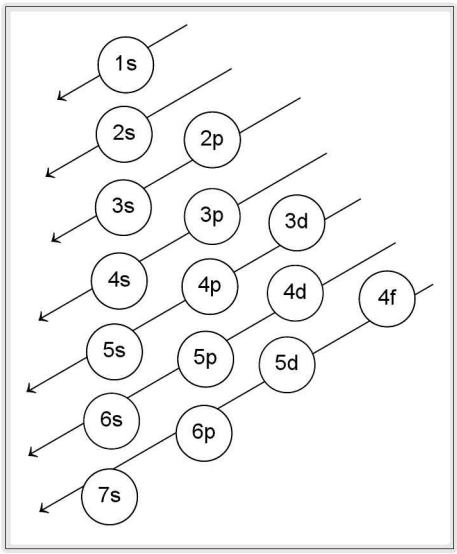


Fig. 1.37

Alternatively, the order of increasing energies of the various orbitals can be calculated on the basis of (n + *l*) rule.

The energy of an orbital depends upon the sum of values of the principal quantum number (n) and the azimuthal quantum number (*l*). This is called (n + *l*) rule. According to this rule,

"In neutral isolated atom, the lower the value of (n+ l) for an orbital, lower is its energy. However, if the two different types of orbitals have the same value of (n+ l), the orbitals with lower value of n has lower energy".

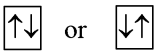
Illustration of (n + *l*) rule

Type of orbitals	*Value of n*	*Values of l*	*Values of (n+ l)*	*Relative energy*
1s	1	0	1 + 0 = 1	Lowest energy
2s	2	0	2 + 0 = 2	Higher energy than 1s orbital
2p	2	1	2 + 1 = 3	2p orbital (n=2) have lower energy than 3s orbital (n=3)
3s	3	0	3 + 1 = 3	

Pauli's exclusion principle

According to this principle, an orbital can contain a maximum number of two electrons and these two electrons must be of opposite spin.

Two electrons in an orbital can be represented by,

 or

Hund's rule of maximum multiplicity

This rule deals with the filling of electrons in the equal energy (degenerate) orbitals of the same sub shell (p, d and f). According to this rule,

"Electron pairing in p,d and f orbitals cannot occur untill each orbital of a given subshell contains one electron each or is singly occupied".

This is due to the fact that electrons being identical in charge, repel each other when present in the same orbital. This repulsion can, however, be minimized if two electrons move as far apart as possible by occupying different degenerate orbitals. All the electrons in a degenerate set of orbitals will have same spin.

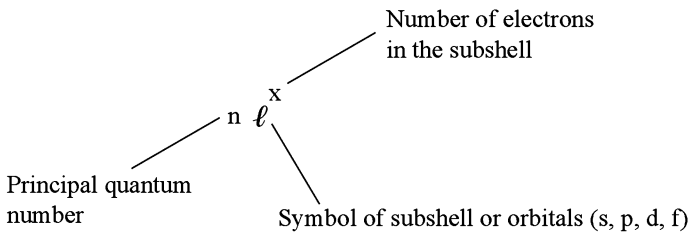
Electronic configuration of elements

Electronic configuration is the distribution of electrons into different shells, subshells and orbitals of an atom.



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Keeping in view the above mentioned rules, electronic configuration of any orbital can be simply represented by the notation.



Alternatively

Orbital can be represented by a box and an electron with its direction of spin by arrow. To write the electronic configuration, just we need to know (i) the atomic number (ii) the order in which orbitals are to be filled (iii) maximum number of electrons in a shell, sub–shell or orbital

To determine the electronic configuration of elements the procedure is to feed electrons in different orbitals obeying certain rules. The aufbau or building up principle is based on the following rules:

1. *Electrons are fed into orbital in order of increasing energy (increasing n) until all the electrons have been accommodated.*
2. *Electrons will tend to maintain maximum spin.* So long as vacant orbitals of similar energy are available for occupation, electrons will prefer to remain unpaired. In other words, electrons tend to avoid the same orbital, that is, hate to share space. This rule is known as Hurd's rule of maximum spin multiplicity (see Chapter 11).
3. *Spin pairing can occur only when vacant orbitals of similar energy are not available for occupation, and when the next available vacant orbital is of a higher energy.*

Hydrogen (atomic number 1) has its only electron in the 1s orbital and this electronic configuration is represented as:

$$\underset{1s}{\uparrow}$$

the bar indicates the orbital and the arrow a single spinning electron in the orbital. In helium (at. No. 2), the second electron has to occupy the 1s orbital since the next available *2s* orbital is of much higher energy. Obeying Pauli principle the configuration 1^2 is represented as:

$$\underset{1s}{\uparrow\downarrow}$$

Lithium (at no. 3) has the configuration $1s^2\ 2s^1$, beryllium $1s^2\ 2s^2$ and boron $1s^2\ 2s^2\ 2p^1$. After boron comes carbon and the next electron can remain unpaired in another *p* orbital of similar energy so that we write the configuration $s^2\ 2s^2\ 2p^2$ of carbon as:

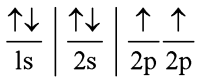
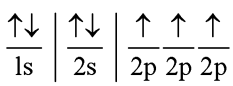
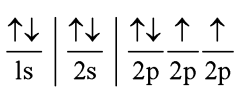
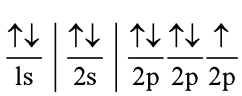
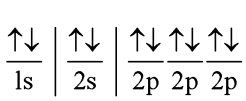
$$\underset{1s}{\uparrow\downarrow} \;\Big|\; \underset{2s}{\uparrow\downarrow} \;\Big|\; \underset{2p}{\uparrow} \; \underset{2p}{\uparrow} \; \underset{2p}{}$$

Continuing in this way we develop Table 1.1. for elements from hydrogen to neon.

Table 1.1 Electronic Configuration of Elements H to Ne

Element	*Atomic Number*	*Electronic Configuration*	*Pictorial Representation*
H	1	$1s^1$	$\underset{1s}{\uparrow}$
He	2	$1s^2$	$\underset{1s}{\uparrow\downarrow}$
Li	3	$1s^2 2s^1$	$\underset{1s}{\uparrow\downarrow} \;\Big|\; \underset{2s}{\uparrow}$
Be	4	$1s^2\ 2s^2$	$\underset{1s}{\uparrow\downarrow} \;\Big|\; \underset{2s}{\uparrow\downarrow}$
B	5	$1s^2\ 2s^2\ 2p^1$	$\underset{1s}{\uparrow\downarrow} \;\Big|\; \underset{2s}{\uparrow\downarrow} \;\Big|\; \underset{2p}{\uparrow}$

(Contd)

C	6	$1s^2\ 2s^2\ 2p^2$	
N	7	$1s^2\ 2s^2\ 2p^3$	
O	8	$1s^2\ 2s^2\ 2p^4$	
F	9	$1s^2\ 2s^2\ 2p^5$	
Ne	10	$1s^2\ 2s^2\ 2p^6$	

After neon the next available orbital is 3s being followed by *3p*. The orbitals are then progressively filled by electrons. The elements concerned are sodium (11), magnesium (12) aluminium (13), silicon (14), phosphorus (15), sulphur (16), chlorine (17) and argon (18). Then the 4s orbital, being of lower energy than the *3d,* is filled. The elements involved are potassium (19) and calcium (20):

$$K : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 \text{ and } Ca : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$$

In scandium (21), the twentyfirst electron goes to a *3d* orbital, the next available orbital of higher energy. There are five 3d orbitals with a capacity of ten electrons. From scandium to zinc these *d* orbitals are being filled up. *Presence of partially filled d orbital generates some very special properties. Elements with partly filled d (or f) orbitals in elementary state or in some oxidation states are called transition.* Table 1.1 summarises the electronic configurations of the elements scandium 10 zinc. The configurations, in Table 1.1 are given on the basis of the aufbau principle. In reality experimental studies on copper and chromium reveal that their electronic configurations are better represented as

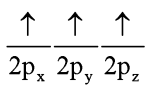
$$\text{Cr (24) } 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$$

$$\text{Cu (29) } 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$$

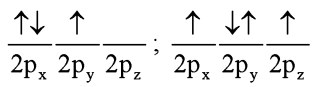
This reordering of electrons is due to an extra stability associated with a half-filled or a filled subshell. Strict adherence to the above definition of transition elements will exclude zinc from the list. An elaborate discussion on these elements is reversed for Part II.

The above discussion explains why chromium and copper in their ground atomic states have a half-filled and filled shell respective .

In the light of exchange interaction we can examine the ground state electron distribution of the nitrogen atom: $1s^2\ 2s^2\ 2p^3$. The three *2p* electrons have to have the following distribution:



The alternative arrangements like,



are rejected because they do not maximise spin and also give lower exchange energy 1K compared to *3K* for the ground state.

Table 1.2 Electronic Configurations of the First Series of Transition Elements

Element	*Atomic Number*	*Electronic Configuration*	*Pictorial Representation*
Scandium	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow}{3d}\ \frac{}{3d}\ \frac{}{3d}\ \frac{}{3d}\ \frac{}{3d}$
Titanium	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{}{3d}\ \frac{}{3d}\ \frac{}{3d}$
Vanadium	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{}{3d}\ \frac{}{3d}$
Chromium	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{}{3d}$
Manganese	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}$
Iron	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow\downarrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}$
Cobalt	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}$
Nickel	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow}{3d}\ \frac{\uparrow}{3d}$
Copper	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow}{3d}$
Zinc	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$	[Ar] $\frac{\uparrow\downarrow}{4s}$ $\frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}\ \frac{\uparrow\downarrow}{3d}$

Interaction Among Electrons and Extra Stability of Half-Filled and Filled Shells

Mutual electrostatic repulsion leads to two types of interaction among electrons. (1) The first is called *charge correlation.* If two electrons are separated by a distance r then the Coulomb energy of each is given by e^2/r where e is the electrostatic charge. This clearly indicates that a two-electron or a multielectron system will get stabilised when r increases *i.e.,* when the electrons stay away from each other. Thus two *d* electrons will be better off in two *d* orbitals rather than in one. (2) The second interaction is known as *spin correlation* and is more important than charge correlation. According to spin correlation electrons of same spin tend to keep away from each other while electrons of opposite spin tend to come closer. Electrons of similar spin develop an *exchange interaction* which leads to the stabilisation of the system. For electrons of similar spin repulsion is less by an amount called *exchange energy.* The greater the number of electrons with parallel spins the greater is the exchange interaction and the greater is the stability. This is the basis of Hund's rule of maximum spin multiplicity. In the absence of any electric or magnetic field electrons with parallel spin and with the same n and l have similar wave functions. They are indistinguishable and can exchange their positions.

For the *d* subshell maximum stability will result if there are five electrons with parallel spins in the five d-orbitals, each orbital having one *i.e.,* when the *d* subshell is half-filled. If it were possible to tag the electrons *as* 1, 2, 3, 4 and 5 we could write as many as ten pairs with parallel spins : (1, 2), (1, 3), (1, 4), (1, 5), (2, 3), (2, 4), (2, 5), (3, 4), (3, 5) and (4, 5). If K stands for the exchange energy per pair of parallel

spins and *n* for the number of electrons with parallel spins then the total *exchange (stabilisation)* energy is given by:

$$E_{exchange} = \frac{n(n-1)}{2}K$$

Thus, for five unpaired electrons with parallel spins, the exchange energy is 10*K*. If one electron is withdrawn we have a d^4 system with exchange (stabilisation) energy *6K*. Instead if we introduce a sixth electron into the d subshell it will have its spin opposed (antiparallel) to all the five parallel spins. Since there are still five electrons with parallel spins the exchange energy will still be 10*K* but there will be significant Coulomb repulsion because of two electrons being in the same orbital, Thus, we see that a half-filled subshell has greater stability than a less than half-filled subshell or a more than half-filled subshell. Similar arguments will convince us of the extra stability of filled d^{10} subshell. We then have as exchange energy as 10K for the five parallel spins and another 10*K* for the five antiparallel spins. For a d^9 shell we would have 10*K* for the five parallel spins and only *6K* for the four antiparallel spins. Thus a d^{10} subshell gains in stability by *4K (= 20K – 16K)* over a d^9 subshell.

(a) Each orbital can accommodate two electrons
(b) The number of electrons to be accomodated in a subshell is 2 × number of degenerate orbitals.

Subshell	*Maximum number of electrons*
s	2
p	6
d	10
f	14

(c) The maximum number of electron in each shell (K,L,M,N…) is given by $2n^2$. where n is the principal quantum number.
(d) The maximum number of orbitals in a shell is given by n^2 where n is the principal quantum number.
(e) The number of nodal planes associated with an orbital is given by l-1.

Importance of knowing the electronic configuration

The chemical properties of an element are dependent on the relative arrangement of its electrons.



Worked-out Example

36. Write the electronic configuration of nitrogen (atomic number = 7)

Solution



Exceptional Configurations

Stability of half filled and completely filled orbital

Cu has 29 electrons. Its expected electronic configuration is,

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

But a shift of one electron from lower energy 4s orbital to higher energy 3d orbital will make the distribution of electron symmetrical and hence will impart more stability.

Thus, the electronic configuration of Cu is

$1s^2\ 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Fully filled and half filled orbitals are more stabl

Total spin and spin magnetic moment

The total spin (s) of an atom is given by $s = \frac{1}{2} \times n$, where n is number of unpaired electrons. The spin magnetic moment of electron (excluding orbital magnetic moment) is given by:

$$\mu_{effective} = \sqrt{[4s(s+1)]}$$

Putting, $s = \frac{1}{2}n$

$$\mu_{effective} = \sqrt{[n(n+2)]} \text{ BM}$$

The magnetic moment is expressed in Bohr Magneton (BM), where 1 BM = 9.27×10^{-24} J/T.

Example

A compound of vanadium has a magnetic moment 1.73 BM. Work out the electronic configuration of vanadium ion in this compound.

Solution

No. of unpaired electrons are given by magnetic moment $= \sqrt{[n(n+2)]}$, where n is no. of unpaired electrons.

or $1.73 = \sqrt{[n(n+2)]}$ or $1.73 \times 1.73 = n^2 + 2n \therefore n = 1$

Now vanadium atom must have one unpaired electron and thus its configuration is

$_{23}V^{4+}$: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$

Magnetic Moment

$\mu = \sqrt{n(n+2)}$ Bohr Magneton (unit of magnetic moment)

n = number of unpaired electrons

$_8O$ ⇅ ⇅ ⇅ 1 1

1s 2s 2p

No. of unpaired electron = 2

$\mu = \sqrt{2(2+2)} = \sqrt{2 \times 4} = \sqrt{8} = 2\sqrt{2}$ B.M.

Compare the magnetic moment of P(15) Mg(12) A1(13) Na^+(11)

P(15) ⇅ ⇅ ⇅ ⇅ ⇅ 1 1 1

$1s^2 2s^2 2p^6 3s^2 3p^3$ $n = 3 = \sqrt{3(5)}$

$\mu = \sqrt{15}$ B.M.

Mg(12) ⇅ ⇅ ⇅ ⇅ ⇅

$1s^2 2s^2 2p^6 3s^2$ $n = 0$

$\mu = 0 \leftarrow$ Diamagnetic

A1(13)

$1s^2\ 2s^2 2p^6 3s^2 3p^1$ 1

$n = 1$

$\mu = \sqrt{2}$

Na^+ (10) ⇅ ⇅ ⇅ ⇅ ⇅

$1s^2 2s^2 2p^6$ $n = 0 \leftarrow$ Diamagnetic

$\mu = 0 \quad \therefore P > A1 > Mg = Na^+$



Worked-out Examples

37. We know that fully filled and half filled orbitals are more stable. Can you write the electronic configuration of Cr(Z = 24)?

Solution Cr (Z = 24)

$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$.

Since half filled orbital is more stable one, 4s electron is shifted to 3d orbital

38. The number of electrons with the azimuthal quantum number $l = 1$ and $l = 2$ in ground state of $_{24}Cr$ is respectively: **[AIEEE-2004]**

(a) 16 and 5 (b) 12 and 5
(c) 16 and 4 (d) 12 and 4

Solution (b) $_{24}Cr : 1s^2, 2s^22p^6, 3s^23p^63d^5, 4s^1$

39. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them: **[AIEEE-2004]**

(a) $(n-1)d^5 ns^2$ (b) $(n-1)d^5ns^1$
(c) $(n-1)d^3 ns^2$ (d) $(n-1)d^8 ns^2$

Solution (a) +7 state can be achieved by five d-electrons and two s-electrons.

40. The spin only magnetic moment (in Bohr magneton, M_B) of Ni^{2+} in aqueous solution would be: **[AIEEE-2006]**

(a) 2.84 (b) 4.90 (c) 0 (d) 1.73

Solution (a) $Ni^{2+} : 1s^2, 2s^2\ 2p^6, 3s^23p^63d^6$
(with two unpaired electrons)
Thus, magnetic moment

$$= \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$$

41. The outer electronic configuration of the ground state chromium atom is $3d^44s^2$. **[IIT-JEE-1982]**

Solution False: The outer electronic configuration of the ground state chromium atom is $3d^5\ 4s^1$, as half filled orbitals are more stable.

42. The outermost electronic configuration of Cr is..... . **[IIT-JEE-1994]**

Solution $3d^5\ 4s^1$; The electronic configuration of Cr is: $1s^2, 2s^2p^6\ 3s^2p^6d^5, 4s^1$
Outermost electronic configuration is $3d^5, 4s^1$

43. The electronic configurati n of an element is $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$. This represents its **[IIT-JEE-2000]**

(a) excited state (b) ground state
(c) cationic form (d) anionic form

Solution (b) $3d^54s^1$ system is more stable than $3d^44s^2$, hence former is the ground state configura tion.

44. If the nitrogen atom has electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^22s^22p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates.

(a) Heisenberg uncertainty principle (b) Hund's rule
(c) Pauli exclusion principle (d) Bohr postulate of stationary orbits

Solution (c) As per Paul! Exclusion Principle "no two electrons in the same atom can have all the four quantum numbers equal or an orbital cannot contain more than two electrons and it can accommodate two electrons only when their directions of spins are opposite".

45. Which of the following satement(s) is (are) correct? **[IIT-JEE-1998]**

(a) The electronic configuration of Cr is [Ar] $3d^5 4s^1$. (Atomic Number of Cr = 24)

(b) The magnetic quantum number may have a negative value.

(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic Number of Ag = 47)

(d) The oxidation state of nitrogen in HN_3 is – 3.

Solution (a, b, c) $_{24}Cr = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1 = [Ar]\ 3d^5, 4s^1$

For magnetic quantum number (m), negative values are possible.

For s-subshell, l = 0, hence m = 0

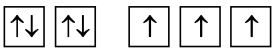
for p-subshell, l = 1, hence m =-1, 0, +1

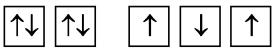
$_{47}Ag = 1s^2, 2s^2\ 2p^6, 3s^2 3p^6 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^1$

Hence, 23 electrons have a spin of one type and 24 of the opposite type.

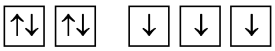
Oxidation state of N in HN_3 is-1/3.

46. Ground state electronic configuration of nitrogen atom can be represented by **[IIT-JEE-1999]**

(a) 

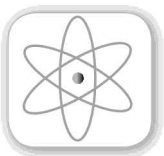
(b) 

(c) 

(d) 

Solution (a, d) Only the configurations (a) and (d) follow Hund's rule.

THE SCRODINGER WAVE EQUATION



For a standing wave of wavelength λ, whose amplitude at any point along x may be described by a function f(x), it can be written that

$$\frac{d^2 f(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2} f(x)$$

If an electron is considered as a wave which moves in only one dimension then

$$\frac{d^2\psi}{dx^2} = \frac{4\pi^2}{\lambda^2}\psi$$

An electron may move in three directions x, y and z so this becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\psi$$

Using the symbol ∇ instead of the three partial differentials, this can be shortened to

$$\nabla^2\psi = \frac{4\pi^2}{\lambda^2}\psi$$

The de Broglie relationship states that,

$$\lambda = \frac{h}{mv}$$

(where) h is Planck's constant, m is the mass of an electron and v its velocity); hence,

$$\nabla^2\psi = \frac{4\pi^2 m^2 v^2}{h^2}\psi$$

or

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \qquad \text{(i)}$$

However, the total energy of the system E is made up of the kinetic energy K plus the potential energy V

$$E = K + V$$

so

$$K = E - V$$

But the kinetic energy $= \frac{1}{2}mv^2$

Therefore, $\frac{1}{2}mv^2 = E - V$

$$v^2 = \frac{2}{m}(E-V)$$

Substituting for v^2 in equation (i) gives the well-known form of the Schrodinger equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

Acceptable solutions to the wave equation, that is solutions which are physically possible, when ψ is finite, continuous, single valued an

- The probability of finding the electron over all the spaces from plus infinity to minus infinity must be equal to one.
  The probability of finding an electron at a point x, , z is ψ^2, so,

$$\int_{-\infty}^{+\infty} \psi^2 \, dx\, dy\, dz = 1$$

Several wave functions called ψ_1, ψ_2, ψ_3.... will satisfy these conditions to the wave equation, and each of these has a corresponding energy E_1, E_2, E_3..... Each of these wave functions ψ_1, ψ_2, etc., is called an orbital, by analogy with the orbits in the Bohr theory. In a hydrogen atom, the single electron normally occupies the lowest of the energy levels E_1. This is called the ground state. The corresponding wave function ψ_1 describes the orbital, that is the volume in space where there is a high probability of finding the electron

For a given type of atom, there are a number of solutions to the wave equation which are acceptable, and each orbital may be described uniquely by a set of three quantum numbers, n, *l* and m.

The subsidiary quantum number *l* describes the shape of the orbital occupied by the electron. *l* may have values 0, 1, 2 or 3. When *l* = 0, the orbital is spherical and is called a p orbital; when *l* = 2,

the orbital is double dumb-bell shaped and is called a d orbital; and when $l = 3$ a more complicated f orbital is formed.

Examination of a list of all the allowed solutions to the wave equation shows that the orbitals fall into groups.

In the first group of solutions, the value of the wave function ψ, and

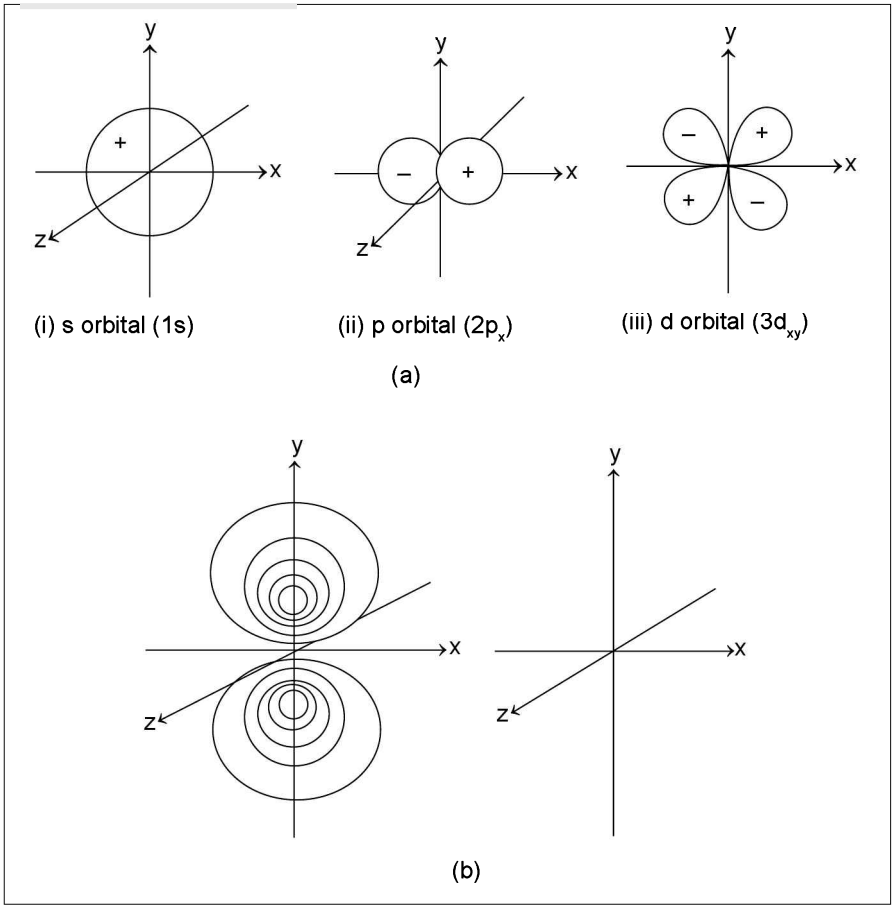


Fig. 1.38 (a) Wave functions ψ for s, p and d atomic orbitals. (Note that the + and – signs refer to symmetry, not charge.) (b) Different ways of representing ψ^2 for a 2p orbital (as a contour diagram or as a 90% boundary surface)

Hence the probability of finding the electron ψ^2, depends only on the distance r from the nucleus, and is the same in all directions.

$$\psi = f(r)$$

This leads to a spherical orbital, and occurs when the subsidiary quantum number l is zero. These are called s orbitals. When $l = 0$, the magnetic quantum number m = 0, so there is only one such orbital for each value of n.

In the second group of solutions to the wave equation, ψ depends both on the distance from the nucleus, and on the direction in space (x, y or z). Orbitals of this kind occur when the subsidiary quantum number $l = 1$. These are called p orbitals and there are three possible values of the magnetic quantum number (m = –1, 0 and +1). There are therefore three orbitals which are identical in energy,

shape and size, which differ only in their direction in space. These three solutions to the wave equation may be written

$\psi_x = f(r) \cdot f(x)$

$\psi_y = f(r) \cdot f(y)$

$\psi_z = f(r) \cdot f(z)$

Orbitals that are identical in energy are termed degenerate, and thus three degenerate p orbitals occur for each of the values of n = 2, 3, 4…..

Principal quantum number n	*Subsidiary quantum number l*	*Magnetic quantum numbers m*	*Symbol*
1	0	0	
2	0	0	
2	1	–1, 0, +1	
3	0	0	
3	1	–1, 0, +1	
3	2	–2, –1, 0, +1, +2	
4	0	0	
4	1	–1, 0, +1	
4	2	–2, –1, 0, +1, +2	
4	3	–3,–2,–1,0,+1,+2,–3	

The third group of solutions to the wave equation depend on the distance from the nucleus r and also on two directions in space, for example,

$\psi = f(r) \cdot f(x) \cdot f(y)$

This group of orbitals has $l = 2$, and these are called d orbitals. There are five solutions corresponding to m = –2, –1, 0, +1 and +2, and these are all equal in energy. Thus five degenerate d orbitals occur for each of the values of n = 3, 4, 5…..

A further set of solutions occurs when $l = 3$, and these are called f orbitals. There are seven values of m; –3, –2, –1, 0, +1, +2 and +3, and seven degenerate f orbitals are formed when n = 4, 5, 6….



Worked-out Examples

47. The electrons, identified by quantum numbers n and l, (i) n = 4, l = 1, (ii) n = 4, l = 0, (iii) n = 3, l = 2, and (iv) n = 3, l = 1 can be placed in order of increasing energy, from the lowest to highest, as **[IIT-1999]**

(a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)

(c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)

Solution (a) The two guiding rules to arrange the various orbitals in the increasing energy are:

(i) Energy of an orbital increases with increase in the value of n + l.

(ii) Of orbitals having the same value of n + l, the orbital with lower value of n has lower energy.

Thus for the given orbitals, we have,

(i) n + l = 4 + 1 = 5

(ii) n + l = 4 + 0 = 4

(iii) n + l = 3 + 2 = 5

(iv) n + l = 3 + 1 = 4

Hence, the order of increasing energy is
(iv) < (ii) < (iii) < (i)

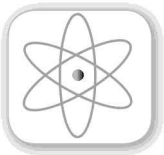
48. The quantum numbers + 1/2 and – 1/2 for the electron spin represent **[IIT-JEE-2001]**
(a) rotation of the electron in clockwise and anticlockwise direction respectively
(b) rotation of the electron in anticlockwise and clockwise direction respectively
(c) magnetic moment of the electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogue

Solution (c) Magnetic moment for an electron exists even if the orbital angular momentum is zero. This is explained by the spin magnetic moment because, it is the spin which produces magnetic moment.

49. When there are two electrons in the same orbital, they have ..... spins. **[IIT-JEE-1982)**

Solution antiparallel;

RADIAL AND ANGULAR FUNCTIONS



The Schrodinger equation can be solved completely for the hydrogen atom, and for related ions which have only one electron such as He^+ and Li^{2+}. For other atoms, only approximate solutions can be obtained. For most calculations, it is simpler to solve the wave equation if the cartesian coordinates x, y and z are converted into polar coordinates, r, θ and ϕ. The coordinates of the point A measured from the origin are x, y, and z in cartesian coordinates, and r, θ and ϕ in polar coordinates. It can be seen from figure that the two sets of coordinates are related by the following expressions:

$$z = r\cos\theta \qquad y = r\sin\theta\sin\phi \qquad x = r\sin\theta\cos\phi$$

The Schrodinger equation is usually written:

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

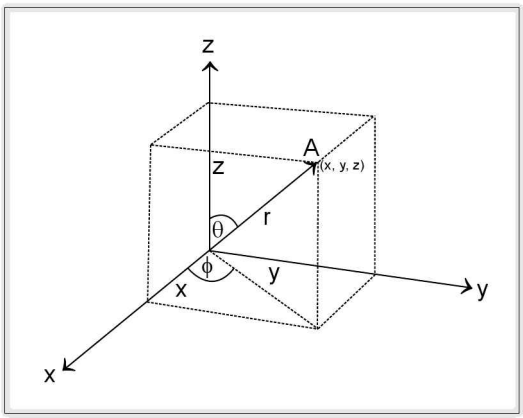


Fig. 1.39 The relationship between Cartesian and polar coordinates

Where,

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

Changing to polar coordinates, $\nabla^2\psi$ becomes,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\varphi^2}+\frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$

The solution of this is of the form,

$$\psi = R(r).\ \Theta(0)\ .\ \Phi(\phi) \qquad \text{(i)}$$

R(r) is a function that depends on the distance from the nucleus, which in turn depends on the quantum numbers n and *l*.

$\Theta(\theta)$ is a function of θ, which depends on the quantum numbers *l* and m

$\Phi(\phi)$ is a function of ϕ, which depends only on the quantum number m

Equation (i) can be written as,

$$\psi = R(r)_{ml}\ .\ A_{ml}$$

This splits the wave function into two parts which can be solved separately:

1. R(r) the radial function, which depends on the quantum numbers n and *l*.
2. A_{ml} the total angular wave function, which depends on the quantum numbers m and *l*.

The radial function R has no physical meaning, but R^2 gives the probability of finding the electron in a small volume dv near the point at which R is measured. For a given value of r, the number of small volumes is $4\pi r^2$, so the probability of the electron being at a distance r from the nucleus is $4\pi r^2R^2$. This is called the radial distribution function. Graphs of the radial distribution function for hydrogen plotted against r are shown in figure.

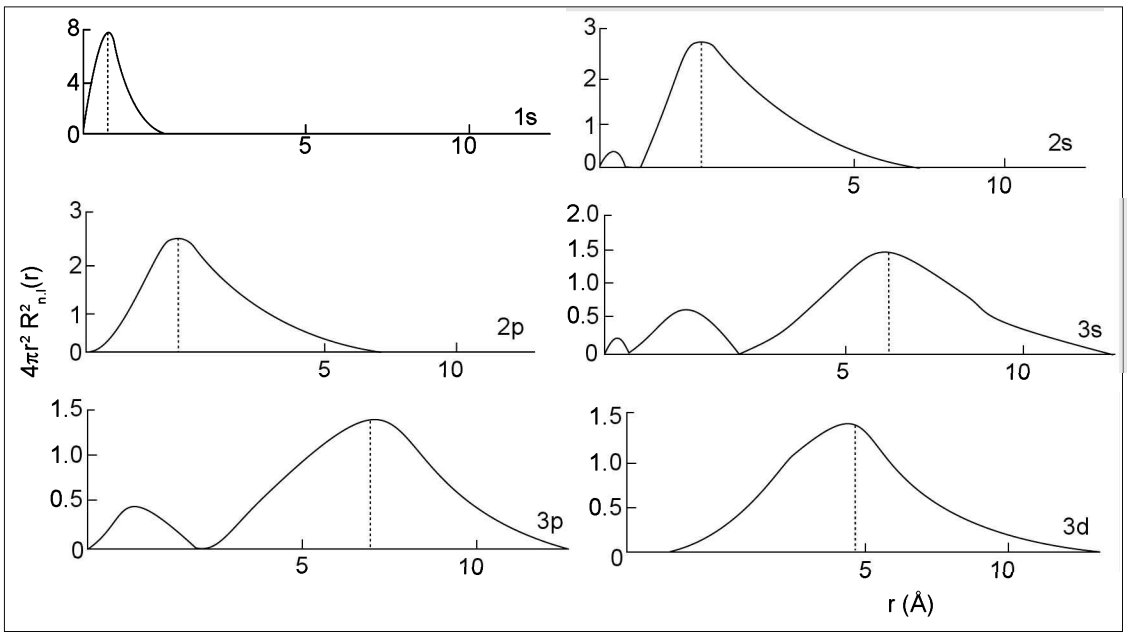


Fig. 1.40

These diagrams show that the probability is zero at the nucleus (as r = 0), and by examining the plots for 1s, 2s and 3s that the most probable distance increases markedly as the principal quantum number increases. Furthermore, by comparing the plots for 2s and 2p, or 3s, 3p and 3d it can be seen that the most

probable radius decreases slightly as the subsidiary quantum number increases. All the s orbitals except the first one (1s) have a shell-like structure, rather like an onion or a hailstone, consisting of concentric layers of electron density. Similarly, all but the first p orbitals (2p) and the first d orbitals (3d) have a shell structure.

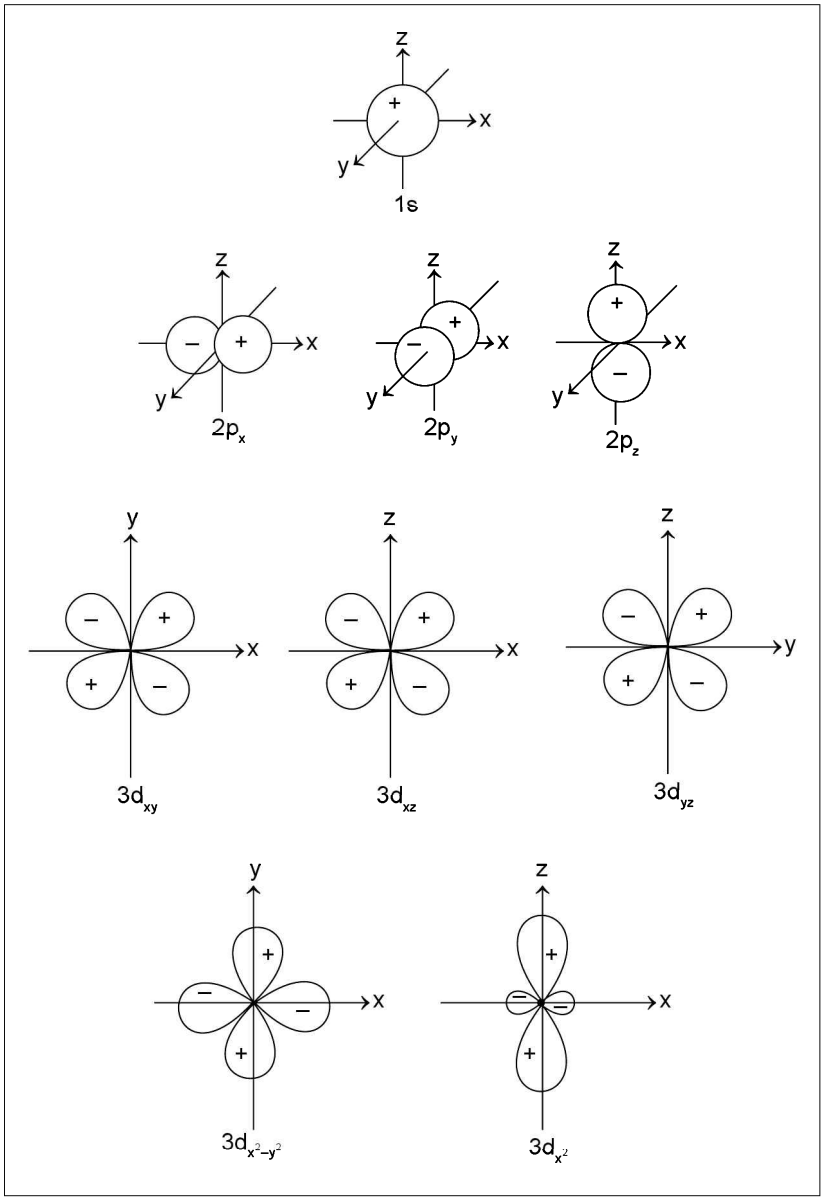


Fig. 1.41 Boundary surface for the angular part of the wave function A(θ, φ) for the 1s, 2p and 3d orbtials for a hydrogen atom shown as polar diagrams.

The angular function A depends only on the direction, and is independent of the distance from the nucleus (r). Thus A^2 is the probability of finding an electron at a given direction θ, ϕ at any distance from the nucleus to infinit . The angular functions A are plotted as polar diagrams in Figure. Polar diagrams do not represent the total wave function ψ, but only the angular part of the wave function. (The total wave function is made up from contributions from both the radial and the angular functions).

$$\psi = R(r) \, . \, A$$

Thus the probability of finding an electron simultaneously at a distance r and in a given direction θ, ϕ is $\psi^2_{r,\theta,\varphi}$.

$$\psi^2_{r,\theta,\varphi} = R^2(r) \,.\, A^2(\theta, \phi)$$

Drawings of the angular part of the wave function, are commonly used to illustrate the overlap of orbitals giving bonding between atoms. Polar diagrams are quite good for this purpose, as they show the signs + and – relating to the symmetry of the angular function. For bonding like signs must overlap. These shapes are slightly different from the shapes of the total wave function. There are several points about such diagrams.

1. It is difficult to picture an angular wave function as a mathematical equation. It is much easier to visualize a boundary surface, that is a solid shape, which for example contains 90% of the electron density. To emphasize that ψ is a continuous function, the boundary surfaces have been extended up to the nucleus in Figure. For p orbitals the electron density is zero at the nucleus, and porbital can be shown as two spheres which do not touch.
2. These drawings show the symmetry for the 1s, 2p, 3d orbitals. However, in the others. 2s, 3s, 4s…… 3p, 4p, 5p…. 4d, 5d….the sign (symmetry) changes inside the boundary surface of the orbital. This is readily seen as nodes in the graphs of the radial function (Figure).

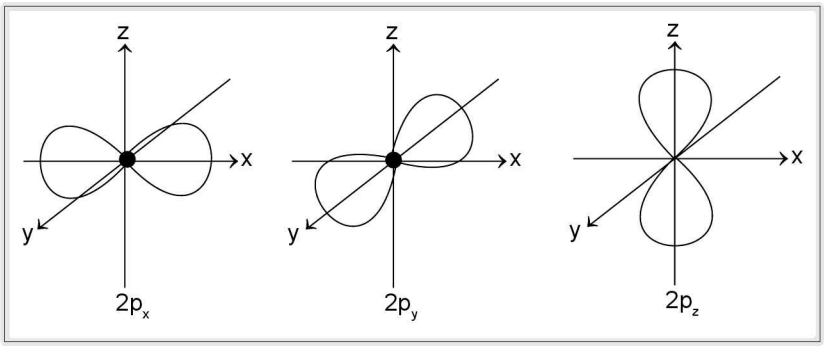


Fig. 1.42

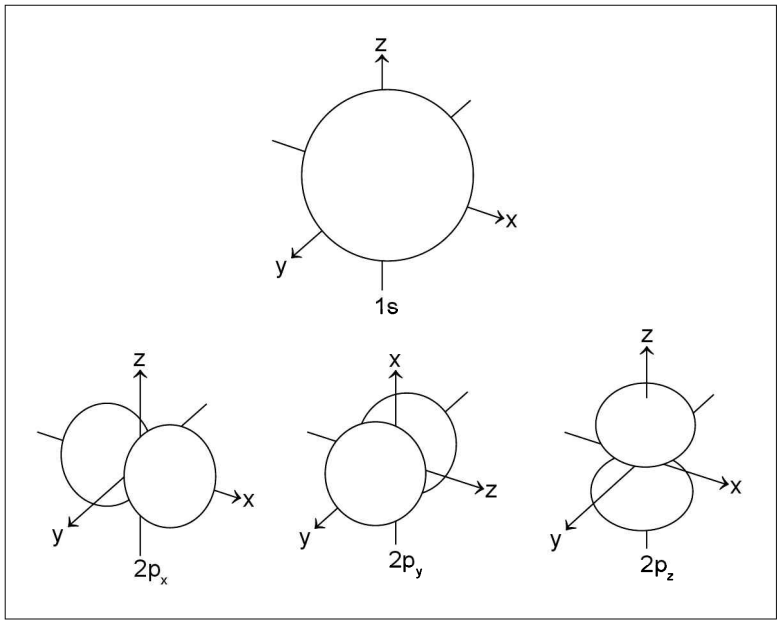


Fig. 1.43 (a)

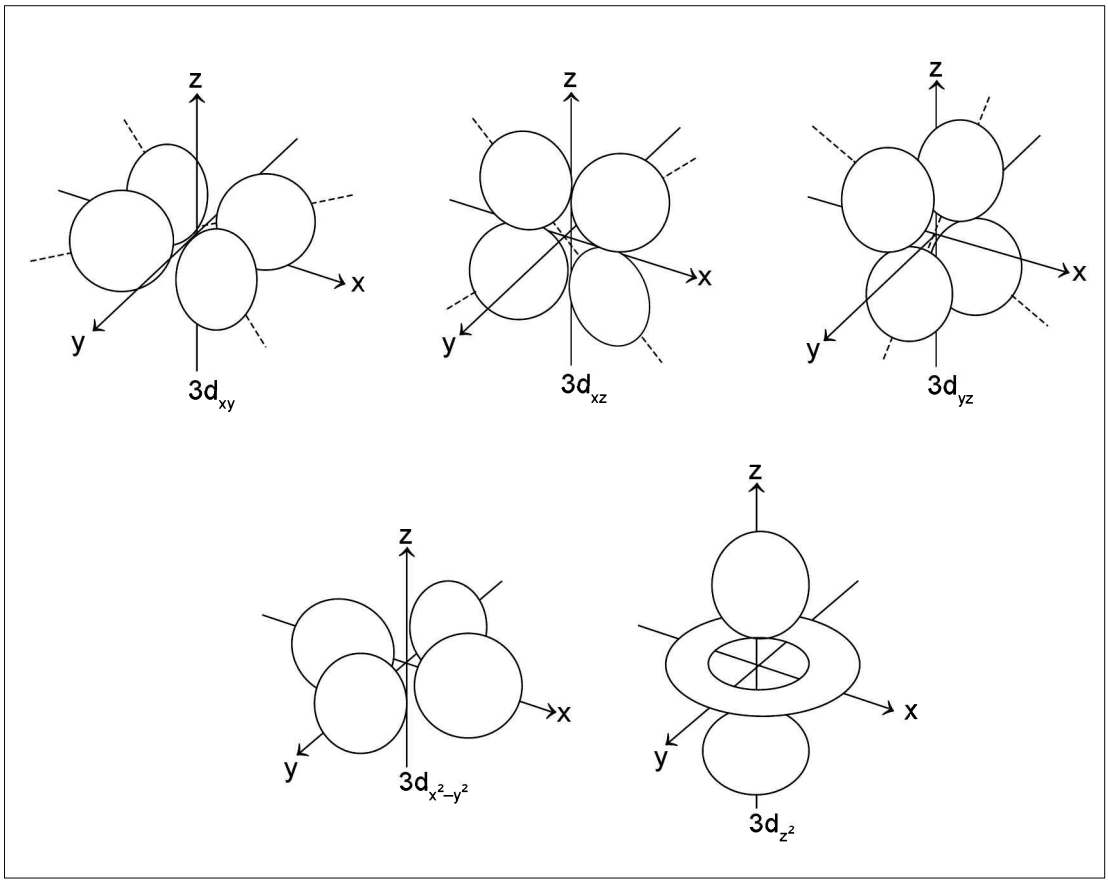


Fig. 1.43 (b)

3. The probability of finding an electron at a direction θ, ϕ is the wave function squared. A^2, or more precisely $\psi_\theta^2 \psi_\varphi^2$. The diagrams in figure are of the angular part of the wave function A, not A^2. Squaring does not change the shape of an s orbital, but it elongates the lobes of porbitals (Figure). Some books use elongated p orbitals, but strictly these should not have signs, as squaring removes any sign from the symmetry.
4. Note that the p orbitals are not simply two spheres, but are ellipsoids of revolution. Thus the $2p_x$ orbital is spherically symmetrical about the x axis, but is not spherical in the other direction. Similarly the p_y orbitl is spherically symmetrical about the y axis, and both the p_z and the $3d_{z^2}$ are spherically symmetrical about the z axis.

Note

1. The plane and point at which zero electron density exists (i.e., $\psi^2 = 0$) is known as nodal plane or nodal point, e.g., the probability of finding electron between 1s and 2s-orbitals or between two lobes of p-orbitals is zero.
2. An orbital with quantum number n and I possesses:
   Angular or non-spherical nodes = l
   Radial or spherical nodes = $n - l - l$
   Thus, total nodes in an orbital = $n - l - 1 + l = n - l$
3. Radial node is defined between the orbitals having same shape or same l value (or same azimithal q. no.)
   Angular node refers to **Nodal Plane.**

It is the plane passing through nucleus but the nucleus should not be considered as a node.

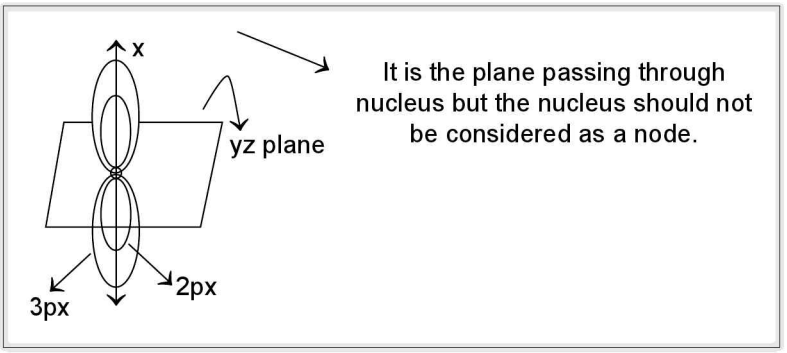


Fig. 1.44

4. Number of angular node depends on shape of orbital only and size of orbital has no role in it where as number of radial nodes is affected by both size and shape.
5. For one electron systems (an atom or an ion) the energy of orbital depends only on the number of nodes, i.e., on n and not on *l* or m. It is therefore, in H-atom or He^+ energy levels of barbitals in a shell are same, i.e., energy level of 3s = 3p = 3d.

Worked-out Examples

50. Wave functions of electrons in atoms and molecules are called..... . **[IIT-JEE-1993]**

Solution orbitals

51. The $2p_x$, $2p_y$ and $2p_z$ orbitals of atom have identical shapes but differ in their..... . **[IIT-JEE-1993]**

Solution orientation in space

52. The energy of the electron in the 3d-orbital is less than that in the 4s-orbital in the hydrogen atom. (Ture/False) **[IIT-JEE-1983]**

Solution False: Although energies of the s and p orbitals for the same principal quantum number are almost close together, the energy of the corresponding d orbitals is much higher. For example, the energy of 3d orbitals is much more than that of 3s and 3p; actually it lies between 4s and 4p orbitals.

53. The electron density in the XY plane in $3d_{x2-y2}$ orbital is zero. (Ture/False) **[IIT-JEE-1986]**

Solution False: The orbital $3d_{x2-y2}$ lie along X and Y axes with its maximum electron probable density.

54. A 3p orbital has: **[IIT-JEE-1995]**

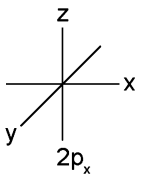
(a) two non spherical nodes
(b) two spherical nodes
(c) one spherical and one non spherical node
(d) one spherical and two non spherical nodes

Solution (c) Total nodes = n-l = 2 No. of radial nodes = n-l-1
For 3p, n = 3, l = 1 $\Rightarrow$ radial nodes = 3-1-1 = 1
Angular nodes = l = 1

55. The number of nodal planes in a p_x orbital is **[IIT-JEE-2000]**

(a) one (b) two

(c) three (d) zero



Solution (a) p orbital being dumbell shaped, number of nodal planes = 1, in y, z plane.

56. The number of radial nodes of 3s and 2p orbitals are respectively **[IIT-JEE-2005]**

(a) 2, 0 (b) 0, 2 (c) 1, 2 (d) 2, 1

Solution (a) Number of radial nodes = (n-l-1)

For 3s: n = 3, l = 0 (Number of radial node = 2) For 2p: n = 2, l = 1 (Number of radial node = 0)

57. The orbital angular momentum of an electron in 2s orbital is: **[IIT-JEE-1996]**

(a) $+\frac{1}{2}.\frac{h}{2\pi}$ (b) Zero

(c) $\frac{h}{2\pi}$ (d) $\sqrt{2}.\frac{h}{2\pi}$

Solution (b) The expression of orbital angular momentum is,

$$L = \sqrt{l(l+1)}(h/2\pi)$$

For 2s orbital, l = 0. Hence, L = 0

58. For a d-electron, the orbital angular momentum is, **[IIT-JEE-1997]**

(a) $\sqrt{6}(h/2\pi)$ (b) $\sqrt{2}(h/2\pi)$

(c) $(h/2\pi)$ (d) $2(h/2\pi)$

Solution (a) The expression for orbital angular momentum is $L = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)$

For d orbital, l = 2. Hence, $L = \sqrt{2(2+1)}\left(\frac{h}{2\pi}\right) = \sqrt{6}\left(\frac{h}{2\pi}\right)$

ONE CORRECT OPTION TYPE QUESTIONS

1. A d-shell containing four unpaired electrons can exchange
(a) four electrons (b) three electrons
(c) sixteen electrons (d) six electrons

2. The electrons, identified by quantum numbers n and l, (i) n = 4, l = 1, (ii) n = 4, l = 0, (iii) n = 3, l = 2, and (iv) n = 3, l = 1 can be placed in order of increasing energy, from the lowest to highest, as
(a) (iv) < (ii) < (iii) < (i)
(b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv)
(d) (iii) < (i) < (iv) < (ii)

3. The velocity of an electron in the first Bohr orbit of a hydrogen atom is 2.19×10^6 m s^{-1}. Its velocity in the second orbit would be
(a) 1.10×10^6 m s^{-1}
(b) 4.38×10^6 m s^{-1}
(c) 5.5×10^5 m s^{-1}
(d) 8.76×10^6 m s^{-1}

4. The ratio of potential energy and total energy of an electron in a Bohr orbit of a hydrogen-like species is
(a) 2 (b) –2
(c) 1 (d) –1

5. If the wavelength of the first line of the Balmer series of hydrogen atom is 656.1 nm, the wavelength of the second line of this series would be
(a) 218.7 nm (b) 328.0 nm
(c) 486.0 nm (d) 640.0 nm

6. Li^{3+} and a proton are accelerated by the same potential, their de Broglie wavelengths λ_{Li} and λ_p have the ratio (assume $m_{Li} = 9m_p$)
(a) 1 : 2 (b) 1 : 4
(c) 1 : 1 (d) $1 : 3\sqrt{3}$

7. When light of frequency 3.2×10^{16} Hz is used to irradiate a metal surface, the maximum kinetic energy of the emitted photoelectron is $\frac{3}{4}$ of the energy of the irradiating photon. What is the threshold frequency of the metal?
(a) 2.4×10^{25} Hz (b) 2.4×10^{16} Hz
(c) 1.6×10^{15} Hz (d) 8×10^{15} Hz

8. If the radius of the first orbit of H-atom is a_0, then de Broglie wavelength of electron in 4th orbit is
(a) $2\pi a_0$ (b) $16\, a_0$
(c) $\frac{a_0}{4}$ (d) $8\pi a_0$

9. The wave number of electronegative radiation emitted during the transition in between two energy levels of Li^{2+} ion whose principal quantum number sum is 4 and difference is 2, is (Atomic No. of Li = 3)
(a) $3.5\, R_H$ (b) $4\, R_H$
(c) $8\, R_H$ (d) $\frac{8}{9} R_H$

10. In an atom two electrons move around the nucleus in circular orbits or radii R and 4R. The ratio of the time taken by them to complete one revolution is:
(a) 1 : 4 (b) 4 : 1
(c) 1 : 8 (d) 8 : 7

11. The radius of first Bohr orbit is x, then de Broglie wavelength of electron in 3rd orbit is nearly
(a) $2\pi x$ (b) $6\pi x$
(c) 9 x (d) x/3

12. The wave number of the first line in the Balmer series of H-atom is 15200 cm^{-1}. The wave number of the first line in the Balmer series of Li^{2+} ion is
(a) 15200 cm^{-1} (b) 60800 cm^{-1}
(c) 76,000 cm^{-1} (d) 136, 800 cm^{-1}

13. If numerical value of mass and velocity are equal then de Broglie wavelength in terms of KE is
(a) $\frac{mh}{2KE}$ (b) $\frac{vh}{2KE}$
(c) both are correct (d) None is correct

14. An electron is accelerated through V volt Its de Broglie wavelength is
(a) $\frac{h}{\sqrt{2m.eV}}$ (b) $\frac{12.27}{\sqrt{V}}$ Å
(c) $\left[\frac{150}{V}\right]^{\frac{1}{2}}$ Å (d) All of these

15. The energy of the electron in the first orbit of He^+ is -871.6×10^{-20} J. The energy of the electron in the first orbit of hydrogen would be
(a) -871.6×10^{-20} J (b) -435.8×10^{-20} J
(c) -217.9×10^{-20} J (d) -108.9×10^{-20} J

16. A hydrogen like atom with atomic number 'Z' is in higher excited state of quantum number 'n'. This xcited state atom can make a transition to the first

excited state by successively emitting two photons of energies 10 eV and 17 eV respectively. Alternatively, the atom from the same excited state can make a transition to the 2nd excited state by emitting two photons of energies 4.25 eV and 5.95 eV respectively. The 'n' and 'Z' are

(a) $n = 6, Z = 3$ (b) $n = 3, Z = 6$

(c) $n = 6, Z = 6$ (d) $n = 5, Z = 5$

17. Photoelectric emission is observed from a surface for frequencies v_1 and v_2 of incident radiations ($v_1 > v_2$). If the maximum kinetic energy of photoelectrons in the two cases are in the ratio of 1 : 2, then threshold frequency v_0 is given by

(a) $\frac{v_2 - v_1}{2-1}$ (b) $\frac{2v_1 - v_2}{2-1}$

(c) $\frac{2v_2 - v_1}{2-1}$ (d) $\frac{v_2 - v_1}{2}$

18. The mass of an electron is *m*. Its charge is *e* and it is accelerated from rest through a potential difference V. The velocity acquired by the electron will be

(a) $\sqrt{V/m}$ (b) $\sqrt{eV/m}$

(c) $\sqrt{2eV/m}$ (d) None of these

19. Indicate among the following, the correct choice. The time taken by an electron for one complete revolution in the n^{th} Bohr orbit of the hydrogen atom is:

(a) inversely proportional to n^2

(b) directly proportional to n^3

(c) directly proportional to $\frac{h}{2\pi}$

(d) proportional to $\frac{n^2}{h^2}$

20. Assuming the nucleus and an atom to be spherical, the radius of the nucleus of mass number A is given by $1.25 \times 10^{-13} \times A^{1/3}$ cm. The atomic radius of atom is 1 $\mathring{A}$. If the mass number is 64, the fraction of the atomic volume that is occupied by the nucleus is:

(a) 1.25×10^{-13} (b) 2.50×10^{-13}

(c) 5×10^{-5} (d) none.

21. The wavelength of a certain electron transition in the hydrogen spectrum is 4864 $\mathring{A}$. Identify the transition.

(a) Third line Balmer

(b) First line Lyman

(c) First line Paschen

(d) Second line Balmer

22. The energy associated with Bohr's orbit in the hydrogen atom is given by expression ; $E_n = \frac{-13.6}{n^2}$ eV. The energy associated with the orbit having a radius 9 r_1 (r_1 is the radius of the first orbit) is given by

(a) –13.6 eV (b) –6.8 eV

(c) –1.51 eV (d) Zero.

23. According to the Bohr theory for the hydrogen atom, the number of revolutions of the electron per second in the orbit of quantum number, n is proportional to

(a) n^{-2} (b) $\sqrt{n}$

(c) n^{-3} (d) n^{-1}

24. An electron in an atom jumps in such a way that its kinetic energy changes from x to $\frac{x}{4}$. The change in potential energy will be

(a) $+\frac{3}{2}x$ (b) $-\frac{3}{8}x$

(c) $+\frac{3}{4}x$ (d) $-\frac{3}{4}x$

25. The mass of an electron is m, charge is e and it is accelerated from rest through a potential difference of V volts. The velocity acquired by electron will be

(a) $\sqrt{\frac{V}{m}}$ (b) $\sqrt{\frac{eV}{m}}$

(c) $\sqrt{\frac{2eV}{m}}$ (d) zero

26. Find the value of wave number ($\bar{V}$) in terms of Rydberg's constant, when transition of electron takes place between two levels of He^+ ion whose sum is 4 and difference is 2.

(a) $\frac{8R}{9}$ (b) $\frac{32R}{9}$

(c) $\frac{3R}{4}$ (d) none of these

27. If the lowest energy X-rays have $\lambda = 3.055 \times 10^{-8}$ m, estimate the minimum difference in energy between two Bohr's orbits such that an electronic transition would correspond to the emission of an X-ray. Assuming that the electrons in other shells exert no influence, at what Z (minimum) would a transition from the second energy level to the first result in the emission of an X-ray?

(a) 1 (b) 2

(c) 3 (d) 4

28. Assuming the nucleus and an atom to be spherical, the radius of the nucleus of mass number A is given by $1.25 \times 10^{-13} \times A^{1/3}$ cm. The atomic radius of atom is 1 Å. If the mass number is 64, the fraction of the atomic volume mat is occupied by the nucleus is

(a) 1.25×10^{-13}
(b) 2.50×10^{-13}
(c) 5×10^{-5}
(d) None of these

29. Calculate the number of quanta of radiations of frequency 4.67×10^{13} s^{-1} that must be absorbed in order to melt 5g of ice (The energy required to melt 1g of ice is 333 J)

(a) 3.36×10^{18} (b) 17
(c) 5.38×10^{22} (d) 30.91×10^{-21}.

30. The number of photons of light having wave number 'x' in 2 J of energy source is

(a) 2 hcx (b) $\frac{hc}{2x}$

(c) $\frac{2}{hcx}$ (d) $\frac{2x}{hc}$

31. The angular momentum produced due to spin of electron is given by

(a) $\frac{1}{2} \times \frac{h}{2\pi}$ (b) $\frac{\sqrt{3}}{2} \times \frac{h}{2\pi}$

(c) $\left(-\frac{1}{2}\right)\frac{h}{2\pi}$ (d) $\sqrt{3}\frac{h}{2\pi}$

32. If the shortest wavelength of hydrogen atom in Lyman series is x, then the longest wavelength in Paschen series of He^+ is

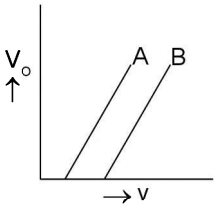
(a) $\frac{9x}{5}$ (b) $\frac{36x}{5}$

(c) $\frac{36x}{7}$ (d) $\frac{5x}{9}$

33. When the speed of electron increases, the value of specific charge (e/m)

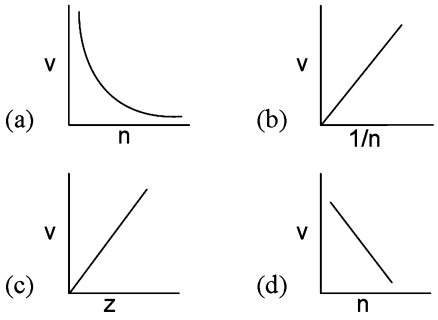
(a) decreases
(b) increases
(c) remains same
(d) None of these

34. The stopping potential as a function of frequency is plotted for two different photoelectric surfaces A and B. The graph shows that the work function of A is

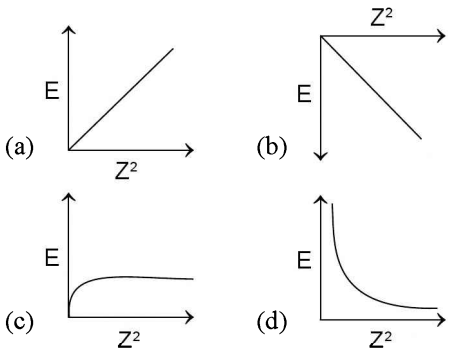


(a) greater than that of B
(b) smaller than that of B
(c) same as that of B
(d) such that no comparison can be done from given graph

35. Select the incorrect graph for velocity of e^- in an orbit VS. Z and n:



36. The energy of an electron moving in nth Bohr's orbit of an element is given by $E_n = \frac{-13.6}{n^2} Z^2$ eV/atom (Z = atomic number). The graph of E Vs Z^2 (keeping "n" constant) will be:



37. A dye absorbs a photon of wavelength A, and re-emits the same energy into two photons of wavelengths λ_1 and λ_2 respectively. The wavelength λ. is related with λ_1 and λ_2 as:

(a) $\lambda = \frac{\lambda_1 + \lambda_2}{\lambda_1 \lambda_2}$ (b) $\lambda = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$

(c) $\lambda = \frac{\lambda_1^2 + \lambda_2^2}{\lambda_1 + \lambda_2}$ (d) $\lambda = \frac{\lambda_1 + \lambda_2}{(\lambda_1 + \lambda_2)^2}$

38. If a_0 be the radius of first Bohr's orbit of H-atom, the de-Broglie's wavelength of an electron revolving in the second Bohr's orbit will be

(a) $6\pi a_0$
(b) $4\pi a_0$
(c) $2\pi a_0$
(d) None of these

39. The Schrodinger wave equation for hydrogen atom is

$$\Psi(\text{radial}) = \frac{1}{16\sqrt{4}}\left(\frac{Z}{a_0}\right)^{3/2}[(\sigma-1)(\sigma^2-8\sigma+12)]e^{-\sigma/2}$$

where a_0 and Z are the constant in which answer can be expressed and $\sigma = \frac{2Zr}{a_0}$ minimum and maximum position of radial nodes from nucleus are ..... respectively.

(a) $\frac{a_0}{Z}, \frac{3a_0}{Z}$ (b) $\frac{a_0}{2Z}, \frac{a_0}{Z}$
(c) $\frac{a_0}{2Z}, \frac{3a_0}{Z}$ (d) $\frac{a_0}{2Z}, \frac{4a_0}{Z}$

40. If λ_0 and λ the threshold wavelength and the wavelength of incident light, the velocity of photo-electrons ejected from the metal surface is:

(a) $\sqrt{\frac{2h}{m}(\lambda_0-\lambda)}$ (b) $\sqrt{\frac{2hc}{m}(\lambda_0-\lambda)}$
(c) $\sqrt{\frac{2hc}{m}\left(\frac{\lambda_0-\lambda}{\lambda\lambda_0}\right)}$ (d) $\sqrt{\frac{2h}{m}\left(\frac{1}{\lambda_0}-\frac{1}{\lambda}\right)}$

41. A light source of wavelength A, illuminates a metal and ejects photo-electrons with $(K.E.)_{max}$ = 1eV Another light source of wavelength $\frac{\lambda}{3}$, ejects photo-electrons from same metal with $(K.E.)_{max}$= 4eV. Find the value of work function?

(a) 1 eV (b) 2 eV
(c) 0.5 eV (d) None of these

42. The ratio of slopes of K_{max} *Vs* ν and V_0 *Vs* v curves in the photoelectric effect gives (v = frequency, K_{max} = maximum kinetic energy, V_0 = stopping potential):

(a) charge of electron
(b) Planck's constant
(c) work function
(d) the ratio of Planck's constant of electronic charge

43. Potential energy of electron present in He^+ is:

(a) $\frac{e^2}{2\pi\varepsilon_0 r}$ (b) $\frac{3e^2}{4\pi\varepsilon_0 r}$
(c) $\frac{-2e^2}{4\pi\varepsilon_0 r}$ (d) $\frac{-e^2}{4\pi\varepsilon_0 r^2}$

44. For a hypothetical hydrogen like atom, the potential energy of the system is given by $U(r) = \frac{-Ke^2}{r^3}$, where r is the distance between the two particles. If Bohr's model of quantization of angular momentum is applicable then velocity of particle is given by:

(a) $v = \frac{n^2h^3}{Ke^2 8\pi^3 m^2}$ (b) $v = \frac{n^3h^3}{8Ke^2\pi^3 m^2}$
(c) $v = \frac{n^3h^3}{24Ke^2\pi^3 m^2}$ (d) $v = \frac{n^2h^3}{24Ke^2\pi^3 m^2}$

45. A small particle of mass *m* moves in such a way that P. E. $= -\frac{1}{2}$ mkr² where k is a constant and *r* is the distance of the particle from origin. Assuming Bohr's model of quantization of angular momentum and circular orbit, *r* is directly proportional to:

(a) n^2 (b) n
(c) $\sqrt{n}$ (d) None of these

46. A beam of specific kind of particles of velocity 2.1×10^7 m/s is scattered by a gold (Z =79) nuclei. Find out specific charge (charge/mass) of this particle if the distance of closest approach is 2.5×10^{-14} m.

(a) 4.84×10^7 C/g (b) 4.84×10^{-7} C/g
(c) 2.42×10^7 C/g (d) 3×10^{-12} C/g

47. What is the angular velocity (ω) of an electron occupying second orbit of Li^{2+} ion?

(a) $\frac{8\pi^3 me^4}{h^3}$ (b) $\frac{8\pi^3 me^4}{9h^3}$
(c) $\frac{64}{9}\times\frac{\pi^3 me^4}{h^3}$ (d) $\frac{9\pi^3 me^4}{h^3}$

48. The velocity of an e^- in excited state of H-atom is 1.093×10^6 m/s. What is the circumference of this orbit?

(a) 3.32×10^{-10} m (b) 6.64×10^{-10} m
(c) 13.30×10^{-10} m (d) 13.28×10^{-8} m

49. When an electron makes a transition from (n +1) state to nth state, the frequency of emitted radiations is related to n according to (n > >1):

(a) $v = \frac{2cRZ^2}{n^3}$ (b) $v = \frac{cRZ^2}{n^4}$

(c) $v = \frac{cRZ^2}{n^2}$ (d) $v = \frac{2cRZ^2}{n^2}$

50. An element undergoes a reaction as shown:

$X + 2e^- \longrightarrow X^{2-}$, energy released = 30.87 eV/atom. If the energy released, is used to dissociate 4 gms of H_2 molecules, equally into H^+ and H*, where H* is excited state of H atoms where the electron travels in orbit whose circumference equal to four times its de Broglie's wavelength. Determine the least moles of *X* that would be required: Given: I.E. of H = 13.6 eV/atom, bond energy of H_2 = 4.526 eV/molecule.

(a) 1 (b) 2

(c) 3 (d) 4

51. If the energy of H-atom in the ground state is *–E*, the velocity of photo-electron emitted when a photon having energy E_p strikes a stationary Li^{2+} ion in ground state, is given by:

(a) $v = \sqrt{\frac{2(E_p - E)}{m}}$ (b) $v = \sqrt{\frac{2(E_p + 9E)}{m}}$

(c) $v = \sqrt{\frac{2(E_p - 9E)}{m}}$ (d) $v = \sqrt{\frac{2(E_p - 3E)}{m}}$

52. At which temperature will the translational kinetic energy of H-atom equal to that for H-atom of first line Lyman transition? (Given $N_A = 6 \times 10^{23}$)

(a) 780 K

(b) 1.32×10^5 K

(c) 7.84×10^4 K

(d) 1000 K

53. For a 3s-orbital $\Psi(3s) = \frac{1}{9\sqrt{3}}\left(\frac{1}{a_0}\right)^{3/2}(6 - 6\sigma + 6\sigma^2)$ $e^{-\sigma/2}$, where $\sigma = \frac{2r.Z}{3a_0}$ What is the maximum radial distance of node from nucleus?

(a) $\frac{(3+\sqrt{3})a_0}{Z}$ (b) $\frac{a_0}{Z}$

(c) $\frac{3}{2}\frac{(3+\sqrt{3})a_0}{Z}$ (d) $\frac{2a_0}{Z}$

54. The energy of a I, II and III energy levels of a certain atom are E, $\frac{4E}{3}$ and 2E respectively. A photon of wavelength λ is emitted during a transition from III to I. What will be the wavelength of emission for transition II to I?

(a) $\frac{\lambda}{2}$ (b) λ

(c) 2λ (d) 3λ

55. In a measurement of quantum efficiency of photosynthesis in green plants, it was found that 10 quanta of red light of wavelength 6850 Å were needed to release one molecule of O_2. The average energy storage in this process is 112 kcal/mol O_2 evolved.

What is the energy conversion efficiency in this experiment? Given: 1 cal = 4.18 *J*; $N_A = 6 \times 10^{23}$; $h = 6.63 \times 10^{-34}$ J.s

(a) 23.5 (b) 26.9

(c) 66.34 (d) 73.1

56. H-atom is exposed to electromagnetic radiation of X = 1025.6 Å and excited atom gives out induced radiations. What is the minimum wavelength of these induced radiations?

(a) 102.6 nm (b) 12.09 nm

(c) 121.6 nm (d) 810.8 nm

ANSWER KEYS

1. (d)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (c)	**6.** (d)	**7.** (d)	**8.** (d)	**9.** (c)	**10.** (c)
11. (b)	**12.** (d)	**13.** (c)	**14.** (d)	**15.** (c)	**16.** (a)	**17.** (b)	**18.** (c)	**19.** (b)	**20.** (a)
21. (d)	**22.** (c)	**23.** (c)	**24.** (a)	**25.** (c)	**26.** (b)	**27.** (b)	**28.** (d)	**29.** (c)	**30.** (c)
31. (b)	**32.** (c)	**33.** (a)	**34.** (b)	**35.** (d)	**36.** (b)	**37.** (b)	**38.** (b)	**39.** (c)	**40.** (c)
41. (c)	**42.** (c)	**43.** (c)	**44.** (c)	**45.** (c)	**46.** (c)	**47.** (d)	**48.** (c)	**49.** (a)	**50.** (b)
51. (c)	**52.** (c)	**53.** (c)	**54.** (d)	**55.** (b)	**56.** (a)				

[redacted]S AND EXPLANATIONS

1. (d) $n_{C_2} = 4_{C_2} = \frac{4!}{2!2!} = 6$.

2. (a) (i) 4p (ii) 4s (iii) 3d (iv) 3p
3p < 4s < 3d < 4p
(iv) < (ii) < (iii) < (i)

3. (a) Since $v \propto 1/n$, the velocity in the second orbital will be
$v_2 = v_1/2 = (2.19 \times 10^6 \text{ m s}^{-1})/2 = 1.1 \times 10^6 \text{ m s}^{-1}$

4. (a) $\frac{PE}{E} = \frac{PE}{KE+PE} = \frac{1}{(KE/PE)+1} = \frac{1}{(-1/2)+1} = 2$

5. (c) First line of Balmer series corresponds to n = 3 → n = 2. Second line this series will correspond to n = 4 → n = 2.
We have

$$\Delta E_1 = R_H\left(\frac{1}{4}-\frac{1}{9}\right) \quad \text{and} \quad \Delta E_2 = R_H\left(\frac{1}{4}-\frac{1}{16}\right)$$

$$\frac{\Delta E_1}{\Delta E_2} = \frac{5/36}{3/16} = \frac{27}{20} \text{ i.e. } \lambda_2 = \lambda_1\left(\frac{20}{27}\right)$$

$$= (656.1 \text{ nm})\left(\frac{20}{27}\right) = 486.0 \text{ nm}$$

6. (d) $\lambda_p = \frac{h}{\sqrt{2eVm_p}}$; $\lambda_{Li^{3+}} = \frac{h}{\sqrt{2\times 3eVm_{Li}}}$

$$= \frac{h}{\sqrt{2\times 3eV\times 9m_p}}$$

Hence, $\frac{\lambda Li^{3+}}{\lambda_p} = \sqrt{\frac{2eVm_p}{2\times 3eV\times 9m_p}} = \frac{1}{3\sqrt{3}}$

7. (d) K.E. $= h(v-v_0) = \frac{3}{4}\times hv$; $v_0 = \frac{v}{4} = \frac{3.2\times 10^{16}}{4}$
$= 8 \times 10^{15}$ Hz

8. (d) $r_n = a_0 \times n^2$, $r_4 = a_0 \times 4^2 = 16a_0$

$$mv = 4.\ \frac{h}{2\pi r_4} = \frac{4h}{2\pi\times 16a_0} = \frac{h}{8\pi a_0} \quad \lambda = \frac{h}{mv} = 8\pi a_0$$

9. (c) $n_1 + n_2 = 4$ …… (i)

$n_2 - n_1 = 2$ …… (ii) $n_1 = 1, n_2 = 3$

$$\bar{\upsilon} = R_H Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = R_H \times 3^2 \times \left[\frac{1}{1^1}-\frac{1}{3^2}\right] = 8R_H$$

10. (c) $T = \frac{2\pi r_n}{u_n} = \frac{2\pi r_1 \times n^2}{u_1/n} (\because r_n = n^2 \times r_1)$ or $T \propto n^3$;

$$\therefore \quad \frac{T_1}{T_2} = \frac{1^3}{n^3} = \frac{1}{8} \quad (n = 2)$$

11. (b) For a particular element, radius of an orbit,
$r_n \propto n^2$
where n is the principal quantum number

$$\therefore \quad \frac{r_1}{r_3} = \frac{1}{3^2}$$

If $r_1 = x$ then $r_3 = 9x$
For third shell,
$2\pi r_3 = 3\lambda$

$$\lambda = \frac{2\pi r_3}{3} = \frac{2\pi.9x}{3} = 6\pi x$$

12. (d) We know that wave number ($\bar{\upsilon}$) of a particular line in Balmer series of H-atom is given by:

$$\bar{\upsilon}_H = R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = R_H\left(\frac{1}{2^2}-\frac{1}{n_2^2}\right)$$

$= 15{,}200 \text{ cm}^{-1}$

The wave number ($\bar{\upsilon}$) of a particular line in Balmer series of H-like species with atomic number Z is given by:

$$\bar{\upsilon} = \bar{\upsilon}_H \times Z^2$$

Since for Li^{2+} ion Z = 3, $\bar{\upsilon}_{Li^{2+}}$ is given by:

$\bar{\upsilon}_{Li^{2+}} = \upsilon_H^- \times (3)^2 = 15{,}200 \times$

13. (c) Given, m = v

$$\therefore \quad \lambda = \frac{h}{mv} = \frac{h}{v^2}$$

Also, $KE = \frac{1}{2}mv^2$

$$\therefore \quad v^2 = \frac{2KE}{m}$$

$$\therefore \quad \lambda = \frac{h}{\left(\frac{2KE}{m}\right)} = \frac{mh}{2KE} \quad \text{hence (a)}$$

14. (d) $KE = \frac{1}{2}m\upsilon^2$

$$\upsilon = \left[\frac{2KE}{m}\right]^{\frac{1}{2}}$$

Put in de-Broglie equation,

$$\lambda = \frac{h}{m\upsilon} = \frac{h}{m.\left[\frac{2KE}{m}\right]^{\frac{1}{2}}}$$

or $\lambda = \frac{h}{\sqrt{2m.KE}}$

As K.E. = Ev

$\therefore \lambda = \frac{h}{\sqrt{2m.eV}}m$

$(B \times C)\ \lambda = \frac{\lambda}{\sqrt{2meV}} = \left[\frac{h^2}{2meV} \times 10^{20}\right]^{\frac{1}{2}} \text{Å}$

On putting the value,

$$\lambda = \left[\frac{150}{V}\right]^{\frac{1}{2}} \text{Å} = \frac{12.27\,\text{Å}}{\sqrt{V}}$$

15. $E_n = \frac{E_{1H}Z^2}{n^2}$

for the electron in the first orbit of He^+ $E_1 = E_{1H}\,2^2 = 4\,E_{1H}$

Hence, $E_{1H} = \frac{E_1}{4} = \frac{-871.6 \times 10^{-20}}{4} J = -217.9 \times 10^{-20}$ J

16. (a) For n = 2 and n = 3, energy differnence = (10 + 17 – 4.25 – 5.95) eV = 16.8 eV

$$16.8 = 13.6\left(\frac{1}{2^2} - \frac{1}{3^2}\right)z^2 \Rightarrow z = 2.98 = 3$$

Energy difference n_2 = n and n_1 = 2 = 10 + 17 = 27 eV

$$27 = 13.6\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \times 3^2$$

$$3.0 = 13.6\left(\frac{1}{4} - \frac{1}{n^2}\right),\ n \simeq 6$$

(b), (c) and (d) are not possible.

17. (b) $hv_1 = hv_0 + (K.E.)_1$

$hv_2 = hv_0 + (K.E.)_2$

$$\frac{h(v_1 - v_0)}{h(v_2 - v_0)} = \frac{(K.E.)_1}{(K.E.)_2} = \frac{1}{2}$$

$2(v_1 - v_0) = v_2 - v_0$

$v_0 = 2v_1 - v_2$

18. (c) $K.E. = \frac{1}{2}m\upsilon^2$

$\upsilon^2 = 2\,KE/m$

$\upsilon = \sqrt{2KE/m}$

As KE = eV

$\therefore \quad \upsilon = \sqrt{\frac{2eV}{m}}$

19. (b) Since, $mvr = \frac{nh}{2\pi}$, we have $2\pi r = \frac{nh}{mv}$. Dividing by v, $\left(\frac{2\pi r}{v}\right) = \left[\frac{nh}{mv^2}\right]$

L.H.S is the time for one revolution in the nth orbit. mv^2 is proportional to the energy which is $mv^2 \propto \frac{1}{n^2}$ so $\frac{2\pi r}{v} \propto \frac{nh}{\frac{1}{n_2}}$. So, $t \propto n^3$

20. (a) $\frac{V_{nucleus}}{V_{atom}} = \frac{4/3\pi r_n^3}{4/3\pi r_a^3} = \frac{r_n^3}{r_a^3}$

$$= \frac{[1.25 \times 10^{-13} \times (64)^{\frac{1}{3}}]^3}{(10^{-8})^3}$$

21. (d) The formula to be used in

$\lambda(\text{Å}) = \left[n_2^2 n_1^2/(n_2^2 - n_1^2)\right] \times 912$

$\frac{4864}{912} = \left[n_2^2 n_1^2/(n_2^2 - n_1^2)\right] = \frac{16}{3}$. The value 4864 Å is in the visible region and thus suggests the Balmer series. By trial n_2 = 4 and n_1 = 2 fits in. Thus, the transition corresponds to the second line of the Balmer series.

22. (c) $r_n = n^2.r_1$

$9r_1 = n^2.r_1$

$\therefore \quad n^2 = 9$ and n = 3

Thus, $E_n = \frac{-13.6}{3^2} = \frac{-13.6}{9}$

$= -1.51$ eV

23. (c) $mvr = \frac{nh}{2\pi}$.

$\therefore 2\pi r = \frac{nh}{mv}$

$$\therefore \frac{2\pi r}{v} = \frac{nh}{mv^2} = \text{time for one revolution.}$$

$$\therefore \frac{v}{2\pi r} = \frac{mv^2}{nh}$$

Now, $mv^2 \propto \frac{1}{n^2}$

$$\therefore \left(\frac{v}{2\pi r}\right) \propto \frac{1}{n^3} \text{ or } n^{-3}$$

24. (a) Change in P.E. $= -\frac{2x}{4} + (2x) \Rightarrow \frac{3}{2}x$

25. (c) When an electron of charge e and mass m is accelerated with a potential difference of V volts K.E. $= eV \Rightarrow \frac{1}{2} mv^2 = eV$ or $v^2 = \frac{2eV}{m}$

$$\Rightarrow v = \sqrt{\frac{2eV}{m}}$$

26. (b) $n_1 + n_2 = 4$; $n_2 - n_1 = 2$; $\therefore n_1 = 1$, $n_2 = 3$

$$\bar{v} = R(2)^2 \left[\frac{1}{1^2} - \frac{1}{3^2}\right] = \frac{32R}{9}$$

27. (b) $\Delta E = \frac{hc}{\lambda} = \frac{(6.63\times10^{-34}\,J-s)(3.00\times10^{8}\,m/s)}{3.055\times10^{-8}\,m}$

$= 6.52 \times 10^{-18}$ J $\Delta E_H = \frac{3}{4}(2.176 \times 10^{-18}\,J)$

$= 1.63 \times 10^{-18}$ J; $\Delta E = \Delta E_H (Z^2)$

$$Z^2 = \frac{\Delta E}{\Delta E_H} = \frac{(6.52\times10^{-18})}{(1.63\times10^{-18})} = 4;$$

Z = 2 (helium)

28. $\frac{V_{nucleus}}{V_{atom}} = \frac{4/3\pi r_n^3}{4/3\pi r_a^3} = \frac{r_n^3}{r_a^3}$

$$= \frac{[1.25\times10^{-13}\times(64)^{\frac{1}{3}}]^3}{(10^{-8})^3}$$

29. Energy required to melt 5g of ice
$= 5 \times 333 = 1665$ J

Energy of one quantum = hv

$= 6.626 \times 10^{-34} \times 4.67 \times 10^{13}$

Number of quanta required to melt 5g of ice

$$= \frac{1665}{30.91\times10^{-21}} = 53.8 \times 10^{21}$$

$\simeq 5.38 \times 10^{22}$

30. $E = nhv = \frac{nhc}{\lambda} = nhc\bar{v} \quad \left(\because \bar{v} = \frac{1}{\lambda}\right)$

as $E = 2J$

$\therefore 2 = nhc\,\bar{v}$

or $n = \frac{2}{hc\bar{v}} = \frac{2}{hcx}$

31. Angular momentum due to spin of electron

$$= \sqrt{s(s+1)}\frac{h}{2\pi} \text{ as } s = \frac{1}{2}$$

$$\therefore \text{ angular momentum} = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\ \frac{h}{2\pi}$$

$$= \sqrt{\frac{1}{2}\times\frac{3}{2}}\frac{h}{2\pi} = \frac{\sqrt{3}}{2}\frac{h}{2\pi}$$

32. For shortest wavelength line (Maximum energy),
$n = 1$, $n_2 = \infty$, $z = 1$

$$\frac{1}{\lambda_{min.}} = R.Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{x} = R.1^2\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = R$$

Now $\frac{1}{x_{max.}} = R \times 4\left[\frac{1}{3^2} - \frac{1}{4^2}\right]$

He^+

For Paschen series, line having longest wavelength, (minimum energy)

$n_1 = 3$

$n_2 = 4$

$$\frac{1}{\lambda_{max.}} = \frac{1}{x}.4\left[\frac{1}{9} - \frac{1}{16}\right]$$

$$= \frac{4}{x}\left[\frac{16-9}{9\times16}\right] = \frac{7\times4}{16\times9\times x}$$

$$\frac{1}{\lambda_{max.}} = \frac{7}{36x} \quad \text{or } \lambda_{max.} = \frac{36x}{7}$$

33. (a) $m_e = \frac{m_e(\text{in rest})}{\sqrt{1-(v/c)^2}}$; the mass of moving electron increases wth increae in velocity and thus e/m decreases.

34. (b) The work function = hv_0. So, it is clear from graph, for zero stopping potential frequency must be threshold which is smaller for A with respect to B metal.

35. (a) $V = V_{1H}\frac{Z}{w} \Rightarrow V_n = \text{contant}$

$\Rightarrow$ rectangular hyperbola

36. (b) $\because E_n \propto -\frac{Z^2}{n^2}$

$\Rightarrow E_n \propto -Z^2$

37. (b) $E = E_1 + E_2;\ \frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$

$\Rightarrow \frac{hc}{\lambda} = hc\left(\frac{\lambda_2+\lambda_1}{\lambda_1\lambda_2}\right);\ \lambda = \frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2}$

38. (b) $mvr_n = \frac{nh}{2\pi}$ and $p = \frac{h}{\lambda} = pr_2 = \frac{2\times h}{2\times\pi}$

$\Rightarrow \frac{h}{\pi}$ or $\frac{h}{\lambda}.r_2 = \frac{h}{\pi}$

$\Rightarrow \lambda = nr_2$,

$\therefore r_2 = 4a_0$;

$\therefore \lambda = 4a_0\pi$

39. (c) Probability of finding e^- is zero implies that, $\Psi^2 = 0$ or $\Psi = 0$

$\Rightarrow (\sigma - 1) = 0$

$\Rightarrow \sigma = 1$

or $r = \frac{a_0}{2z}$ or $(\sigma^2 - 8\sigma + 12) = 0$

$\Rightarrow (\sigma - 6)\ (\sigma - 2) = 0$

$\Rightarrow \sigma = 6$

$\Rightarrow r = \frac{6a_0}{z}$ and $\sigma = 2$

$\Rightarrow r = \frac{a_0}{z}$

$r_1 = \frac{a_0}{2z}, \frac{a_0}{z}, \frac{3a_0}{z}$

40. (c) As per Einstein's equation of photoelectric effect, $hv = hv_0 + \text{K.E.}$

$\therefore \frac{1}{2}mv^2 = hv - hv_0 = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}v^2 = \frac{2hc}{m}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$;

$v = \left[\frac{2hc}{m}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)\right]^{1/2}$

$\Rightarrow \left[\frac{2hc}{m}\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right)\right]^{1/2}$

41. (c) $\frac{hc}{\lambda} = 1 + \phi$ .... (1)

$3 \times \frac{hc}{\lambda} = 4 + \phi$ .... (2)

from equation (1) and (2) $\phi = 0.5$ eV

42. (a) $hv = hv_0 + eV_0;\ eV_0 = hv - hv_0$

or $V_0 = \frac{h}{e}v - \frac{h}{e}v_0;\ \text{slope}_1 = \frac{h}{e}$

Similarly, $hv = hv_0 + K_{max}$

or $K_{max} = hv - hv_0$;

$\text{slope}_2 = h,\ \frac{\text{slope}_2}{\text{slope}_1} = \frac{h}{h/e} = e$

43. (c) $\text{P.E.} = \frac{1}{4\pi\varepsilon_0}\frac{(+Ze)(-e)}{r} = \frac{1}{4\pi\varepsilon_0}\frac{(+2e)(-e)}{r}$ e $2\pi\varepsilon_0 r$

$= -\frac{e^2}{2\pi\varepsilon_0 r}$

44. (c) $\frac{d[U(r)]}{dr} = \frac{3Ke^2}{r^4} \Rightarrow$ Magnitude of the force

$\therefore \frac{3Ke^2}{r^4} = \frac{mv^2}{r}$

and we know $mvr = \frac{nh}{2\pi}$ or $r = \frac{nh}{2\pi m.v}$,

$3Ke^2 \times \frac{8\pi^3m^3v^3}{n^3h^3} = mv^2,\ v = \frac{n^3h^3}{24Ke^2\pi^3m^2}$

45. (c) $-\frac{1}{2} \times \text{P.E.} = \text{K.E} = -\frac{1}{2}\left(-\frac{1}{2}mkr^2\right) = \frac{1}{2}mv^2$,

$mvr = \frac{nh}{2\pi}$,

$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$;

$r^4 = \frac{n^2h^2}{2\pi^2m^2k^2}$ or $r \propto \sqrt{n}$

47. (d) $v = r\omega$ where $r_n = \frac{n^2h^2}{4\pi^2me^2Z}$ and $v_n \frac{2\pi.Z.e^2}{n.h}$

$\therefore \frac{2\pi Ze^2}{n.h} = \frac{n^2h^2}{4\pi^2me^4Z} \times \omega$;

$\omega = \frac{8\pi^3me^4.Z^2}{n^3.h^3} = \frac{9\pi^3me^4}{h^2}$ ($\because$ n = 2 and Z = 3)

48. (c) $v_n = 2.186 \times 10^6 \frac{Z}{n} \Rightarrow 1.093 \times 10^6 = 2.186 \times 10^6 \times \frac{1}{n}$; n = 2

from Bohr theory we know $2\pi r = n\lambda$

$\Rightarrow 2\lambda$, where, $\lambda = \frac{h}{mv}$

or $r = 0.529 \frac{n^2}{Z}$

$\Rightarrow 0.529 \times 4$ Å

$\therefore$ Circumference of the orbit,

$\Rightarrow 2 \times \frac{22}{7} \times 0.529 \times 4 \times 10^{-10}$

$\Rightarrow 13.30 \times 10^{-10}$ m

49. (a) $\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$, where $n_1 = n$, $n_2 = n + 1$

$\therefore \frac{1}{\lambda} = RZ^2\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right)$

$\Rightarrow \frac{1}{\lambda} = \left(\frac{2n+1}{n^2(n+1)^2}\right) RZ^2$

Since, n > > 1; Therefore, 2n + 1 ≈ 2n
and $(n + 1)^2 \approx n^2$

$\therefore \frac{1}{\lambda} = RZ^2\left(\frac{2n}{n^2.n^2}\right) \Rightarrow \frac{v}{c} = \frac{RZ^2}{n^3}$

or $v = \frac{2cRZ^2}{n^3}$

50. (b) $2\pi r = 4\lambda$; n = 4

Total energy required + total energy released = 0

$2 \times 4.526 \text{ eV} \times N_A + 2 \times 13.6 \times N_A + 2 \times 13.6 \times \left(1 - \frac{1}{16}\right) \times N_A - 30.87 \times x \times N_A = 0$

x = 2 $\therefore$ moles of X required = 2

51. (c) Work function for Li^{2+} = 9E.

$E_p = w + \frac{1}{2}mv^2$; $E_p = 9E + \frac{1}{2}mv^2$

$v = \sqrt{\frac{2(E_p - 9E)}{m}}$

52. (c) $E = hc\bar{v} \Rightarrow 1.63 \times 10^{-18}$ J

where $\bar{v} = R(1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \Rightarrow \frac{3}{4}R$

Translational K.E. of H-atom $= \frac{3}{2} \times \frac{R}{N_A} \times T$

$\frac{3}{2} \times \frac{8.314}{6 \times 10^{23}} \times T = 1.63 \times 10^{-18}$ $T = 7.84 \times 10^4$ K

53. (c) Radial node occurs where probability of finding e^- is zero.

$\therefore \psi^2 = 0$ or $\psi = 0$

$\therefore 6 - 6\sigma + 6\sigma^2 = 0$; $\sigma = 3 \pm 1\sqrt{3}$

For maximum distance $r = \frac{3}{2}\frac{(3+\sqrt{3})a_0}{Z}$

54. (d) For II to I transition,

$\Delta E = \frac{4E}{3} - E = \frac{hc}{\lambda_{II \to I}}$

For III to I transition,

$\Delta E = 2E - E = \frac{hc}{\lambda}$ or $E = \frac{hc}{\lambda}$

$\therefore \frac{hc}{3 \times \lambda} = \frac{hc}{\lambda_{II-I}}$ $\lambda_{II-I} = 3\lambda$

55. (b) $E = \frac{hc}{\lambda} = 2.9 \times 10^{-19}$ J

Total energy of 10 quanta $\Rightarrow 10 \times 2.9 \times 10^{-19}$ J

Energy stored for process = $\frac{112 \times 4.18 \times 10^3}{6 \times 10^{23}}$

$= 7.80 \times 10^{-19}$ J

% efficiency = $\frac{7.8 \times 10^{-19}}{29 \times 10^{-19}} \times 100 \Rightarrow 26.9\%$

56. (a) $\Delta E = \frac{hc}{\lambda} \Rightarrow \frac{1240 \text{ eV} - \text{nm}}{1025.6 \times 10^{-10} \times 10^9}$

$\Delta E = 12.09$ eV

In three different radiations, minimum wavelength for $3 \rightarrow 2$ transition,

$\lambda_{3-1} = \frac{hc}{\Delta E}$

$\Rightarrow \frac{1240 \text{ eV} - \text{nm}}{12.09 \text{ eV}} \approx 102.6$ nm

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. For the radical probability distribution curves ($4\pi r^2$. $R_{n,l}$ Vs r graph), which of the following is/are correct?
- (a) The number of maxima is $n - l$
- (b) The number of nodal points is $n - l - 1$
- (c) The radius of maximum charge density (r_{max}) increases in the order; $3s < 3p < 3d$
- (d) The number of angular nodes is l

2. According to Bohr's atomic theory, which of the following relations is/are correct?
- (a) Kinetic energy of electron $\alpha \frac{z^2}{n^2}$
- (b) The product of velocity of electron and the principal quantum number αz^2
- (c) Frequency of revolution of the electron in an orbit $\alpha \frac{z^2}{n^3}$
- (d) Coulombic force of attraction on the electron $\alpha \frac{z^3}{n^4}$

3. Choose the correct statements among the following:
- (a) A node is a point in space where the wavefunction ψ^2 has zero amplitude.
- (b) The number of maximas (peaks) in radial distribution is $n - l$.
- (c) Radial probability density is $4\pi r^2 R^2_{n,l}(r)$.
- (d) ψ^2 represents probability of finding electron.

4. Which of the following statements are correct?
- (a) The total spectral lines obtained from a single line during Zeeman effect is $(2l + 1)$.
- (b) In the Lyman series as the energy liberated during transition increases then the distance between the spectral lines goes on decreasing.
- (c) The highest probability of finding an electron in 1s orbital is in the vicinity of the circumference.
- (d) The highest probability of finding an electron in 1s orbital is exactly at the middle between nucleus and circumference.

5. Each orbital has a nodal plane. Which of the following statements about nodal planes is not true?
- (a) A plane on which there is zero probability that the electron will be found.
- (b) A plane on which there is maximum probability that the electron will be found.
- (c) A plane with variable probability of finding the electron.
- (d) That orbital has a nodal plane is incorrect.

6. In which of the following situations the heavier of the two particles have smaller de Broglie wavelength? The two particles
(a) move with the same speed
(b) move with same linear momentum
(c) move with the same kinetic energy
(d) have fallen through the same height

7. Which of the following is/are correct for H-atom?
(a) $1s < 2s < 2p < 3s < 3p$
(b) $1s < 2s = 2p < 3s = 3p$
(c) $1s < 2p < 3d < 4s$
(d) $1s < 2s < 4s < 3d$

8. The correct statement(s) among the following is (are):
(a) All d-orbitals except d_{z^2} have two angular nodes
(b) $d_{x^2-y^2}$ and d_{z^2} orbitals lie on the axis or axes
(c) The degeneracy of p-orbital remains unaffected in a homogeneous external magnetic fiel
(d) The angle between the Z-component of orbital angular momentum of p_z-electron and Z-axis is 90°

9. Electromagnetic radiations of frequency 'v' consists of a stream of particle called photons. Which of the following statements is/are true about photons?
(a) As the frequency increases, the number of photons in the beam increases.
(b) As the intensity of light increases, the number of photons in the beam increases.
(c) The number of photons in the beam are independent of frequency.
(d) The number of photons in the beam are independent of the intensity of light.

10. Atomic emission spectra of an element cannot be used to:
(a) identify the element
(b) determine the mass number of the nucleus of the atom
(c) measure the difference in energy between pairs of stationary states of the atom
(d) calculate the ionization energy of the atom

ANSWER KEYS

1. (abd) **2.** (acd) **3.** (abcd) **4.** (abc) **5.** (b,c) **6.** (acd) **7.** (bc) **8.** (abcd) **9.** (c) **10.** (b)

HINTS AND EXPLANATIONS

3. (abcd) Explanation : All statements are correct.

7. (bc) (b) is correct because energy of orbital of hydrogen depends upon 'n' and not on 'l'
(c) is also correct as explained above
(ad) are not correct for H-atom.

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

Dual Nature of Matter: Light and other electromagnetic radiations have dual nature i.e., wave and particle nature. Interference and diffraction phenomenon show the wave nature of light whereas the photoelectric effect and black body radiation phenomenon support the particle nature of light. Louis de Broglie (1924) suggested on the same grounds that all moving material particles (microscopic as well macroscopic) also have the dual nature i.e., wave and particle nature. However, the wave associated with matter, known as matter wave has characteristics different from the electromagnetic wave.

The two characters of matter are related by de Broglie equation as:

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad \text{..... (h = Planck's constant)} \qquad \text{..... (1)}$$

Where λ denotes the wavelength associated with the moving matter object of mass m and velocity v, and p denotes the momentum of the object.

Davission and Germer determined the wavelength of matter wave associated with electrons (accelerated by a exactly known electric potential) by studying their diffraction patterns from nickel crystal and using he relation:

$$2d\sin\theta = n\lambda \qquad \text{.....(2)}$$

where d denotes the spacing of lattice planes in nickel crystal, θ the grazing angle of incidence on the planes and n (1, 2, 3 etc.) the order of reflection

The experimentally determined value of λ from Eq. (2) is found to be in excellent agreement with the value of wavelength calculated using de Broglie equation as:

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

Where e is the electronic charge (coulombs) and V (volts) is the accelerating potential.

1. The momentum of hydrogen atom is given by

(a) $p = \frac{hv}{c}$ (b) $p = \frac{hv}{mc^2}$

(c) $p = \frac{mv}{h}$ (d) Cannot be predicted

2. The wavelength of matter wave associated with an electron passing through an electric potential of 5000 V is given by (h = electronic charge in coulombs and m = mass of electron in kg.)

(a) $\frac{h\times10^{-4}}{\sqrt{me}}$m (b) $\frac{h\times10^{-2}}{\sqrt{me}}$m

(c) $\frac{\sqrt{me}}{h}\times10^{-2}$m (d) $\frac{\sqrt{me}}{h}\times10^{4}$m

3. If λ is the wavelength associated with the electron in the second circular orbit of H-atom, the radius of the orbit is given by

(a) $\frac{\lambda}{2\pi}$ (b) $\frac{2\pi}{\lambda}$

(c) $\frac{\lambda}{\pi}$ (d) $\frac{\pi}{\lambda}$

4. If the Planck's constant is 6.6×10^{-34} J.s, the de Broglie wavelength of a particle of mass 3.3×10^{-27} kg and velocity 200 ms^{-1} will be

(a) 2 Å (b) 5 Å

(c) 20 Å (d) 10 Å

COMPREHENSION-II

Excited atoms emits radiations consisting of only certain discrete frequencies or wavelengths. In spectroscopy it is often more convenient to use frequencies or wave numbers than wavelength because frequencies and wave numbers are proportional to energy, and spectroscopy involves transitions between different energy levels. The line spectrum shown by an mono electronic excited atom (a finger print of an atom) can be given as:

$$\frac{1}{\lambda} = \bar{v} = R_H \cdot Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

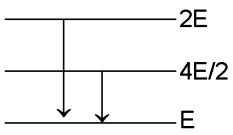
where Z is atomic number of mono electronic atom and n_1, n_2 are integers and if $n_2 > n_1$, then emission spectrum is noticed and if $n_2 < n_1$, then absorption spectrum is noticed. Every line is spectrum can be represented as a difference of two terms $\frac{R_H.Z^2}{n_1^2}$ and $\frac{R_H.Z^2}{n_2^2}$.

5. The ratio of wavelength for II line of Balmer series and I line of Lyman series is:

(a) 1/4 (b) 2

(c) 3 (d) 4

6. The given diagram indicate the energy levels of certain atom. When an electron moves from 2E level to E level, a photon of wavelength λ is emitted. The wavelength of photon emitted during its transition from $\frac{4E}{3}$ level to E level is:



(a) $\frac{\lambda}{3}$ (b) $\frac{3\lambda}{4}$

(c) $\frac{4\lambda}{3}$ (d) 3λ

7. H-atoms in ground state (13.6 eV) are excited by monochromatic radiations of photon of energy 12.1 eV. The number of spectral lines emitted in H-atom will be:

(a) 1 (b) 2

(c) 3 (d) 6

COMPREHENSION-III

The behavious of an electron in an atom is described mathematically by a wave function, or orbital. It turns out that each wave function contains three variables, called quantum numbers, which are represented as n, l and m_l. These quantum numbers describe the energy level of an orbital and define the shape and orientation of the region in space where the electron will be found.

8. Which quantum number determines orientation of the electron?

(a) Principal (b) Secondary

(c) Magnetic (d) Spin

9. Orbital angular momentum is quantised and is given by:

(a) $\sqrt{l(l+1)}\,\hbar$ (b) $\sqrt{n(n+2)}\,\hbar$

(c) $\sqrt{m(m+1)}\,\hbar$ (d) $\sqrt{s(s+1)}\,\hbar$

10. Radial nodes are maximum in:

(a) 4s (b) 4p

(c) 3d (d) 5 f

11. Total number of electrons in any energy level is:

(a) $\sum_{l=1}^{l=n} 2(2l+1)$ (b) $\sum_{l=1}^{l=n-1} 2(2l+1)$

(c) $\sum_{l=0}^{l=n+1} 2(2l+1)$ (d) $\sum_{l=0}^{l=n-1} 2(2l+1)$

12. Consider following statements:

A: Splitting of spectral line occurs when placed in a magnetic field or in an electric fiel

B: In case of 1s-orbital, the density of the charge cloud is the greatest at the nucleus and falls off with the distance. The density (at a particular distance is uniform)

C: Electron-density is concentrated along a particular direction in case of 2p-orbital

D: A p-orbital can take maximum of six electrons select correct statement (s):

Select correct statement(s):

(a) A, B, D (b) A, B, C

(c) B, C, D (d) A, C, D

ANSWER KEYS

1. (d) **2.** (b) **3.** (c) **4.** (d) **5.** (a) **6.** (d) **7.** (c) **8.** (c) **9.** (a) **10.** (a)
11. (d) **12.** (b)

[redacted]TS AND EXPLANATIONS

COMPREHENSION-I

1. (d) Momentum cannot be calculated as the velocity of hydrogen atom is not given.

2. (b) Wavelength of electron accelerated by potential of V volt $= \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{2me \times 5000}} = \frac{h}{100 \times \sqrt{me}} m$

3. (c) The angular momentum of electron in second orbit is given by $mvr = n\frac{h}{2\pi} = \frac{2h}{2\pi}$. Hence, $r = \frac{h}{\pi mv} = \frac{\lambda}{\pi}$

4. (d) deBroglie wavelength $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{3.3 \times 10^{-27} \times 200}\theta$
$= 10^{-9}$ m = 10 Å

COMPREHENSION-II

1. (a) $\frac{1}{\lambda_1} = Rz^2\left(\frac{1}{4} - \frac{1}{16}\right) = \frac{Rz^2}{4} \times \frac{3}{4}$; $\frac{1}{\lambda_2} = Rz^2\left(\frac{1}{1} - \frac{1}{4}\right) = Rz^2 \times \frac{3}{4}$
$= Rz^2 \times \frac{3}{4}$; $\frac{\lambda_1}{\lambda_2} = 4 : 1$

2. (d) $\Delta E_1 = E = \frac{hc}{\lambda}$, $\therefore \lambda = \frac{hc}{E}$;

$\Delta E_2 = \frac{4E}{3} - E = \frac{E}{=} \frac{hc}{\lambda_2}$;

$\frac{hc}{\lambda_2} = \frac{E}{3}, \lambda_2 = \frac{3hc}{E} = 3\lambda$

3. (c) $1.5 = \frac{13.6}{n^2}, n = 3$ number of spectral line $= \frac{n(n-1)}{2}$
$= 3$

MATCH THE COLUMN TYPE QUESTIONS

1. Electron of charge e (coulombs) and mass m_e(kg) is accelerated by a potential of 50V. Match the following:

Column–I	**Column–II**
(i) Velocity of Electron (ms^{-1})	(a) $\frac{h}{10\sqrt{em_e}}$
(ii) K.E. of electron (j)	(b) $10\sqrt{em_e}$
(iii) Momentum of electron	(c) 50e
(iv) Wavelength of wave associated with e^-	(d) $10\sqrt{e/m_e}$

2. If the shortest wavelength of spectral line of H-atom in Lyman series is x, then match the following for Li^{2+}

Column –I	**Column–II**
(i) Shortest wavelength in Lyman series	(a) $\frac{4x}{5}$
(ii) Longest wavelength in Lyman series	(b) $\frac{4x}{9}$
(iii) Shortest wavelength in Balmer series	(c) $\frac{x}{9}$
(iv) Longest wavelength in Balmer series	(d) $\frac{4x}{27}$

3. According to Bohr's theory
E_n = Total energy K_n = Kinetic energy
V_n = Potential energy r_n = Radius of nth orbit

Match the following:

Column–I	**Column II**
(i) V_n/K_n = ?	(a) 0
(ii) If radius of nth orbit $\propto E_n^x$, x = ?	(b) –1
(iii) Angular momentum in lowest orbital	(c) –2
(iv) $\frac{1}{r^n} \propto Z^y$, y = ?	(d) 1

ANSWER KEYS

1. (i) d; (ii) c; (iii) b (iv) a **2.** (i) e (ii) d (iii) b (iv) a **3.** (i) c; (ii) d; (iii) b (iv) a

HINTS AND EXPLANATIONS

1. (i) → c, (ii) → b, (iii) → a, (iv) → d

According to Bohr's theory

Total energy is $E_n = K_n + V_n$

Kinetic energy $= K_n = \frac{1}{8\pi\varepsilon_0}.\frac{Ze^2}{r}$

Potential energy $= V_n = \frac{1}{4\pi\varepsilon_0}.\frac{Ze^2}{r}$

$\therefore \quad E_n = \frac{1}{8\pi\varepsilon_0}.\frac{Ze^2}{r} - \frac{1}{4\pi\varepsilon_0}.\frac{Ze^2}{r}$

Radius of nth orbit $(r_n) = \frac{n^2h^2\varepsilon_0}{\pi mZe^2}$

$\therefore \quad E_n = -\frac{me^4}{8\varepsilon_0^2h^2} \times \frac{1}{n^2}$

(a) $\frac{V_n}{K_n} = \frac{-\frac{1}{4\pi\varepsilon_0}.\frac{Ze^2}{r}}{\frac{1}{8\pi\varepsilon_0}.\frac{Ze^2}{r}} = -2$

Hence, (a) match with (R).

(b) $E_n \propto \frac{1}{n^2}$ or $E_n \propto \frac{1}{r_n}$

Radius of n^{th} orbit $r_n \propto E_n^x$

$\therefore \quad x = -1$

Hence, (b) match (Q).

(c) Angular momentum $= \frac{h}{2\pi}\sqrt{l(l+1)}\,l$

$= 0, 1, 2, \ldots\ldots$

For the lower orbit n = 1

$\therefore \quad l = 0$ and m = 0

(c) match with (P)

(d) $\frac{1}{r^n} \propto Z^y$

as $r_n \propto \frac{1}{Z}$

$\therefore \quad y = 1$

Hence, (d) match with (S).

TRUE/FALSE TYPE QUESTIONS

1. An electronic emission spectrum will contain more lines than the corresponding absorption spectrum.

2. If uncertainty in position and momentum are equal then uncertainty in velocity is $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$.

3. Electron density in the xy plane in $3d_{(x^2-y^2)}$ orbital is zero.

4. Total energy of the electron in a given orbit = – kinetic energy of the electron.

ANSWER KEYS

1. T **2.** T **3.** F **4.** T

ASSERTION/REASON TYPE QUESTIONS

Instructions: In the following questions, an Assertion (A) is given followed by a Reason (R). Mark your responses from the following options.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'
(b) Both Assertion and Reason are true and Reason is not the correct explanation of 'Assertion'
(c) Assertion is true but Reason is false
(d) Assertion is false but Reason is true

1. **Assertion:** The kinetic energy of the photoelectron ejected increase with the frequency of incident light.
   Reason: Increase in intensity of incident light increases the photoelectric current.

2. **Assertion:** Electromagnetic radiation will be emitted for the transition $2p_z \rightarrow 2p_x$.
   Reason: No transition of electron takes place between $2p_z$ and $2p_x$ orbital.

3. **Assertion:** Elecromagnetic radiations will be emitted for the transition of 2p to 2s-orbital in H-atom.
   Reason: Both 2p and 2s orbital in H-atom have same energy level and thus, no transition.

4. **Assertion:** The total number of spectral line or, different number of photons from orbit 7 to ground state is 21.
   Reason: Since total number of spectral lines or, different number of photons falling from higher orbit n to ground state is $\frac{n(n-1)}{2}$.

5. **Assertion:** Photoelectric current is directly proportional to the intensity of photon falling on the metal surface. For photon having frequency greater than or, equal to threshold frequency.
   Reason: As the intensity of photon with frequency equal to or greater than, falling on the metal surface increases, more number of electrons eject out which is responsible for photoelectric current.

ANSWER KEYS

1. (b) **2.** (d) **3.** (d) **4.** (a) **5.** (a)

HINTS AND EXPLANATIONS

1. (b) K.E. = $h(\upsilon - \upsilon_0)$; K.E. increase linearly with υ, the frequency. The rate of emission of photoelectrons i.e., the photoelectric current is proportional to the rate of impinging photons.

2. (d) $2p_x$ and $2p_z$ orbitals are degenerate i.e., they are of equal energies and hence no transition of electron between is possible.

3. (d) In H atom energy, of an orbital is decided by 'n' only and not by 'l'.

SUBJECTIVE TYPE QUESTIONS

1. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å.
2. Why electron cannot exist inside the nucleus according to Heisenberg's uncertainty principle?
3. Find out the energy of H-atom in first excitation state. The value of permittivity factor $4\pi\varepsilon_0 = 1.11264 \times 10^{-10}\ C^2N^{-1}\ m^{-2}$.
4. Oxygen consists of isotopes of O^{16}, O^{17} and O^{18} and carbon consists of isotopes of C^{12} and C^{13}. How many types of CO_2 molecule can be formed? Also report their mol. wt.
5. It has been found that gaseous Iodine molecules dissociate into seperated atoms after absorption of light at wavelengths less than 4995Å. If each quantum is absorbed by one molecule of I_2, what is the minimum input in kcal/mole, needed to dissociate I_2 by this photo chemical process?
6. Show that frequencies of emitted photons are additive but their wavelengths are not.
7. Wavelength of the K_α characterisic X-rays of iron and potassium are 1.931×10^{-8} and 3.737×10^{-8} cm respectively. What is the atomic number and name of the element for which characteristic K_α wave length is 2.289×10^{-8} cm?

   At. No of K = 19, and Fe = 26

   Velocity of light $= 3 \times10^{10}$ cm/sec

   According to Mosly's law, the frequency of emitted X-ray $\nu \propto Z^2$
8. O_2 undergoes photochemical dissociation into one normal oxygen and one excited oxygen atom, 1.967 eV more energetic than normal. The dissociation of O_2 into two normal atoms of oxygen atoms requires 498 KJ $mole^{-1}$. What is the maximum wavelength effective for photochemical dissociation of O_2?
9. Number of waves made by a Bohr electron in one complete revolution in 3rd orbit is
   (a) 2 (b) 3
   (c) 4 (d) 1
10. Photoelectric emission is observed from a surface for frequencies ν_1 and ν_2 of the incident radiation ($\nu_1 > \nu_2$). If the maximum kinetic energies of the photoelectrons in two cases are in ratio 1 : K then the threshold frequency ν_0 is given by

    (a) $\frac{\nu_2 - \nu_1}{K-1}$ (b) $\frac{K\nu_1 - \nu_2}{K-1}$

    (c) $\frac{K\nu_2 - \nu_1}{K-1}$ (d) $\frac{\nu_2 - \nu_1}{K}$

HINTS AND EXPLANATIONS

1. If an electron accelerated by potential V, has velocity 'u' and associated de Broglie's wavelength λ,

   $1/2\ mv^2 = eV$ ... (i)

   $\lambda = \frac{h}{mu}$ ... (ii)

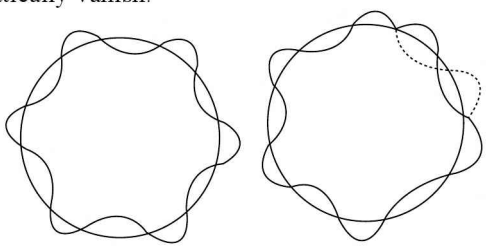
   From equation (ii) $\mu = \frac{h}{m\lambda}$ $\therefore$ $1/2\ m\left(\frac{h}{m\lambda}\right)^2 = e \times V$

   $\Rightarrow V = \frac{h^2}{2m\lambda^2 c}$

   $= \frac{(6.625\times10^{-34})^2}{2\times9.108\times10^{-31}\times(1.54\times10^{-10})^2\times1.602\times10^{-19}}$

   = 63.3 volt

De Broglie further said that electron can reside only in those orbits where the number of waves are complete, because only in those orbits, in which the number of waves are complete, the waves will be in phase i.e., constructive interference will taken place i.e., wave will be there i.e., electron will be there. The orbits in which number of waves will be incomplete, the waves will be out of phase i.e., destructive interference will take place and the orbit will automatically vanish.



(a) The number of waves around the orbit is a whole number (6) times the wavelength.

(b) The number of waves around the orbit is not a while number multiple of the wavelength.When the wave goes around the orbit many times,In cancles itself out. Necessary condition for an electron to be present in an orbit is $2\pi r = n\lambda$ [for complete waves in an orbit n can take only integral values i.e., if the number of wave present in an orbit is n].

$$2\pi r = n\frac{h}{mv} \qquad \text{or} \qquad mvr = \frac{nh}{2\pi}$$

But from Bohr theory n is number of orbit. So number of waves formed in any orbit = orbit number.

De Broglie said that electron will be present only in those orbits where number of waves are complete constructive interference will take place only in all those orbits, to such orbits Bohr called them as stationary orbits and in these orbits electrons does not radiate energy because of the formation of stationary waves because for stationary orbits $\Delta E = 0$.

2. Diameter of the atomic nucleus is of the order of 10^{-15} m

The maximum uncertainty in the position of electron is 10^{-15} m.

Mass of electron = 9.1×10^{-31} kg

$$\Delta x \,.\, \Delta p = \frac{h}{4\pi}$$

$$\Delta x \times (m.\Delta v) = h/4\pi$$

$$\Delta v = \frac{h}{4\pi} \times \frac{1}{\Delta x.m} = \frac{6.63\times10^{-34}}{4\times\frac{22}{7}} \times \frac{1}{10^{-15}\times9.1\times10^{-31}}$$

$$\Delta v = 5.80 \times 10^{10}\ ms^{-1}$$

This value is much higher than the velocity of light and hence not possible.

3. In M.K.S. system

$$E_n = -\frac{2\pi^2 Z^2 me^2}{(4\pi\varepsilon_0)^2 n^2 h^2}$$

$$= \frac{2\times(3.14)^2\times(1)^2\times9.108\times10^{-31}\times(1.602\times20^{-19})^4}{(1.11264\times10^{-10})^2\times(2)^2\times(6.625\times10^{-34})^2}$$

$$= \mathbf{5.443 \times 10^{-19}\ joule}$$

4. Total number of molecules of CO_2 = 12

[1] $C^{12}O^{16}O^{16}$	Mol. wt. = 44
[2] $C^{12}O^{17}O^{17}$	= 46
[3] $C^{12}O^{18}O^{18}$	= 48
[4] $C^{12}O^{16}O^{17}$	= 45
[5] $C^{12}O^{16}O^{18}$	= 46
[6] $C^{12}O^{17}O^{18}$	= 47

Similarly, six molecules with C^{13} isotopes.

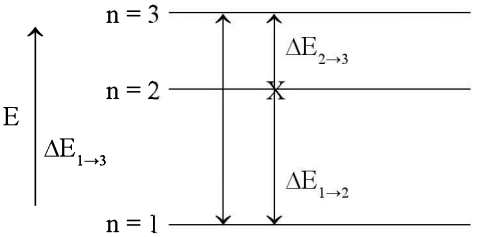
5. E (per mole) = $N_A h\nu$

$$E = N_a \frac{hc}{\lambda}$$

$$= \frac{(6.023\times10^{23}\ mol^{-1})(6.626\times10^{-34}\ Js)\times3\times10^{8}\ ms^{-1}}{4995\times10^{-10}\ m}$$

$$= 239.5\ kJ/mol\left(\frac{1\ kcal}{4.184\ kJ}\right) = 57.1\ kcal/mole$$

6.



$$\because\ \Delta E_{1\to3} = \Delta E_{1\to2} + \Delta E_{2\to3}$$

$$\therefore\ h\nu_{1\to3} = h\nu_{1\to2} + h\nu_{2\to3}$$

$$\therefore\ \nu_{1\to3} = \nu_{1\to2} + \nu_{2\to3}$$

i.e., frequencies like energies are additive, on the other hand

$\because \quad \Delta E_{1\to3} = \Delta E_{1\to2} + \Delta E_{2\to3}$

$$\therefore \quad \frac{hc}{\lambda_{1\to3}} = \frac{hc}{\lambda_{1\to2}} + \frac{hc}{\lambda_{2\to3}}$$

$$\therefore \quad \frac{1}{\lambda_{1\to3}} = \frac{1}{\lambda_{1\to2}} + \frac{1}{\lambda_{2\to3}}$$

$$\therefore \quad \frac{1}{\lambda_{1\to3}} = \frac{\lambda_{2\to3} + \lambda_{1\to2}}{\lambda_{1\to2}\lambda_{2\to3}}$$

$$\therefore \quad \lambda_{1\to3} = \frac{\lambda_{1\to2}\lambda_{2\to3}}{\lambda_{1\to2} + \lambda_{2\to3}}$$

i.e., wavelengths are not additive.

7. Frequency $\nu = \frac{c}{\lambda} \propto Z^2 = \frac{c}{\lambda}K(Z)^2$

$$\frac{\lambda_2}{\lambda_1} = \left(\frac{Z_1}{Z_2}\right)^2 \quad \ldots (1)$$

$$\frac{\lambda_3}{\lambda_2} = \left(\frac{Z_2}{Z_3}\right)^2 \quad \ldots (2)$$

λ_1 (Fe) $= 1.931 \times 10^{-8}$, $Z_1 = 26$

λ_3(K) $= 3.737 \times 10^{-8}$, $Z_3 = 19$

λ_2 (u) $= 2.289 \times 10^{-8}$, $Z_2 = ?$

From equation (1) $\frac{2.289\times10^{-8}}{1.931\times10^{-8}} = \left(\frac{26}{Z_2}\right)^2$

On solving we get $Z_2 = 23.88 = 24$

From equation (2)

$$\frac{3.737\times10^{-8}}{2.289\times10^{-8}} = \left(\frac{Z_2}{19}\right)^2$$

$Z_2 = 24.27 =$ **24**

Thus, the atomic number of that element is 24 and it is chromium.

8. $O_2 \longrightarrow O_N + O_{excited}$

$O_2 \longrightarrow O_N + O_N$

$E = 498 \times 10^3$ J/mole

$$= \frac{498\times10^3}{6.023\times10^{23}} \text{ J per molecule} = 8.268 \times 10^{-19} \text{ J}$$

Energy required for excitation = 1.967 eV = 3.146×10^{-19}J

Total energy required for photochemical dissociation of $O_2 = 8.268 \times 10^{-19} + 3.146 \times 10^{-19} = 11.414 \times 10^{-19}$ J

$$\frac{hc}{\lambda} = 11.414 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{6.626\times10^{-34}\times3\times10^8}{11.414\times10^{-19}}$$

$= 1.7415 \times 10^{-7}$ m **= 1741.5 Å**

9. Circumference of 3rd orbit = $2\pi r_3$

According to Bohr angular momentum of electron in 3rd orbit is,

$$mvr_3 = 3\frac{h}{2\pi}$$

or $\frac{h}{mv} = \frac{2\pi r_3}{3}$

by de Broglie equation,

$$\lambda = \frac{h}{mv}$$

$$\therefore \quad \lambda = \frac{2\pi r_3}{3}$$

$$\therefore \quad 2\pi r_3 = 3\lambda$$

i.e., circumference of 3rd orbit is three times the wavelength of electron or number of waves made by Bohr electron in one complete revolution in 3rd orbit is three.

$\therefore$ (b)

10. $KE_1 = h\nu_1 - h\nu_0$

$KE_2 = h\nu_2 - h\nu_0$

It is given that,

$$\frac{KE_1}{KE_2} = \frac{1}{K}$$

$$\frac{h\nu_1 - h\nu_0}{h\nu_2 - h\nu_0} = \frac{1}{K}$$

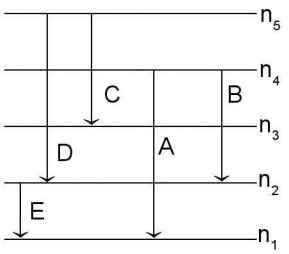
$$(K\nu_1 - \nu_2) = \nu_0(K-1)$$

$$\nu_0 = \frac{K\nu_1 - \nu_2}{K-1} \quad \therefore \text{ (b)}$$

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

1. For a hypothetical H like atom which follows Bohr's model, some spectral lines were observed as shown. If it is known that line 'E' belongs to the visible region, then the lines possibly belonging to ultra violet region will be (n_1 is not necessarily a ground state)



[Assume for this atom, no spectral series shows overlaps with other series in the emmission spectrum]

(a) B and D (b) D only
(c) C only (d) A only

2. Ratio of frequency of revolution of electron in the 2nd excited state of He and 2nd state of hydrogen is

(a) $\frac{32}{27}$ (b) $\frac{27}{32}$
(c) 1/54 (d) 27/2

3. A proton accelerated from rest through a potential difference of 'V' volts has a wavelength λ associated with it. An alpha particle in order to have the same wavelength must be accelerated from rest through a potential difference of

(a) V volt (b) 4V volt
(c) 2V volt (d) $\frac{V}{8}$ volt

4. 4000 A photon is used to break the iodine molecule, then calculate the % of energy converted to the K.E. of iodine atoms if bond dissociation energy of I_2 molecule is 246.5 kJ/mol.

(a) 8% (b) 12%
(c) 17% (d) 25%

ASSERTION/REASON TYPE QUESTIONS

5. **Statement-1:** 'He' has lowest ionization energy among all the elements.
Statement-2: Addition of extra electrons even in fully filled orbitals releases energy

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

6. **Statement-1:** If an electron is located within the range of 0.2 Å then the uncertainty in velocity is approximately 6×20^6 m/s.
Statement-2: Trajectory (path of motion) of above electron can be defined
[$h = 6.6 \times 20^{-34}$, $m_e = 9.2 \times 20^{-31}$ kg]

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

If hydrogen atoms (in the ground state) are passed through an homogeneous magnetic field, the beam is split into two parts. This interaction with the magnetic field shows that the atoms must have magnetic moment. However, the moment cannot be due to the orbital angular momentum since $\ell = 0$. Hence, one must assume existence of intrinsic angular momentum, which as the experiment shows, has only two permitted orientations.

Spin of the electron produces angular momentum equal to $S = \sqrt{s(s+1)}\frac{h}{2\pi}$ where $S = \frac{1}{2}$.

Total spin of an atom $= +\frac{n}{2}$ or $-\frac{n}{2}$

Where, n is the number of unpaired electron.

The substances which contain species with unpaired electrons in their orbitals behave as paramagnetic substances. The paramagnetism is expressed in terms of magnetic moment.

The magnetic moment of an atom

$$\mu_s = \sqrt{s(S+1)} = \frac{eh}{2\pi mc} = \sqrt{\frac{n}{2}\left(\frac{n}{2}+1\right)}\frac{eh}{2\pi mc}$$

$$s = \frac{n}{2}$$

$$\Rightarrow \quad \mu_s = \sqrt{n(n+2)}\text{B.M}$$

n - number of unpaired electrons

1. B.M. (Bohr magneton) $= \frac{eh}{4\pi mc}$

If magnetic moment is zero the substance is di-magnetic.

7. If an ion of $_{25}Mn$ has a magnetic moment of 3.873 B. M. Then Mn is in which state.

(a) +2 (b) +3
(c) +4 (d) +5

8. Which of the following is a paramagnetic substance.

(a) Mg^{2+} (b) Cu^{+}
(c) Mn^{+7} (d) Ti^{+2}

9. The number of unpaired electrons in Mn^{4+} (Z = 25) is –

(a) Four (b) Two
(c) Five (d) Three

COMPREHENSION-2

The French physicist Louis de Broglie in 1924 postulated that matter, like radiation, should exhibit a dual behaviour. He proposed the following relationship between the wavelength λ of a material particle, its linear momentum p and planck constant h.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

The de Broglie relation implies that the wavelength of a particle should decrease as its velocity increases. It also implies that for a given velocity heavier particles should have shorter wavelength than lighter particles. The waves associated with particles in motion are called matter waves or de Broglie waves. These waves differ from the electromagnetic waves as they

(i) have lower velocities
(ii) don't have electrical and magnetic fields and
(iii) are not emitted by the particle under consideration.

The experimental confirmation of the de Broglies relation was obtained when Davisson and Gerber, in 1927, observed that a beam of electrons is diffracted by a nickel crystal. As diffraction is a characteristic property of waves, hence, the beam of electron behaves as a wave, as proposed by de broglie.

10. If proton, electron and a-particle are moving with same kinetic energy then the order of their de-Broglie's wavelength is

(a) $\lambda p > \lambda e > \lambda a$ (b) $\lambda a > \lambda p > \lambda e$
(c) $\lambda a < \lambda p < \lambda e$ (d) $\lambda e = \lambda p < \lambda a$

11. Using Bohr's theory, find out the transition, in which-the electrons de-Broglie wavelength becomes 3 times of its original value in He^{+} ion will be

(a) $2 \rightarrow 6$ (b) $2 \rightarrow 4$
(c) $1 \rightarrow 4$ (d) $1 \rightarrow 6$

12. De-Broglie wavelength of an electron travelling with speed equal to 1% of the speed of light

(a) 400 pm (b) 120 pm
(c) 242 pm (d) 375 pm

COMPREHENSION-3

If an electron is in any higher state n = n and makes a transition to ground state, then total number of different photons emitted is equal to $\frac{n \times (n-1)}{2}$.

If an electrons is in any higher state $n = n_2$ and makes a transition to another excited state $n = n_1$, then total number of different photons emitted is equal to $\frac{\Delta n(\Delta n+1)}{2}$, where, $\Delta n = n_2 - n_1$.

Note: In case of single isolated atom if electron makes transition from n^{th}state to the ground state then maximum number of spectral lines observed = (n – 1).

13. Two samples are taken, in Ist sample mole ratio of H to H^+ is 1: 2. In IInd sample mole ratio of H to He^+ is 2: 1. If n_1 is number of spectral lines produced by Ist sample and number of spectral lines produced by IInd sample is n_2 then n_1: n_2 will be –
(There is sufficient number of both types of atom and both are in same excited state in both sample)
(a) 2 : 1 (b) 1 : 2
(c) 1 : 1 (d) None of these

14. Which of the following statements is/are true?
(I) If H atoms are in 3rd state, then number of maximum spectral line produced by 2 atoms will be equal to number of maximum spectral lines produced by 3 H-atoms
(II) For third excited state, maximum number of spectral line produced by He^+ and maximum number of spectral line produced by 4 H^- atom are not equal.
(III) Energy evolved from 3 to 2 transitions in He cannot used for any transition in Li^{2+}.
(a) I & III (b) II & III
(c) All (d) I & II.

15. In a sample, one H atom is in Ist excited state, two He^+ ions is in IInd excited state and three Li^{2+} ions is in IIIrd excited state are present, then maximum number of spectral line which can be obtained when all possible transitions are terminated at n = 1 are
(a) 11 (b) 12
(c) 13 (d) 17

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

16. The wave functions of 3s and $3p_z$ orbitals are given by

$$\psi_{3s} = \frac{1}{9\sqrt{3}}\left(\frac{1}{4\pi}\right)^{1/2}\left(\frac{z}{a_0}\right)^{3/2}\left(6-\frac{4zr}{a_0}+\frac{4}{9}\frac{z^2r^2}{a_0^2}\right)e^{-zr/3a_0}$$

$$\frac{1}{9\sqrt{6}}\left(\frac{3}{4\pi}\right)^{1/2}\left(\frac{z}{a_0}\right)^{3/2}\left(4-\frac{2zr}{3a_0}\right)\left(\frac{2zr}{3a_0}\right)e^{-zr/3a_0}\cos\theta$$

From these we can conclude
(a) number of nodal surface for $3p_z$ & 3s orbitals are equal
(b) the angular nodal surface of $3p_z$ orbital has the equation $\theta = \pi/2$
(c) The radial nodal surfaces of 3s orbital and $3p_z$ orbitals are at equal distance from the nudes
(d) 3s electron have greater penetrating power into the nucleus in comparison to 3p, electrons

17. A hydrogen like atom in ground state absorbs 'n' photons having the same energy and it emits exactly 'n' photons when electronic transition takes place. Then the energy of the absorbed photon may be
(a) 91.8 eV
(b) 40.8 eV
(c) 48.4 eV
(d) 54.4 eV

18. In a hydrogen like sample, two different types of photons A and B are produced by electronic transition. Photon B has it's wavelength in infrared region. If photon A has more energy then B, then the photon A may belong to the region.
(a) ultraviolet
(b) visible
(c) infrared
(d) None

19. Hydrogen atoms in a particular excited state 'n', when all returned to ground state, 6 different photons are emitted. This of the following is/are incorrect.
(a) Out of 6 different photons only 2 photons have speed equal to that of visible light.
(b) If highest energy photon emitted from the above sample is incedent on the metal plate having work function 8 eV, AKE of liberated photo-electron may be equal to or less than 4.75 eV.
(c) Total number of radial nodes in all the orbitals of nth shell is 24.
(d) Total number of angular nodes in all the orbitals in (n-1)th shell is 23.

20. In a H-like sample electrons make transition from 4th excited state to 2nd state then
(a) 10 different spectral lines are observed
(b) 6 different spectral lines are observed
(c) number of lines belonging to the balmier series is 3
(d) Number of lines belonging to paschen series is 2.

MATCH THE COLUMN TYPE QUSTIONS

21. Match the following:
B.E. – Binding energy
I.E. – Ionization energy:

Column-I	Column-II
(a) Of He atom in an excited state	(p) Infrared region
(b) 7 → 3 transition in H-atom	(q) 3.4 eV
(c) 5 → 1 transition in H-atom	(r) 13.6 eV
(d) Series limit of Balmer series in H-atom	(s) 10 Spectral lines observed

ANSWER KEYS

1. (d)	**2.** (a)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (c)	**7.** (b)	**8.** (d)	**9.** (d)	**10.** (c)
11. (a)	**12.** (c)	**13.** (c)	**14.** (a)	**15.** (a)	**16.** (a, b, d)	**17.** (a, b)	**18.** (a, b, c)	**19.** (a, c, d)	
20. (b, c, d)	**21.** (a – q, r), (b – p, s), (c – s), (d – q)								

HINTS AND SOLUTIONS

1. (d) In the given figure, if line 'E' is in visible region then line belonging to ultraviolet region will have more energy than 'E' i.e., line A

2. (a) $\frac{f_1}{f_2} = \frac{z_1^2}{n_1^3} \times \frac{z_2^3}{z_2^2} \quad \begin{matrix} n_1 = 3 \\ z_1 = 2 \end{matrix} = \begin{matrix} n_2 = 3 \\ z_2 = 1 \end{matrix}, \frac{2^2}{3^3} \times \frac{32}{27}$

3. (d) $\lambda = \frac{h}{\sqrt{2m_p eV}}$

$\lambda\alpha = \frac{h}{\sqrt{2m_a (2e) V_a}} \quad 2 \times 4 \times m_p \times 2eV\alpha$

$\Rightarrow \quad V\alpha = \frac{V}{8}$

4. (c) Energy of one photon = $\frac{12400}{4000}$ = 3.1 ev

Energy supplied by one mole photon in KJ/mole = $3.1 \times 1.6 \times 10^{-19} \times 6 \times 10^{23} \times 10^{-3} = 297$ kJmol^{-1}

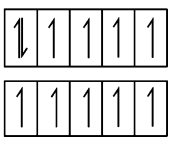
% of energy converted to K. E.

$= \frac{297 - 246.5}{297} = 17\%$

5. (d) 'He' has highest first ionization energy therefore, assertion is wrong and also addition of extra electron to the outer most shelf of fully filled orbitals absorbes energy. Hence, reason is also wrong.

6. (c) $m\Delta V \Delta x = \frac{h}{4\pi}$

$\Rightarrow \quad \Delta v = \frac{6.62 \times 10^{-34}}{9.1 \times 10^{31} \times 4 \times 3.14 \times 10^{11}} = 6 \times 106 \text{m/s}$



as uncertainty in velocity is very high so, we cannot define the trajectory of an electron.

7. (b) Magnetic moment = $\sqrt{n(n+2)} = 3.873$

$\Rightarrow$ number of unpaired electron n=3

$\therefore$ $_{25}$Mn – [Ar] $3d^5\ 4s^2$ therefore, Mn should be in + 4

8. (d) There are two unpaired electron in Ti^{2+}

9. (d) Mn^{4+} – [Ar] $3s5\ 4s^3$

16. (a, b, d)

3s orbital has two radial nodes at the values of radius given by solutions of $\left(6-\frac{4Zr}{a_0}+\frac{4}{9}.\frac{Z^2r^2}{a_0^2}\right)=0$

$3p_z$ orbital has on radial nodal surface at $\left(4-\frac{4Zr}{3a_0}\right)$ = 0 & one angular node at $\theta = \pi/2$

for $3\ p_z$, at r = 0 $\psi = 0$ while for

3 s at r = 0 ψ = maximum so, 3s has greater penetrating power than $3p_z$ orbital

17. (a, b)

Since it obsorbes 'n' photons and also emits exactly n-photons therefore, transition must have taken place from 1 to 2.

$\therefore$ Energy of photon $=10.2\ Z^2$

where, Z = 1, 2, 3, 4.

18. (a, b, c)

Since B is in infrared region and A has more energy than B hence, it will have lesser wave length i.e., ultra violet, visible or infrared region.

21. (a – q, r), (b – p, s), (c – s), (d – q)

(a) B.E. of He^+ atom $= \frac{13.6\times 2^2}{n^2}$ n = 1, 2, 3 ……

Hence, it cane be 13.6 ev, 3.4ev both

(b) In $7 \rightarrow 3$ transition

$\Delta n = 7 - 3 = 4$

$\therefore$ Maximum number of spectral line observed $= \frac{4(4+1)}{2} = 10$

It is line of paschen series. Hence, infrared region

(c) $5 \rightarrow 1$ – 10 lines

(d) Series limit of Balmer series is the last line having 3.4 ev energy.

INTEGER ANSWER TYPE QUESTIONS

1. A hydrogen-like atom (atomic number Z) is in a higher excited state of quantum number n. This excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV respectively. Alternatively, the atom from the same excited state can make a transition to the second excited state by successively emitting two photons of energy 4.25 eV and 5.95 eV respectively. Determine the values of n and Z.

Sol. Total energy liberated during transition of electron from nth shell to first excite state (i.e., 2nd shell) = $10.20 + 17.0 = 27.20\text{eV} = 27.20 \times 1.602 \times 10^{-12}$ erg

$\because \quad \frac{hc}{\lambda} = R_H \times Z^2 hc\left[\frac{1}{2^2}-\frac{1}{n^2}\right]$

$\therefore \quad 27.20\times 1.602\times 10^{-12} = R_H \times Z^2 \times h \times c\left[\frac{1}{2^2}-\frac{1}{n^2}\right]$ ...(1)

Similarly, total energy liberated during transition of electron from *n*th shell to second excited state (i.e., 3rd shell)

$= 4.25 + 5.95 = 10.20$ eV

$= 10.20 \times 1.602 \times 10^{-12}$ erg

$\therefore \quad 10.20 \times 1.602 \times 10^{-12}$

$= R_H \times Z^2 \times h \times c\left[\frac{1}{3^2}-\frac{1}{n^2}\right]$ ...(2)

Dividing Eq. (1) by Eq. (2), **n = 6**

On substituting the value of n in Eqs. (1) or (2),

Z = 3

2. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He^+ spectrum?

Sol. For He^+, $\frac{1}{\lambda} = R_H \cdot Z^2\left[\frac{1}{2^2}-\frac{1}{4^2}\right]$

For H, $\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

Since λ is same

$\therefore \quad Z^2\left[\frac{1}{2^2}-\frac{1}{4^2}\right] = \left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

$\because \quad Z = 2$

$\therefore \quad \left[\frac{1}{1^2}-\frac{1}{2^2}\right] = \left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$

$\therefore \quad n_1 = \mathbf{1}$ and $n_2 = \mathbf{2}$

3. Find the quantum number 'n' corresponding to the excited state of He^+ ion. If on transition to the ground state that ion emits two photons in succession with wavelengths 108.5 and 30.4 nm.

Sol. Given, $\lambda_2 = 30.4 \times 10^{-7}$ cm

$\lambda_1 = 108.5 \times 10^{-7}$ cm

Let excited state of He^+ be n_2. It comes from n_2 to n_1 and then n_1 to 1 to emit two successive photon

$$\frac{1}{\lambda_2} = R_H . Z^2 \left[\frac{1}{1^2} - \frac{1}{n_1^2}\right]$$

$$\frac{1}{30.4 \times 10^{-7}} = 109678 \times 4 \left[\frac{1}{1^2} - \frac{1}{n_1^2}\right]$$

$\therefore \quad n_1 = 2$

Now for λ_1 : $n_1 = 2$ and n_2 : ?

$$\frac{1}{\lambda_1} = R_H Z^2 \left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{108.5 \times 10^{-7}} = 109678 \times 4 \left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$$

$\therefore \quad \mathbf{n_2 = 5}$

Thus, excited state for He is 5th orbit.

4. Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbital.

Sol. r_n for H = $r_1 \times n^2$

r_3 for H = $0.529 \times 9 \times 10^{-8}$ cm $\qquad (\because r_1 = 0.529 \text{ Å})$

Also, $\quad u_n = \frac{u_1}{n}$

$$\therefore \quad u_3 = \frac{2.19 \times 10^8}{3} \text{ cm sec}^{-1}$$

$(\because u_1 = 2.19 \times 10^8 \text{ cm sec}^{-1})$

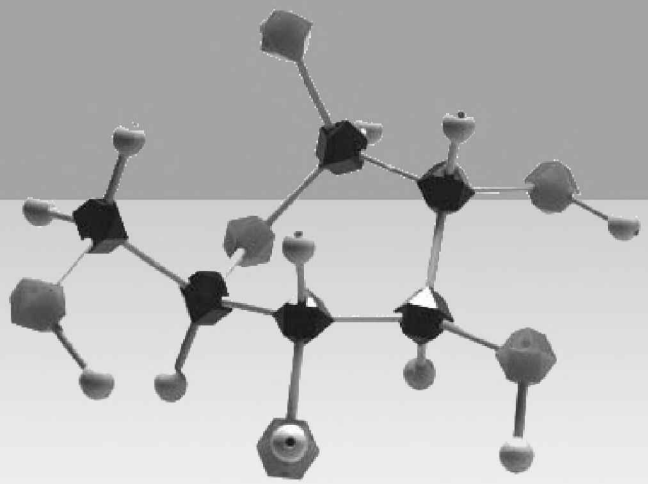
$\therefore$ No. of waves in one round

$$= \frac{2\pi r_3}{\lambda} = \frac{2\pi r_3}{h / m u_3}$$

$$= \frac{2\pi r_3 \times u_3 \times m}{h}$$

$$= \frac{2 \times 22 \times 0.529 \times 9 \times 10^{-8} \times 2.19 \times 10^8 \times 9.108 \times 10^{-28}}{7 \times 3 \times 6.62 \times 10^{-27}}$$

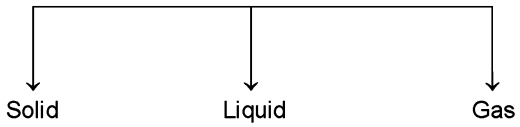
$\mathbf{= 3}$



CHAPTER 2

Gaseous State

Pure substance can exist mainly in three different phases:

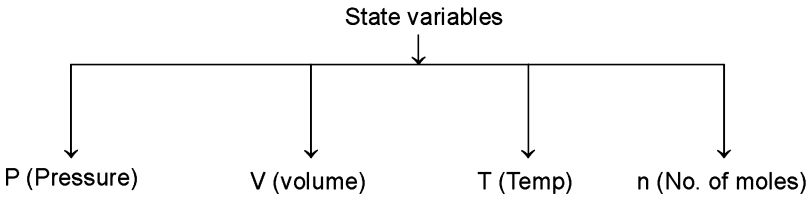


Most of the things around you are solids, substances whose constituent atoms, molecules, or ions are held rigidly together in a definite way, giving the solid a definit volume and shape. Other substances are liquids, whose constituent atoms or molecules are held together less strongly, giving the liquid a definite volume but a changeable and indefinite shape. Still other substances are gases, whose constituent atoms or molecules have little attraction for one another and are therefore free to move about in whatever volume is available.

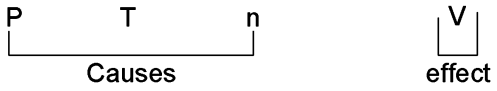
Though gases are few in number—only about a hundred substances are gases at room temperature—their study was enormously important in the historical development of chemical theories. We will look briefly at this historical development in this chapter, and we'll see how the behaviour of gases can be described.

Within the same phase the state (condition) can change.
For example, nitrogen gas can remain under one atmospheric pressure and two atmospheric pressure, its state will be different in different pressure condition but the phase will remain the same (gas).

Different parameters required to describe the state of a gas are called state variables.
There are four state variables:



There is one equation which can combine these four variables.
We know, that Number of equation = Number of dependent variable
Hence, any three of them can be independent variable the fourth one will become dependent variable.
(i.e., if three of them are assigned definite values, the fourth one will have a fixed valu



RESPONSE OF VOLUME TOWARDS STATE VARIABLES

Gas Laws

Boyle's Law: Boyle's law states that at constant temperature, the volume of a definite mass of gas is inversely proportional to the pressure of gas.

$V \propto \frac{1}{P}$. When n and T are constant

Or $PV = K$ (constant)

Or $P_1V_1 = P_2V_2 = P_2V_3$ etc

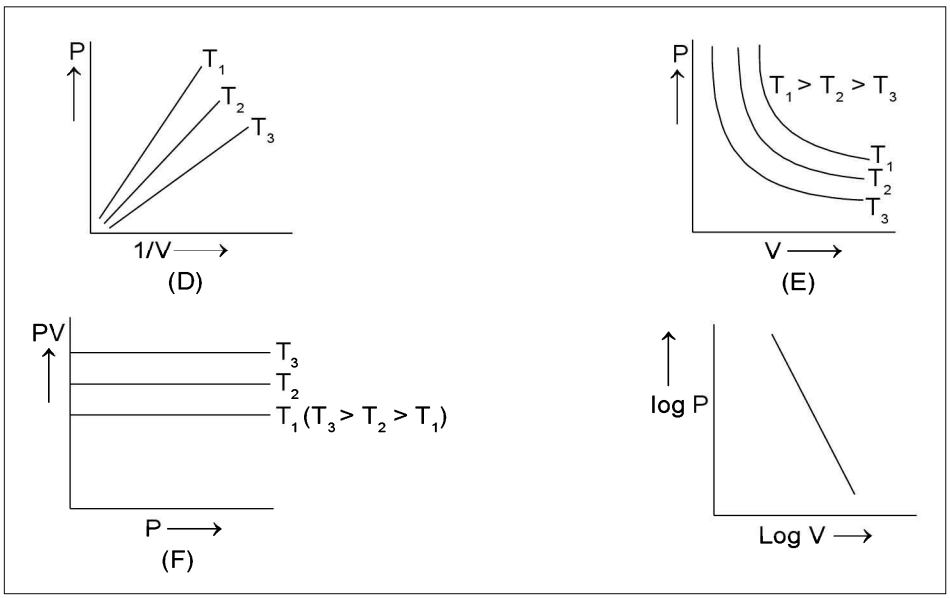


Fig. 2.1

Plots showing variation in pressure with volume at constant temperature. These plots of pressure volume of constant temperature for a given gas are known as isotherms.

Charles Law

The law states that at constant pressure, the volume of a definit mass of a gas is directly proportional to its absolute temperature.

$V \propto T$, when n and P are constant

or $\frac{V}{T} = \text{constant}$

$\therefore \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3}$

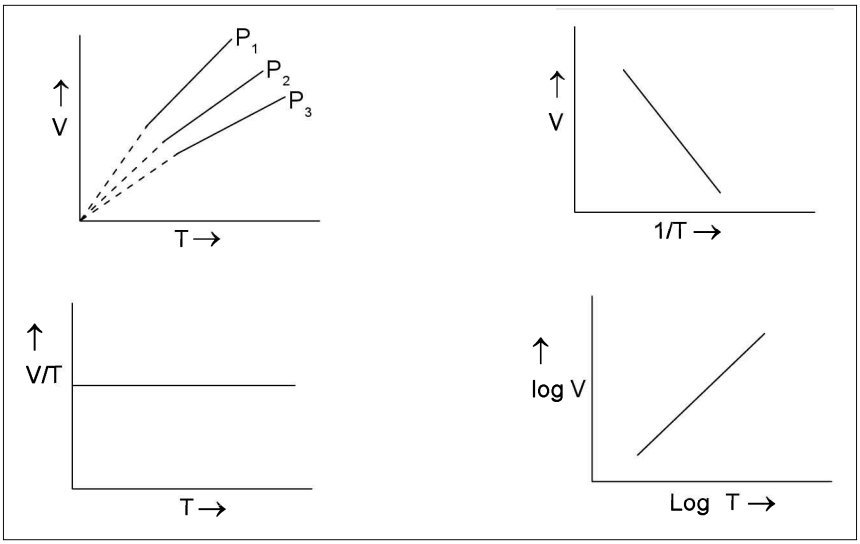


Fig. 2.2 (a) Plots showing variation of volume with temperature at constant pressure

Fig. 2.2 (b) Plots between V and T at constant pressure are known as isobars.

Charle's–Gay-Lussac Law

In 1787, Jacques Charles and in 1808 Gay Lussac discovered that if the pressure is kept constant, the volume of a gas sample increases linearly with the temperature for a fixed amount of gas. This law led to the idea of temperature. The unit of temperature used is Kelvin.

$T(K) = T(^\circ C) + 273. \qquad \therefore V \propto T$ (P and n are constant)

or $\frac{V}{T} = \text{Constant}$

Avogadro's Law

In 1812, Amadeo Avogadro stated that samples of different gases which contain the same number of molecules (any complexity, size, shape) occupy the same volume at the same temperature and pressure. It follows from Avogadro's hypothesis that $V \propto n$ (when T and P are constant).

Ideal Gas Equation

These three laws can be combined as,

$$V \propto \frac{nT}{P} \text{ or } PV = nRT$$

where R is the constant of proportionality called molar gas constant. As the value of R does not depend upon the nature of the gas its value is constant for all gases and hence called universal gas constant.

The above equation is known as ideal gas equation and gases which obey this equation are called ideal gases and the gases which do not obey this equation are called real gases. Unfortunately, no gases are known which obey this equation at all temperatures and pressure.

Dimension of molar gas constant R

$$PV = nRT;\ R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{No. of moles} \times \text{Temp in K}}$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{length})^2};\ V = (\text{length})^3$$

$$R = \frac{\frac{\text{Force}}{(\text{length})^2} \times (\text{length})^3}{\text{No. of moles} \times \text{Temp. in K}} = \frac{\text{Force} \times \text{length}}{\text{No. of moles} \times \text{Temp.}}$$

R = Work done per K per mole

Case I

Unit of R

P $\Rightarrow$ atm

V $\Rightarrow$ litre

T $\Rightarrow$ K

$R = \frac{PV}{nT} \Rightarrow$ lit atm mol^{-1} k^{-1}

R = 0.0821 L atm mol^{-1} K^{-1}

Another unit of R = feet pound K^{-1} pound mol^{-1}

Case II

S.I Unit

$P = N/m^2 \Rightarrow Pa$

$V = m^3$

T = K

$$R \Rightarrow \frac{PV}{nT} \Rightarrow \frac{(N/m^2)(m^3)}{nK} \Rightarrow (Nm)\ mol^{-1}\ K^{-1}$$

$\Rightarrow J\ mol^{-1}\ K^{-1}$

$R = 8.314\ J\ mol^{-1}\ K^{-1}$

$= 1.987\ Cal\ mol^{-1}\ K^{-1}$

Case III

CGS unit

$P \Rightarrow$ dyme cm^{-2} $\quad R \approx 2\ cal\ mol^{-1}\ K^{-1}$

$V \Rightarrow cm^3 = cc = ml$

T $\Rightarrow$ K

$$R \Rightarrow \frac{PV}{nT} \Rightarrow \frac{(dyne/cm^2)(cm^3)}{mol\ K}$$

dyne cm = erg

$\Rightarrow$ (dyne cm) mol^{-1} K^{-1}

$\Rightarrow 8.314 \times 10^7$

$\Rightarrow$ erg mol^{-1} K^{-1}

Unit of Pressure

1 atm = 760 mmHg = 76 cm Hg = 760 torr

= 101.325 K Pa = 101.325 × 10^3 Pa

= 1.01 × 10^5 Pa

1 atm ≈ 10^5 Pa

1 bar = 100 K Pa

1 atm ≈ 1 bar

1 atm is slight greater than 1 bar.

1 dyne cm^{-2} = 10^{-5} N cm^{-2}

= 10^{-5} × 10^4 N m^{-2}

= 10^{-1} Pa

1 dyne cm^{-2} = 0.1 Pa

cm^{-2} = 10^4 m^{-2}

$1m^2$ = $(100\ cm)^2$

= 10^4 cm^2

Unit of Volume

1 litre = 1 dm^3

$1\ m^3$ = 10^3 litre

= 10^6 ml

1 dn = 10 cm

1 dn^3 = 10^3 cm^3

1 dn^3 = 1000 cm^3

= 1000 cc

1 L = 1000 ml



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry



Worked-out Examples

1. 2 moles of He gas can exert 'x' N m^{-2} pressure at 27°C in a container of $1m^3$ volume. Calculate x.

Solution PV = nRT

$$P = \frac{nRT}{V} = \frac{2 \times (8.314\ J\,mol^{-1}K^{-1})300K}{1m^3}$$

$$= (8.134 \times 2 \times 300)\ (Nm)\ (m^{-3})$$

$$= (8.134 \times 2 \times 600)\ Nm^{-2}$$

$$= \frac{2 \times 8.134 \times 3.00}{10^5}\ atm = 49.88\ atm$$

$1m^3$ = 10^3 L = V P ⇒ atm

T = 300 K

$$P = \frac{nRT}{V} = \frac{2 \times (0.0821 L\,atm\,mol^{-1}\,K^{-1})(300K)}{10^3 L} = 49.26\ atm$$

PV = nRT $n = \frac{W}{M}$ Total mass in 'g' molar mass (unitless).

$PV = \frac{W}{M}RT$ ↓ g mol^{-1} mass of 1 mole

% atomic mass

$$\frac{W}{V} = \frac{PM}{RT} = d \qquad d(\text{density}) = \frac{\text{Mass}}{\text{Volume}}$$

$$d = \frac{PM}{RT} = \frac{P(\text{atm}) \times M(\text{g mol}^{-1})}{R(\text{lit atm mol}^{-1}\text{K}^{-1})T(\text{K}^{+})} = \text{g/L}$$

Hence density increases proportionally with pressure and varies inversely with temperature.

2. For an ideal gas, number of moles per litre in terms of its pressure P, gas constant R and temperature T is: **[AIEEE-2002]**

(a) PT/R (b) PRT

(c) P/RT (d) RT/P

Solution (c) $\frac{n}{V} = \frac{P}{RT}$

3. If the temperature of a gas is increased by 10% what will be the % decrease in density? (under constant pressure)

Solution $d_1 = \frac{PM}{RT_1} \quad T_1 = x$

$$d_2 = \frac{PM}{RT_2} \quad T_2 = \frac{110}{100}x \quad ? \quad \frac{d_1}{d_2} = \frac{T_2}{T_1} = \frac{11}{10} \quad \Rightarrow \% \text{ decrease in density} = \frac{(d_1 - d_2) \times 100}{d_1}$$

$$\Rightarrow \quad \left(1 - \frac{10}{11}\right) \times 100 = \frac{100}{11} = 9.09\,\%$$

4. Calculate density of CO_2 under 10^4 Pa of pressure at 27°C. Molar Mass = 44

Solution $d = \frac{PM}{RT} \quad P = 0.1 \text{ atm} \qquad T = 300 \text{ K}$

$$= \frac{0.1 \times 44}{0.0821 \times 300} = \frac{440000}{821 \times 3000} = \frac{440}{2463} = 0.2 \text{ g/L}$$

5. The density of neon will be highest at **[IIT-1990]**

(a) S.T.P. (b) 0°C, 2 atm

(c) 273°C, 1 atm (d) 273°C, 2 atm

Solution (b) Since $V_m \propto (nT/p)$, hence at 0°C and 2 atm neon would produce the least molar volume and thus the highest density.

6. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of N_2O_4 (g) decomposes to NO_2 (g).The resultant pressure is: **[IIT-1996]**

(a) 1.2 atm (b) 2.4 atm

(c) 2.0 atm (d) 1.0 atm

Solution (b)

According to ideal gas equation, at two conditions

At 300 K $\quad P_0V = n_0RT_0$

$$1 \times V = 1.08 \times R \times 300 \qquad \ldots \text{(i)}$$

At 600 K $\quad P_1V = n_1RT_1$

$$P_1 \times V = (0.86 + 0.43) \times R \times 600 \qquad \ldots \text{(ii)}$$

Divide (ii) by (i)

$$\frac{P_1}{1} = \frac{1.29 \times 600}{1.08 \times 300};\ P_1 = \frac{1.29 \times 2}{1.08} = 2.38 \text{ atm.}$$

	N_2O_4	$\rightleftharpoons$	$2NO_2(g)$
At start	100/92 mol		0
	=1.08 mol		
At equilibrium	80/92 mol		20/46 mol
	= 0.86		= 0.43 mol

7. A gas will approach ideal behaviour at **[IIT-1999]**

(a) low temperature and low pressure
(b) low temperature and high pressure
(c) high temperature and low pressure
(d) high temperature and high pressure

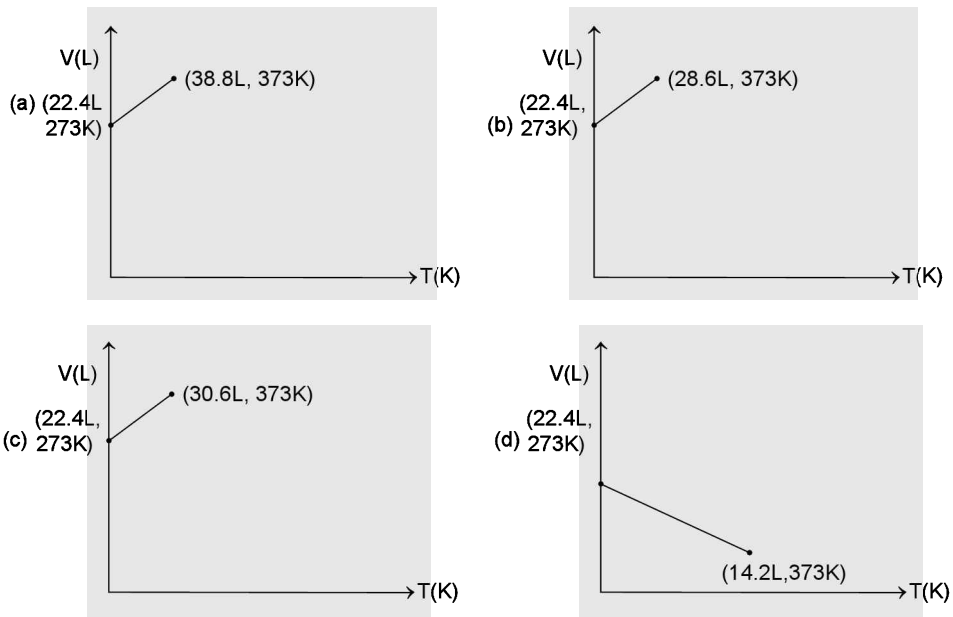
Solution (c) For an ideal-gas behaviour, the molecules of a gas should be far apart. The factors favouring this condition are high temperature and low pressure.

8. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at that temperature is **[IIT-2000]**

(a) 6 cm^3 (b) 60cm^3
(c) 0.6 cm^3 (d) 0.06 cm^3 **[IIT-2000]**

Solution (c) Mass of 1 L water vapour = 0.6 g, V = m/d=0.6g/1.0gcm^{-3}=0.6 cm^3

9. Which of the following volume (V)-temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure? **[IIT-2002]**



Solution (c) Volume of 1 mole of an ideal gas at 273 K and 1 atm is 22.4 Land that at 373 K and 1 atm pressure is calculated as; V = RT/P = 0.082 × 373/1 = 30.58 L

10. The value of PV for 5.6 litres of an ideal gas is..... RT, at N.T.P. **[IIT-1987]**

Solution $0.25; \left(\because 5.6/ \equiv \frac{1}{4} \text{mol of an ideal gas} \right)$

11. A mixture of ideal gases is cooled upto liquid helium temperature (4.22 K) to form an ideal solution. (True/False) **[IIT-1996]**

Solution False: An ideal gas cannot be liquefied as there exists no intermolecular attraction between molecules.

Standard States

N.T.P	S.T.P
Normal Temp.	Standard temperature
and Pressure	and Pressure
P = 1 atm	P = 1 bar
T = O°C	T = O°C = 273K

SATP

Standard Ambient Temperature and Pressure

T = 25°C = 298 K; P = 1 bar

Actual density

For an ideal gas, PV = nRT or PV = $\frac{w}{M}RT$, where w = mass of the gas in gms. and M = Molecular wt. in g/mole.

$\therefore$ $PM = \frac{w}{V} RT$ or $PM = \rho RT$, where ρ is the density of the gas.

$\therefore$ $\rho = \frac{PM}{RT}$

Vapour Density

For gases another term which is often used is vapour-density. Vapour density of a gas is defined as the ratio of the mass of the gas occupying a certain volume at a certain temperature and pressure to the mass of hydrogen occupying the same volume at the same temperature and pressure i.e.,

$$W(gas) = \frac{PVM}{RT}$$

and $W_{H_2} = \frac{PV \times 2}{RT}$ ($\because$ mol. wt.of Hydrogen is 2)

$\therefore$ $\frac{W_{gas}}{W_{H_2}} = \frac{M}{2}$ = Vapour density of gas

Vapour density of a gas is same at any temperature, pressure and volume.

Molar Volume $\overline{V}_m$

It is the volume occupied by 1 mole of a gas.

$$PV = nRT$$

V = Volume of 'n' moles

$$\overline{V}_m = \frac{V}{n} = \text{molar volume}$$

$$PV = nRT \Rightarrow P\left(\frac{V}{n}\right) = RT$$

$$P(\overline{V}_m) = RT$$

$$\overline{V}_m = \frac{RT}{P}$$

$$\overline{V}_m = \frac{RT}{P}.$$

Hence the molar volume of a gas will be constant under constant temperature and pressure.
But density will be different under constant temperature and pressure (because of different molar mass).



Worked-out Example

12. Calculate molar volume under NTP.

Solution P = 1 atm

T = 273 K

$$\overline{V}_m = \frac{RT}{P} = \frac{(0.0821 \text{lit atm Mol}^{-1}\ \text{K}^{-1})(273\text{K})}{1\text{atm}} = 22.414 \text{ lit mol}^{-1}$$

Molar Volume of all Gases at NTP = 22.4 Lit

Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP)* will have same volume. Standard temperature and pressure means 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol^{-1}

Standard Ambient Temperature and Pressure

(SATP), Conditions are also used in some scientific works. SAT conditions means 298.15 K and 1 bar (i.e., exactly 10^5 Pa). At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol^{-1}.

Density of Gas

$$d = \frac{PM}{RT} = \frac{M}{\left(\frac{RT}{P}\right)} = \frac{M}{\overline{V}_m}$$

$$\text{density} = \frac{\text{Molar Mass}}{\text{Molar volume}}$$

*The previous standard is still often used, and applies to all chemistry data more than a decade old. In this definition, STP denotes the same temperature of 0°C (273.15 K), but a slightly higher pressure of 1 atm (101.325 kPa). One mole of any gas of a combination of gases occupies 22.413996 L of volume at STP.

Worked-out Examples

13. Calculate density of CH_4 (Molar mass = 16) at NTP.

Solution $d = \frac{M}{\overline{V}_m} \quad \frac{PM}{RT} = \frac{1\times16}{0.0821\times273} = \frac{160}{224} = 0.71\,g/l$

14. An iron cylinder contains helium at a pressure of 250 k Pa at 300 K. The cylinder can withstand a pressure of 10^5 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts. MP = 1800 K.

Solution V = Constants

n = Constant Then, $P \propto T$

$$\frac{P_1}{P_2} = \frac{T_1}{T_2} \Rightarrow \frac{250\,K\,Pa}{10^3\,KPa} = \frac{300\,K}{T_2(K)}$$

$$T_2 = 1200\ K$$

Thus, cylinder will blow up.

15. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at STP from a cylinder containing the gas at 20 atm and 27°C. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up.

Solution We must understand first that the gas in the cylinder is at 20 atm and 27°C while its filling in the balloons requires STP conditions. If we calculate the volume of the gas at STP, it comes out to be,

$$V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} = \frac{20\times2.82}{300}\times\frac{273}{1}$$

$$V_2 = 51.324\ L$$

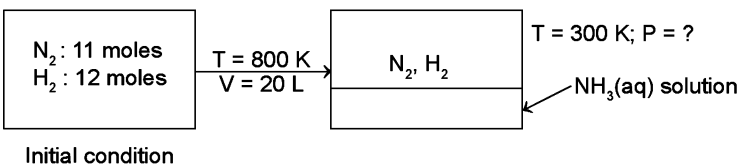
This means as we fill the gas at STP, the volume of the gas expands to 51.324 L. It is this expansion that leads to filling of the gas in balloons. But since the cylinder's volume is 2.82 L, this much gas would be inside the cylinder while the rest of the volume escapes out, filling the balloons Therefore the volume that is actually filled,

$$= (51.324 - 2.82)\ L = 48.504\ L$$

$$\text{Volume of one balloon} = \frac{4}{3}\pi r^3 = \frac{4}{3}\times\frac{22}{7}\times\left(\frac{21}{2}\right)^3 = 4.8504\ L$$

$\therefore$ **Number of balloons filled up** $= \frac{48.504}{4.851} = 10$

16. 11 moles N_2 and 12 moles of H_2 mixture reacted in 20 litre vessel at 800 K. After equilibrium was reached, 6 mole of H_2 was present. 3.58 litre of liquid water is injected in equilibrium mixture and resultant gaseous mixture suddenly cooled to 300K. What is the final pressure of gaseous mixture? Negative vapour pressure of liquid solution. Assume (i) all NH_3 dissolved in water (ii) no change in volume of liquid (iii) no reaction of N_2 and H_2 at 300 K



(a) 18.47 atm (b) 60 atm
(c) 22.5 atm (d) 45 atm

Solution (c) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Initial moles 11 12 0

at equilibrium 9 6 4

moles of N_2 and H_2 present at equilibrium = 15

after addition of water

$NH_3(g) + H_2O(l) \longrightarrow NH_4OH(l)$

Volume of vessel available for gaseous mixture of N_2 and H_2 = 20 – 3.58 $\Rightarrow$ 16.42 L

Pressure exerted by gaseous mixture at 300 K = $\frac{15 \times 0.821 \times 300}{16.42} \Rightarrow 22.5$ atm

17. 3.2g S is heated if occupy a volume of 780 ml at 450°C and 723 mm pressure. Formula of sulphur is

(a) S_2 (b) S
(c) S_4 (d) S_8

Solution (d) $PV = \frac{w}{M}RT$ given $P = \frac{723}{760}$atm , $V = \frac{780}{1000}$ lit

$$\frac{723}{760} \times \frac{780}{1000} = \frac{3.2}{M} \times 0.0821 \times 683$$

$$M = 256$$

$\therefore$ atomicity = $\frac{256}{32} = 8$

18. Two closed vessel A and B of equal volume containing air at pressure P_1 and temperature T_1 are connected to each other through a narrow open tube. If the temperature of one is now maintained at T_1 and other at T_2 (where $T_1 > T_2$) then that what will be the final pressure?

(a) $\frac{T_1}{2P_1T_2}$ (b) $\frac{2P_1T_2}{T_1 + T_2}$

(c) $\frac{2P_1T_1}{T_1 - T_2}$ (d) $\frac{2P_1}{T_1 + T_2}$

Solution (b) Let $T_1 > T_2$; final pressure will be same in both container, but different from the initial pressure which was same in both container. Initial pressure in both container = P_1 given. Let final pressure in both container = P_A. Let x mole transfer from A to B vessel.

$\therefore$ $P_AV = (n - x)RT_1$ 1

and $P_AV = (n + x)RT_2$ 2

By Eq. 1 and 2

$\therefore$ $x = \frac{n(T_1 - T_2)}{T_1 + T_2}$; $V = \frac{nRT_1}{P_1}$

Put the value of x and b in equation 1

$\therefore$ $P_A \times \frac{nRT_1}{P_1} = \left(n - \frac{n(T_1 - T_2)}{(T_1 + T_2)}\right)RT_1$ $P_A = \frac{2P_1T_2}{T_1 + T_2}$

Hydrostatic pressure

- Open end manometer: It consists of a U-shaped glass tube partially filled with non-volatile liquid generally mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel which contains the gas and the longer limb is open. The mercury in the longer limb is subjected to the atmospheric pressure while in the shorter limb to the pressure of the gas.

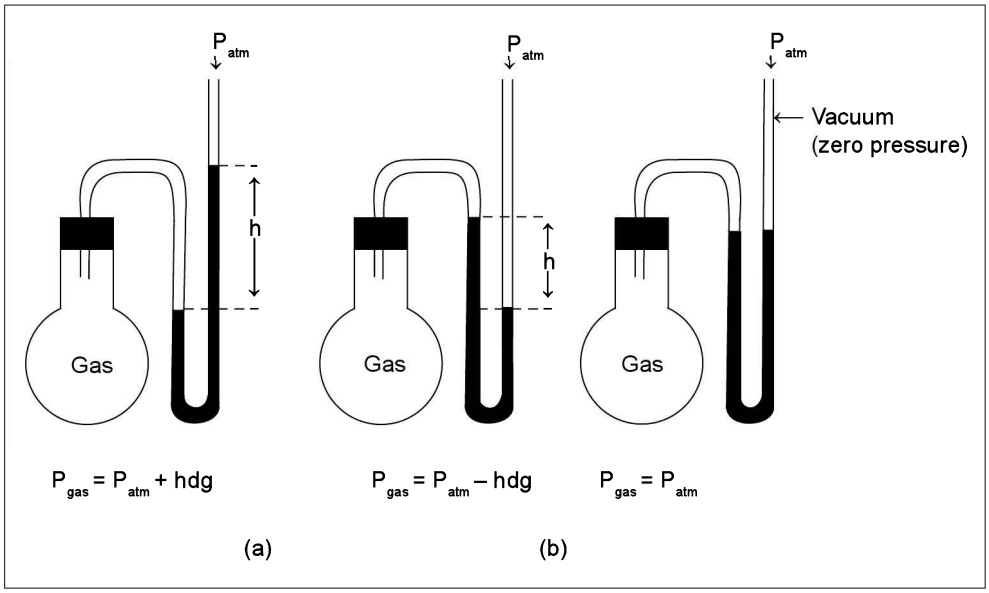


Fig. 2.3

There are three possibilities:

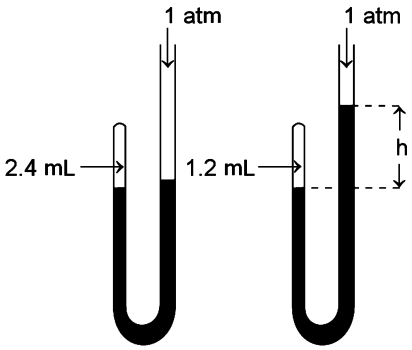
(i) If Hg level in the two limbs is the same, then
Gas pressure = Atmospheric pressure (Pa)

(ii) If Hg level in the longer tube is higher
Gas pressure = Pa + h (difference between the two levels)

(iii) If Hg level in the shorter tube is higher
Gas pressure = Pa – h (difference between the two levels)

Worked-out Example

19. By taking two J-tubes at constant temperature what is the difference in the levels of mercury in two columns?



Solution It is the case of Boyle's law when temperature is constant.

Initially $P_1 = 1 \text{ atm} = 760 \text{ mm}$

$V_1 = 2.4 \text{ mL}$

Finally $P_2 = ((760 + h) \text{ mm}$

$V_2 = 1.2 \text{ mL}$

By Boyle's law $P_1V_1 = P_2V_2$

$760 \times 2.4 = (760 + h)\ 1.2$

$\therefore$ $h = 760 \text{ mm}$

Dalton's Law of Partial Pressure

Just as the gas laws apply to all pure gases, regardless of chemical identity, they also apply to mixtures of gases, such as air. The pressure, volume, temperature, and amount of a gas mixture are all related by the ideal gas law.

What is responsible for the pressure in a gas mixture? Since the pressure of a pure gas at constant temperature and volume is proportional to its amount (P = nRT/V), the pressure contribution from each individual gas in a mixture must also be proportional to its amount in the mixture. In other words, the total pressure exerted by a mixture of gases in a container at constant V and T is equal to the sum of the pressures each individual gas in the container would exert alone, a statement known as **Dalton's law of partial pressures.**

Dalton's Law of Partial Pressures

$$P_{total} = P_1 + P_2 + P_3 + \ldots\ldots \text{ At constant V and T}$$

The individual pressures of the various gases in the mixture, P_1 P_2, and so on, are called partial pressures and refer to the pressure of each individual gas would exert if it were alone in the container. That is why, It is applicable to non-reacting gases.

Let us consider gaseous mixture of A and B in close container

$$P_TV = n_TRT$$

Here, P_T = total pressure and n_T= total number of moles

$$P_TV = (n_A + n_B)\ RT \qquad \ldots. 1$$

Case I

The gas (B) is taken out entirely from the mixture. So gas A is left and it will occupy the whole volume of container.

$$P_AV = n_A\ RT \qquad \ldots.2$$

(P_A = Partial pressure of gas A)

Partial Pressure → It is defined for each gas present in a mixture of gases. It is the pressure, the component (the particular gas) can exert when it is allowed to occupy the entire volume of gas mixture alone in the container.

Case II

The gas A is taken out and B is present in container

$$P_BV = n_BRT \qquad \ldots..3$$

(P_B = Partial pressure of gas B)

Adding equation (2) and (3)

$$P_A V + P_B V = n_A RT + n_B RT$$

$$(P_A + P_B)\, V = (n_A + n_B)\, RT \quad \ldots.4$$

Comparing 1 and 4

$$P_T = P_A + P_B$$

Total Pressure = sum of partial pressures of different gases.

$$P_T = \Sigma P_i$$

Sum of partial pressures of all components

Dividing (2) by (1) Dividing (3) by (1)

$$\frac{P_A}{P_T} = \frac{(n_A)}{(n_A + n_B)} = X_A \quad \frac{P_B}{P_T} = \frac{n_B}{n_A + n_B} = X_B$$

Mole fraction

components: A B

no.of moles: ↓ ↓

n_A n_B

X_A = mole fraction of A

$$X_A = \frac{\text{no. of moles of A}}{\text{Total no. of moles}} \Rightarrow \frac{n_A}{n_A + n_B}$$

$$X_B = \frac{n_B}{n_A + n_B} \qquad X_A + X_B = 1$$

Sum of mole fraction of all components in the mixture is unity.

$$P_A = P_T X_A$$

$$P_B = P_T X_B$$

$$P_i = P_T X_i$$

$$\Sigma P_i = \Sigma P_T X_i$$

$$= P \Sigma X_i$$

$$\Sigma P_i = P_T \qquad \Sigma X_i = 1$$

Now Dividing (2) by (3) $\frac{P_A}{P_B} = \frac{n_A}{n_B}$

Hence the ratio of partial pressure will be the ratio of number of moles.

Vapour Pressure

It is the pressure exerted by a vapour when the vapour is in equilibrium with its liquid.

The magnitude depends (1) on the nature of the liquid and (2) on its temperature. (It is not proportional to temperature but increases with temperature. The exact variation will be given in the chapter "liquid solution and colligative properties").

The vapour pressure does not change with volume or any other parameter.

The pressure of a moist gas can be expressed as follows:

$$P_{moist} = P_{dry} + P_{vapour\ pressure}$$

The vapour pressure is constant for a given liquid at constant temperature.

Note that:

1. The pressure of dry gas only changes with volume according to Boyle's Law.
2. The gas collected by the displacement of water is always a moist gas.

Relative Humidity

Relative humidity (RH) at a given temperature is given by:

$$RH = \frac{\text{partial presure of water in air}}{\text{vapour pressure of water}}$$



Worked-out Examples

20. On a humid day in summer, the mole fraction of gaseous H_2O (water vapour) in the air at 25°C can be as high as 0.0287. Assuming a total pressure of 0.977 atm, what is the partial pressure of H_2O vapours in the air? What is partial pressure of dry air?

Solution $P_{H_2O} = X_{H_2O} P_{Total}$

$= 0.0287 \times 0.977 = 0.028$ atm

Also $P_{Total} = P_{dry\ air} = P_{H_2O}$

$\therefore$ $P_{dry\ air} = P_{Total} - P_{H_2O} = 0.977 - 0.028 = 0.949$ atm

21. At a temperature of 20°C, vapour pressure of water is 17.5 Torr. If relative humidty is 45%, calculate the moles of water present is, one litre of air at 20°C.

Solution Relative humidity $= \frac{\text{partial pressure of } H_2O \text{ in air}}{\text{vapour pressure of } H_2O}$

$$0.45 = \frac{p_{H_2O}}{17.5}$$

$\therefore$ $P_{H_2O} = 0.45 \times 17.5 = 7.88$ Torr $= 0.0104$ atm

Since, $PV = nRT$

$\therefore$ $n = \frac{PV}{RT} = \frac{0.0104 \times 1}{0.0821 \times 293} = 4.3 \times 10^{-4}$ mol

22. Assume that air contains 79% N_2 and 21% O_2 by volume. Calculate the density of moist air at 25°C and 1 atm pressure when relative humidity is 60%. The vapour pressure of water at 25°C is 23.78 mm of Hg. Relative humidity is given by percentage relative humidity

$$= \frac{\text{Partial pressure of water}}{\text{vapour pressure of water at that temperature}} \times 100$$

Solution First of all it is important to understand the distinction between vapour pressure and partial pressure of vapour.

When a liquid is in equilibrium with its vapours, the vapours exert a pressure on the surface of the liquid called vapour pressure. This is the maximum possible pressure exerted by the vapours of the liquid at that tempreature. If we assume that vapours of a liquid exist in a container without the liquid, then the vapours behave just like any other gas, obeying all the gas laws. The pressure exerted by the vapours now can be anything which is less than or equal to that of vapour pressure. This is called partial pressure of vapour. If the partial pressure somehow becomes more than vapour pressure, the vapours start liquefying to form liquid till vapours would be in equilibrium with liquid, exerting the vapour pressure.

To this problem let us look at what we are supposed to calculate. We need to find the density of moist air. From the ideal gas equation,

$$PV = \frac{w}{M}RT$$

$$\Rightarrow \quad \rho = \frac{w}{V} = \frac{PM}{RT}$$

Therefore, we need to find the molecular weight of moist air. To find the molecular weight of a mixture of gas, we need the molar composition or mole fraction of the gas mixture.

$$\text{Partial pressure of water (vapour)} = \frac{60}{100} \times \frac{23.78}{760} = 0.0187 \text{ atm.}$$

$$\therefore \quad \text{mole fraction of water vapour} = \frac{0.0187}{1} = 0.0187$$

$$\text{Pressure of } (N_2+O_2) = (1-0.0187) \text{ atm} = 0.9813 \text{ atm}$$

Let the pressure of N_2 be 79 x, then pressure of O_2 is 21 x (they are in that molar ratio)

$$\therefore \quad 79x + 21x = 0.9813 \text{ atm}$$

$$x = \frac{0.9813}{100}$$

$$x = 0.009813 \text{ atm}$$

$$\therefore \quad p_{N_2} = 79x = 0.7752 \text{ atm}$$

$$\therefore \quad p_{O_2} = 0.2061 \text{ atm.}$$

$$\text{Mole fraction of } N_2 = \frac{0.7752}{1} = 0.7752$$

$$\text{Mole fraction of } O_2 = \frac{0.2061}{1} = 0.2061$$

$\therefore$ Effective molecular weight of moist air

$$= (0.0187 \times 18) + (0.7752 \times 28) + (0.2061 \times 32) = 28.63 \text{ g/mol}$$

$$\therefore \quad \rho = \frac{1 \times 28.63}{0.082 \times 298}$$

$$= \mathbf{1.1716 \text{ g/L}}$$

Average Molar Mass

Molecular wt. of a gas mixture or effective molecular weight: Suppose we have to find the molecular weight of air and we are told that air contains 79% nitrogen and 21% oxygen (by mole or volume).



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

First of all, let us understand what is meant by molecular wt. of a gas. Molecular wt. of a gas is the weight in gms of one mole of the gas (hence the unit gm/mole). Now if we take one mole of air it would contain 79/100 moles of Nitrogen and 21/100 moles of oxygen. The weight of one mole of air would be $0.79 \times 28 + 0.21 \times 2 = 22.54$ gm/mole.

$$\therefore \quad M_{effective} = \Sigma X_i M_i = \Sigma \text{ mole fraction of a gas } \times \text{ mol. wt. of a gas.}$$

$$X_i \text{ (Mole fraction) of a gas is } = \frac{n_i}{\Sigma n_i} = \frac{\text{moles of a gas}}{\text{Total moles of gas}}$$



Worked-out Examples

23. The average molar mass of a mixture of N_2 and O_2 is 29. Calculate
(a) molar % of N_2 (b) mass % of N_2

Solution $N_2 \rightarrow x\%$ (molar percentage)

$O_2 \rightarrow (100–x)$ % (molar percentage)

$$M_{av} = 29 = \frac{n_{N_2} \times 28 + n_{O_2} \times 32}{n_{N_2} + n_{O_2}}$$

$$29 = \frac{x \times 28 + (100 - x)32}{100}$$

$$2900 = 28x + 3200 - 32x$$

$$x = 75\%$$

$$N_2 = 75\% \; O_2 = 25\%$$

$$\frac{W_{N_2}}{W_{O_2}} = \frac{n_{N_2} \times 28}{n_{O_2} \times 32} = \frac{75 \times 28}{25 \times 32} = \frac{21}{8}$$

$$\text{Mass\% of } N_2 = \left(\frac{W_{n_2}}{W_{n_2} + W_{O_2}}\right) \times 100 = \frac{21}{21+8} \times 100\% = \frac{21}{29} \times 100 = 72.4\%.$$

$$d_{mix} = \frac{P_T M_{av}}{RT}; \; M_{av} = \frac{d_{mix} RT}{P_T} = d_{mix} \, \overline{V}_m$$

24. A mixture of N_2 and O_2 has density 1.3 g/L under S.T.P. Calculate molar % and mass % of O_2.

Solution $M_{av} = d \times \overline{V}_m = 1.3 \times 22.4 = 29.12$ g

$$M_{av} = \frac{n_{N_2} \times 28 + n_{O_2} \times 32}{n_{N_2} + n_{O_2}}$$

$$n_{N_2} + n_{O_2} = 100; \; n_{N_2} = x; \; n_{o_2} = (100 - x)$$

$$2912 = x \times 28 + 3200 - 32x$$

$$288 = 4x$$

$$x = 72\% \leftarrow N_2$$

$$O_2 \rightarrow 28\%$$

$$\frac{W_{n_2}}{W_{o_2}} = \frac{72 \times 28}{28 \times 32} = 2.25 = \frac{9}{4}$$

$$\text{Mass \% of } O_2 = \frac{W_{o_2}}{W_{n_2} + W_{o_2}} \times 100 = \frac{4}{13} \times 100 = \frac{400}{13} = 30.7\%$$

25. Inside the spherical glass flask A of radius 1 m containing 300 g of H_2, there was a rubber balloon B containing some N_2. Inside the balloon B was another rubber balloon C containing some O_2. At 27°C it was found that the balloon B had a radius of 60 cm and balloon C had a radius of 30 cm. Calculate total weight of gases inside the flask. If another 50 g of H_2 was not introduced in flask A, what would be the volume of B and C. If the flask is now dipped in a bath containing acetone and dry ice (–78°C) for sufficient time the temperature of the entire contents would react with the bath temperature. Assuming that at this temperature rubber cracks up and both the balloons burst, what would be pressure inside flask

Solution Volume of flask A $= \frac{4}{3}\pi(1)^3 = \frac{4}{3}\pi$

$$\text{Volume of balloon B} = \frac{4}{3}\pi\left(\frac{60}{100}\right)^3 = 0.216 \times \frac{4}{3}\pi$$

$$\text{Volume occupied by } H_2 \text{ in A} = \frac{4}{3}\pi - \frac{4}{3} \times 0.216\pi$$

$$= 3.284 \text{ m}^3 = 3284 \text{ lit}$$

$$\text{Pressure in A} = \frac{150 \times 0.082 \times 300}{3284} = 1.123 \text{ atm}$$

$$\text{Pressure in B} = 1.123 \text{ atm}$$

$$\text{Volume of } N_2 \text{ in B} = \frac{4}{3}\pi\left(\frac{60}{100}\right)^3 - \frac{4}{3}\pi\left(\frac{30}{100}\right)^3$$

$$= 0.7917 \text{ m}^3 = 791.7 \text{ lit}$$

$$\text{Moles of } N_2 = \frac{1.123 \times 791.7}{0.082 \times 300} = 36.14$$

$$\text{Mass of } N_2 = (36.14 \times 28) = 1011.92\text{g}$$

$$\text{Mass of } O_2 \text{ in C} = \frac{1.123 \times 113.09 \times 32}{0.082 \times 300} = 165.12\text{g}$$

Total weight of all the gases (165.2 + 300 + 1011.92)g = 1477.12g

Total pressure inside the flask of –78°C after the balloon cracks u

$$= \frac{(150 + 36.14 + 5.16) \times 0.082 \times 195}{\frac{4}{3}\pi \times 1000} = \mathbf{0.73 \text{ atm}}$$

26. The pressure of a moist gas at 27°C is 2 atm. The volume of the container is doubled at the same temperature. The new pressure of the moist gas (Given vapour pressure of water at 27°C = 0.2 atm)

(a) 1 atm (b) 0.9 atm

(c) 1.2 atm (d) 1.1 atm

Solution (d) $P_{moist} = p_{dry} + P^{\circ}_{H_2O}$ $2atm = P_{dry} + 0.2$ atm

$\Rightarrow P_{dry} = 1.8$ atm

Final pressure of dry gas = $P'_{dry} = 0.9$ atm

(volume is doubled hence pressure of dry gas will be half)

$P^{\circ}_{H_2O} = 0.2$ atm (Does not change with volume only changes with temperature)

P_{moist} (final) = $P'_{dry} + P^{\circ}_{H_2O} = (0.9 \text{ atm} + 0.2 \text{ atm}) = 1.1$ atm

27. At 27 °C vapour density of the mixture of NO_2 and N_2O_4 is 38.3. Calculate the moles of NO_2 in 100 g mixture.

Solution V.D. of mixture = 38.3, M.Wt. of mixture = 2×38.3, Wt. of mixture = 100 g

Number of moles present $= \dfrac{100}{2 \times 38.3}$ ... (1)

Suppose mass of NO_2 = a gram Mass of N_2O_4 = (100–a) gram

Moles of NO_2 = w/M = a/46

Moles of N_2O_4 = w/M = (100–a)/92

Total moles $\dfrac{a}{46} + \dfrac{100-a}{92}$ ... (2)

Equating equation (1) and (2)

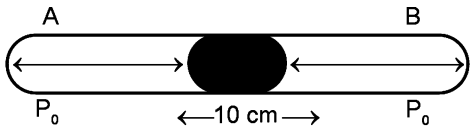
$$\frac{100}{2 \times 38.3} = \frac{a}{46} + \frac{100-a}{92}$$

$\therefore$ Moles of NO_2 = w/M = 20.1/46 = 0.43

28. A column of Hg of 10 cm in length is contained in the middle of a narrow 1 m long tube which is closed at both ends. Both the halves of the tube contained air at a pressure 76 cm of Hg. By what distance will the column of Hg be displaced if the tube is held vertical?

Solution Let initially the length of air column on each side be L, then 2L + 10 = 100

$\therefore$ L = 45 cm



If the tube is held vertificall , let the Hg column be displaced downwards by y to attain same pressure above and below the column of Hg. Then,

$P_B + 10 = P_A$ (Pressure taken in terms of length of Hg) ... 1

For end A: Since mole remains same on two sides,

$$\frac{P_0 \times L \times a}{RT} = \frac{P_A (L - y) \times a}{RT}$$

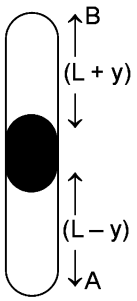
$$P_A = \frac{LP_0}{(L - y)} \quad \ldots (2)\ (V = L \times \text{area})$$

For end B: $$\frac{P_0 \times L \times a}{RT} = \frac{P_B \times (L + y) \times a}{RT} \quad \ldots (3)$$

From (1), (2) and (3)

$L = 45$ cm, $P_0 = 76$ cm

$y =$ **3 cm**



29. A thin tube of uniform cross section is sealed at both ends. It lies horizontally. The middle 5 cm containing Hg and the two equal ends containing air at the same pressure P_0. When the tube is held at an angle 60° with the vertical, the length of air column above and below the mercury are 46 and 44.5 cm respectively. Calculate the pressure P_0 in cm of Hg (the temperature of the system is kept at 30°C).

Solution Let initially, the length of air column in tube be L cm, then

$$2L + 5 = 46 + 5 + 44.5$$

$\therefore$ $$L = 45.25 \text{ cm}$$

When the tube is held vertically at 60.4 the Hg will be displaced to lower end. So that

$$P_B + 5\cos 60° = P_A$$

or $$P_A - P_B = 2.5 \text{ cm} \quad \ldots (1)$$

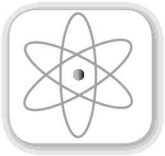
For end A: $$\frac{P_0 \times a \times 45.25}{RT} = \frac{P_A \times 44.5 \times a}{RT} \quad \ldots (2)$$

For end B: $$\frac{P_0 \times a \times 45.25}{RT} = \frac{P_B \times a \times 46}{RT} \quad \ldots (3)$$

From equation (1), (2) and (3)

$P_O =$ **75.4 cm of Hg**

DIFFUSION AND EFFUSION



Gas has infinite expansibility and gravitation has very little to do with the velocity of gas molelecule

When gases are mixed, the molecules of each gas will try to occupy the entire volume available to them.

It happens due to their random ceaseless motion and infinite expansibilit .

As a result of that a homogeneous solution is formed.

This is known as diffusion.

Effusion is movement of gas molecules through the orifice of a containe .

Diffusion is large mass transfer and effusion is small mass transfer.

Graham's Law of Effusion

Graham's Law of effusion is valid for real as well as for ideal gases i.e., all kinds of gases.

$$\text{Rate of effusion} = \frac{\text{Volume of gas effused out}}{\text{time taken}} \text{ or, } \frac{\text{No. of moles of gas diffused}}{\text{Time taken}}$$

$$\text{or, } \frac{\text{distance travelled by effused gas}}{\text{time taken}}$$

Graham in 1829 postulated a law, commonly known as the Graham's law of diffusion. This law states that,

"Under identical condition, rate of diffusion of a gas is inversely proportional to the square root of its density."

Thus, mathematically,

$$\text{Rate of diffusion, } (r) \propto \frac{1}{\sqrt{\text{Density of gas}(d)}}$$

$$r \propto \frac{1}{\sqrt{d}} \quad \text{or} \quad r = k\frac{1}{\sqrt{d}}$$

where r = rate of diffusion d = density of the gas, k = a constant

If there are two gases with densities d_1 and d_2 respecively under similar conditions of temperature and pressure, then their rates of diffusion r_1 and r_2 can be written as,

$$r_1 = k\frac{1}{\sqrt{d_1}}$$

$$r_2 = k\frac{1}{\sqrt{d_2}}$$

$$\text{Hence, } \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Since densities of gases are proportional to their vapour densities, hence

$$\frac{r_1}{r_2} = \sqrt{\frac{\text{Vapour density of gas 2}}{\text{Vapour density of gas 1}}}$$

Vapour density is related to the molecular mass by the relation, Molecular mass = 2 × Vapour density
So, the above equation can be written as,

$$\frac{r_1}{r_2} = \sqrt{\frac{\text{Molecular mass of gas 2}}{\text{Molecular mass of gas 1}}} = \sqrt{\frac{M_2}{M_1}}$$

Thus, the rate of diffusion of a gas is inversely proportional to the square root of its molecular mass. This indicates that a gas with lower molecular mass will diffuse faster. A light molecule diffuses quickly than a heavy molecule.

The rate of diffusion is measured in terms of the volume of the gas which gets diffused in one second (or any other convenient unit of time). If t_1 and t_2 are the times taken for the diffusion of volumes V_1 and V_2 respectively of gas 1 and 2, then,

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{M_2}{M_1}}$$

If equal volumes are made to diffuse out, $V_1 = V_2 = V$ (say). Then,

$$\frac{V/t_1}{V/t_2} = \sqrt{\frac{M_2}{M_1}}$$

or
$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

Thus, the time taken by a certain volume of a gas to diffuse out of a porous membrane is directly proportional to the square root of its molar mass.

Or

$r \propto P_{inside}$ [When A (area of orifice) and M (molar mass) are cons ant]

P_{inside} = Pressure of gas inside conainers

$r \propto A$ [When P_{inside} and M are constant]

$r \propto \frac{1}{\sqrt{M}}$ [A and P_{inside} are constant]

$\therefore \quad r \propto \frac{P_{inside}A}{\sqrt{M}}$ r = rate of effusion

Case I Comparison of rate of effusion of two gases in two different containers with different area of orifice and at di ferent pressure.

$$\frac{r_1}{r_2} = \frac{P_1A_1}{P_2A_2}\sqrt{\frac{M_2}{M_1}}$$

Case II Comparison of rate of effusion of two gases in same container.

$A_1 = A_2$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\frac{\sqrt{M_2}}{\sqrt{M_1}} \text{ [Where } P_1 \text{ and } P_2 \text{ will be partial pressure]} = \frac{n_1(\text{inside})}{n_2(\text{inside}}\sqrt{\frac{M_2}{M_1}}$$

Note: $\frac{P_1}{P_2} = \frac{n_1(\text{inside})}{n_2(\text{inside})} = \frac{x_1}{x_2}$ [Ratio of partial pressure = Ratio of number of moles = Ratio of their mole fraction]

Case III Comparison of gas mixture (a + b) with another gas (c) in separate container at same temperature.

$$\frac{r_{(a+b)}}{r_C} = \frac{P_T A_1}{P_C A_2}\sqrt{\frac{M_C}{M_{avg}}}$$

Case IV If two gases diffused for the same time through same orifice

$$\frac{r_1}{r_2} = \frac{n_1(\text{diffused})}{n_2(\text{diffused})} = \frac{n_1(\text{inside})}{n_2(\text{inside})}\sqrt{\frac{M_2}{M_1}}$$

Case V
$$\frac{r_1}{r_2} = \frac{d_1(\text{distance travelled})}{d_2(\text{distance travelled})} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

Triple point: The temperature at which solid ice, liquid water and water vapour i.e., all the three states of the substance exist together is called triple point. Its value for H_2O is 0.0098°C at 4.58 mm pressure.

$$\text{Bolzmann constant (k)} = \text{Gas constant per molecule} = \frac{R}{N_0} = \frac{8.314\ \text{JK}^{-1}\ \text{mole}^{-1}}{6.023\times10^{23}\ \text{molecules mole}^{-1}}$$

$$= 1.38 \times 10^{-23}\ \text{JK}^{-1}\ \text{molecule}^{-1}$$

Atmolysis: The process of separation of two gases on the basis of their different rates of diffusion due to difference in their densities is called atmolysis. It has been applied with success for the separation of isotopes and other gaseous mixture.



Worked-out Examples

30. There are 100 persons sitting at equal distances in a row XY. N_2O gas (laughing gas) is released from the side X and tear gas (mol. Mass = 176) from side Y at the same moment and at the same pressure. The person who will have a tendency to laugh and weep simultaneously is

(a) 34th from side X (b) 67th from side X

(c) 76th from side X (d) 67th from side Y

Solution (b) Amongst 100 persons, number of equidistant spaces = 99

Let n^{th} be the person from side X.

Then, $\frac{r_{NO_2}}{r_{tear}} = \sqrt{\frac{M_{tear}}{M_{NO_2}}} = \sqrt{\frac{176}{44}} = 2$

or $\frac{n-1}{99-(n-1)} = \frac{n-1}{100-n} = 2 \Rightarrow n = 67$

31. A mixture containing 1.12 litre of H_2 and 1.12 litre of D_2 (deuterium) at STP is taken inside a bulb connected to another bulb by a stop-cock with a small opening. The second bulb is fully evacuated, the stop-cock is opened for a certain time and then closed. The first bulb is found to contain 0.05 g of H_2. Determine the percentage composition by weight of the gases in the second bulb.

Solution In the first bulb:

$$\text{Initial moles of } H_2 = \frac{1.12}{22.4} = \frac{1}{20}$$

$$\text{Initial moles of } D_2 = \frac{1.12}{22.4} = \frac{1}{20}$$

Now after opening of stop-cock, mass of H_2 left in the first bulb = 0.05 g

$$\Rightarrow \quad \text{moles of } H_2 = \frac{0.05}{2} = \frac{1}{40}$$

$\Rightarrow$ moles of H_2 effused into second bulb

$$= \frac{1}{20} - \frac{1}{40} = \frac{1}{40}$$

Let n be number of moles of D_2 effused. Now using Graham's Law, we have:

$$\frac{n}{1/40} = \sqrt{\frac{2}{4}}$$

$$\Rightarrow \quad n = \frac{\sqrt{2}}{80} = \text{mole of } D_2 \text{ in second bulb}$$

In second bulb:

$$\text{The mass of } H_2 \text{ gas} = \frac{1}{40} \times 2 = 0.05 \text{ g}$$

$$\text{The mass of } D_2 \text{ gas} = \frac{\sqrt{2}}{80} \times 4 = 0.07 \text{ g}$$

$\Rightarrow$ Total mass = 0.05 + 0.07 = 0.12

$$\% \text{ of } H_2 = \frac{0.05}{1.12} \times 100 = 41.67\%$$

$$\% \text{ of } D_2 = \frac{0.07}{1.12} \times 100 = 58.13\ \%$$

32. What would be the final pressure of O_2 in following experiment? A collapsed polethylene bag of 30 litre capacity is partially blown up by the addition of 10 litres of N_2 at 0.965 atm at 298 K. Subsequently enough O_2 is pumped into bag so that at 298 K and external pressure of 0.990 atm, the bag contains 30 litres N_2.

Solution Given pressure of N_2 = 0.965 atm

Volume of N_2 = 10 litre. Temperature of N_2 = 298 K

$\therefore$ For N_2 when bag is fully expanded,

Volume of N_2 (alone) = 30 litre at 298 K

$$P_1V_1 = P_2V_2$$

$$0.965 \times 10 = P_2 \times 30$$

$\therefore$ P_{N_2} (alone) in 30 litre bag at 298 K = 0.322 atm

$$\text{Now } P_M = P_{O_2} + P_{N_2}$$

$$0.990 = P_{O_2} + 0.332 \qquad \therefore P_{O_2} = \mathbf{0.668\ atm.}$$

In order to derive the theoretical aspect of the various gas laws based on simple experimental facts, Maxwell proposed the following postulates under the heading of kinetic theory of gases.

33. The rate of diffusion of gas is..... proportional to both ..... and square root of molecular mass. **[IIT-1986]**

Solution inversely, time; $\left[\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}=\frac{t_2}{t_1}=\sqrt{\frac{M_2}{M_1}}\right]$

34. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is **[IIT-1990]**

(a) 64.0 (b) 32.0

(c) 4.0 (d) 8.0

Solution (a) $\frac{r_{CH_4}}{r_x}=2=\sqrt{\frac{M_x}{M_{CH_4}}}=\sqrt{\frac{M_x}{16}}$, or $M_x=64$

35. X ml of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is: **[IIT-1996]**

(a) 10 seconds : He (b) 20 seconds : O_2

(c) 25 seconds : CO (d) 55 seconds : CO_2

Solution (b) Under identical conditions, $\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}$

As rate of diffusion is also inversely proportional to time, we will have, $\frac{t_2}{t_1}=\sqrt{\frac{M_2}{M_1}}$

Thus, For He, $t_2=\sqrt{\frac{4}{2}}(5s)=5\sqrt{2}s\neq 10s$; For O_2, $t_2=\sqrt{\frac{32}{2}}(5s)=20s$

For CO, $t_2=\sqrt{\frac{28}{2}}(5s)\neq 25s$; For CO_2, $t_2=\sqrt{\frac{44}{2}}(5s)\neq 55s$

36. According to Graham's law, at a given temperature the ratio of the rates of diffusion r_A/r_B of gases A and B is given by **[IIT-1998]**

(a) $(P_A/P_B)\,(M_A/M_B)^{1/2}$ (b) $(M_A/M_B)(P_A/P_B)^{1/2}$

(c) $(P_A/P_B)(M_B/M_A)^{1/2}$ (d) $(M_A/M_B)(P_B/P_A)^{1/2}$

(Where P and M are pressures and molecular weights of gases A and B respectively.)

Solution (c) According to Graham's law of diffusion for two gases undergoing diffusion at different pressures through same hole

$$\frac{r_A}{r_B}=\sqrt{\frac{M_B}{M_A}}\times\frac{P_A}{P_B}\quad\left(r\propto P\times\sqrt{\frac{1}{M}}\ \text{At constant temperature}\right)$$

37. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be

(a) 4 (b) 2

(c) 1 (d) 0.5

Solution (b) $\frac{r_{HE}}{r_{CH_4}}=\sqrt{\frac{M_{CH_4}}{M_{He}}}=\sqrt{\frac{16}{4}}=2$

38. At constant volume, for a fixed number of moles of a gas the pressure of the gas increases with rise to temperature due to **[IIT-1992]**

(a) Increase in average molecular speed
(b) Increased rate of collisions amongst molecules
(c) Increase in molecular attraction
(d) Decrease in mean free path

Solution (a) Due to increase in the temperature, the kinetic energy of the gas molecules increases resulting in an increase in average molecular speed. The molecules are bombarded to the walls of the container with a greater velocity resulting in an increase in pressure.

The Postulates

(i) Each gas is made up of a large number of small (tiny) particles known as molecules.
(ii) The volume of a molecule is so small that it may be neglected in comparison to total volume of gas.
(iii) The molecules are never in stationary state but they are believed to be in chaotic (random) motion. They travel in straight line in all possible directions with altogether different but constant velocities. The direction of motion is changed by the collision with container or with other molecules.
(iv) The molecules are perfectly elastic and bear no change in energy during collison.
(v) The effect of gravity on molecular motion is negligible.
(vi) The temperature of gas is a measure of its kinetic energy. KE $\propto$ absolute temperature.
(vii) The pressure of the gas is thus due to the continuous collision of molecules on the walls of container.

Pressure $P = \frac{\text{Force(F)}}{\text{Area(A)}}$.

The Kinetic Equation

Maxwell also derived an equation on the basis of above assumption as

$$PV = \frac{1}{3}mnu^2$$

Where, P = Pressure of gas
V = Volume of gas
m = mass of one molecule of gas
n = number of molecules of gas
u = root mean square velocity of molecules
For 1 mole n = N is Avogadro number
$m \times N$ = Molecular mass M.

$$\therefore \quad PV = \frac{1}{3}Mu^2 \text{ or } u^2 = \frac{3PV}{M} = \frac{3RT}{M} \text{ or } u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}}$$

Kinetic Energy of Gas

As per kinetic equation $PV = \frac{1}{3}mnu_{rms}^2$

For 1 mole $m \times n$ = Molecular Mass (M)

$$\therefore \quad PV = \frac{1}{3}Mu_{rms}^2 = \frac{2}{3} \times \frac{1}{2}Mu^2 = \frac{2}{3} \times \text{K.E./ mole or } \frac{\text{K.E.}}{\text{mole}} = \frac{3}{2}RT.$$

Also, $\frac{\text{K.E.}}{\text{molecule}} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT$

Where k is the Boltzmann constant $\left(k = \frac{R}{N}\right)$



Worked-out Examples

39. The K.E. of N molecule of O_2 is x Joules at –123°C. Another sample of O_2 at 27°C has a KE of 2x Joules. The latter sample contains

(a) N molecules of O_2
(b) 2N molecules of O_2
(c) N/2 molecules of O_2
(d) N/4 molecule of O_2

Solution (a) $KE = \frac{3}{2}RT$; $T = -123 + 273 = +150$ K

$\frac{3}{2} \times R \times 150 = 3 \times 8.314 \times 75 = xJ = 225 \times 8.314 = xJ$

At 27°C = 27+ 223 = 300K

KE for = 2x Joule = $\frac{3}{2} \times 8.314 \times 300$ N molecules $\quad \therefore$ x Joule = $3 \times 8.314 \times 75$

In both the cases x Joules correspond to N molecules.

40. Find out the percentage of molecule in a gas at 1 atm and 27°C whose kinetic energy lies in the range of E and E + 0.01E.

[Where $E = \frac{3}{2}KT$]

Solution

We have,

$$E = \frac{3}{2}KT = \frac{3}{2} \times 1.38 \times 10^{-16} \times 300$$

$$= 6.2 \times 10^{-14} \text{ ergs}$$

$$dE = 0.01\ E = 6.2 \times 10^{-16} \text{ ergs}$$

$$\frac{dnE}{n} = 2\pi\left(\frac{1}{\pi kt}\right)^{3/2} E^{1/2} e^{-EK/T} dE$$

$$= 2 \times 3.4 \times \left(\frac{1}{3.14 \times 1.38 \times 10^{-16} \times 300}\right)^{3/2} \times (6.2 \times 10^{-14})^{1/2} \times e^{-3/2} \times (6.2 \times 10^{-16}) = \mathbf{0.0046}$$

$\therefore$ **46%**

41. At what temperature will the total K.E. of 0.3 mol of He be the same as the total K.E. of 0.4 mol of Ar at 400 K?

(a) 400 K (b) 300 K
(c) 346 K (d) 533 K

Solution K.E. of n moles of a gas,

$$\text{K.E.} = \frac{3}{2}nRT$$

$$\text{K.E}_1 = \frac{3}{2}n_1RT_1$$

$$\text{K.E}_2 = \frac{3}{2}n_2RT_2$$

$$\text{K.E}_1 = \text{K.E}_2$$

$$n_1T_1 = n_2T_2$$

$$0.3 \times T_1 = 0.4 \times 400$$

$$T_1 = \frac{1600}{3} = 533\ \text{K}$$

42. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor: **[AIEEE-2004]**

(a) 2 (b) $\sqrt{\frac{313}{293}}$

(c) $\frac{313}{293}$ (d) $\frac{1}{2}$

Solution (c) $\text{K.E.} = \frac{3}{2}RT \quad E_1 = \frac{3}{2} \times R \times 293$

$$E_2 = \frac{3}{2} \times R \times 313 \qquad E_2 = \frac{313}{293} \times E_1$$

43. Eight gram each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of..... . **[IIT-1989]**

Solution $1:16; \frac{\text{K.E.}_{O_2}}{\text{K.E.}_{H_2}} = \frac{(3/2)n_{O_2}RT}{(3/2)n_{H_2}RT} = \frac{n_{O_2}}{n_{H_2}} = \frac{8/32}{8/2} = \frac{1}{16}$

44. The absolute temperature of an ideal gas is..... to/than the average kinetic energy of the gas molecules. **[IIT-1997]**

Solution Less; $E_k = \frac{3}{2}RT. \Rightarrow E_k > T$

45. Kinetic energy of a molecule is zero at 0°C. **[IIT-1985]**

Solution **False:** K.E.= –KT, and cannot be zero at 0°C or 273 K.

46. According to kinetic theory of gases, for a diatomic molecule **[IIT-1991]**

(a) the pressure exerted by the gas is proportional to mean velocity of the molecule.

(b) the pressure exerted by the gas is proportional to the root mean velocity of the molecule.

(c) the root mean square velocity of the molecule is inversely proportional to the temperature.

(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature.

Solution (d) Pressure exerted by the gas, $P = \frac{1}{3}\frac{mnu^2}{v}$

Here, u = root mean square velocity
M = mass of a molecule, n = Number of molecules of the gas

Hence (a) and (b) are clearly wrong.

Again, $u^2 = \frac{3RT}{M}$ [explained from (1)]

Here, M = Molecular wt. of the gas: Hence (c) is wrong

Further Average K.E. $= \frac{3}{2}KT$; Hence (d) is true.

47. Kinetic theory of gases proves: **[AIEEE-2002]**
(a) Only Boyle's law
(b) Only Charle's law
(c) Only Avogadro's law
(d) All of these

Solution (d) Various gas laws can be easily derived from kinetic equation obtained as a result of kinetic theory of gases.

48. According to kinetic theory of gases in an ideal gas, between two successive collisions a gas molecule travels: **[AIEEE-2003]**
(a) In a straight line path
(b) With an accelerated velocity
(c) In a circular path
(d) In a wavy path

Solution (a) It is one of the assumption of kinetic theory of gases.

Velocities of Gas Molecules

Average Velocity

As per kinetic theory of gases, each molecule is moving with altogether different velocity. Let 'n' molecules be present in a given mass of gas, each one moving with velocity $v_1, v_2, v_3 \ldots v_n$. The average velocity or U_{aV} = average of all such velocity terms.

$$\text{Average velocity} = \frac{u_1 + u_2 + u_2 + \cdots u_n}{n} = \frac{n_1u_1 + n_2u_2 + n_3u_3}{n_1 + n_2 + n_3 \cdots}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}}$$

Root Mean Square Velocity

Maxwell proposed the term U_{rms} as the square root of means of square of all such velocities.

$$U_{rms}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + \cdots}{n} = \frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 +}{n_1 + n_2 + n_3}$$

Also $U_{rms} = \sqrt{\frac{3RT}{M}}$

Most probable velocity

It is the velocity which is possessed by maximum number of molecules.

$$V_{mp} = \sqrt{\frac{2RT}{M}}$$

Furthermore, $U_{MP} : U_{AV} : U_{rms} :: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$

$$\sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$1 : 1.128 : 1.224$$

Also $U_{av} = U_{rms} \times 0.9213$



Worked-out Examples

49. Calculate V_{rms} of O_2 at 273K and 1×10^5 Pa pressure. The density of O_2 under these conditions is 1.42 kg/m³.

Solution $V_{rms} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 10^5}{1.42}} = 460$ m/s

Also $V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 273}{32 \times 10^{-3}}} =$ **461.28 m/s.**

Note: In calculation of velocities pressure should be taken in Pascal's or N/m² units, density in kg/m³ units, molar mass of gas in kg units, R = 8.314 J/mole K to get velocity in m/s units.

50. Let the most probable velocity of hydrogen molecules at a temp t°C is V_o. Suppose all the molecules dissociate into atoms when temp is raised to (2 t + 273)°C then the new r.m.s velocity is

(a) $\sqrt{2/3}\ V_o$ (b) $\sqrt{3(2+273/t)}\ V_o$

(c) $2\sqrt{3}\ V_o$ (d) $\sqrt{6}\ V_o$

Solution (d) $V_o = \sqrt{\frac{2R(t+273)}{2}}$ $V_{rms} = \sqrt{\frac{3R(t+273)2}{1}} = \sqrt{6R(t+273)} = \sqrt{6}\ V_o$

51. For two gases, A and B with molecular weights M_A and M_B, it is observed that at a certain temperature, T, the mean velocity of A is equal to the root mean square velocity of B. Thus, the mean velocity of A can be made equal to the mean velocity of B, if:

(a) A is at temperature, T, and B at T', T > T'

(b) A is lowered to a temperature $T_2 <$ T while B is at T

(c) Both A and B are raised to a higher temperature

(d) Both A and B are placed at lower temperature

Solution (b) $\mu_{AV-A} = \sqrt{\frac{8RT}{\pi M_A}}; u_{rms-B} = \sqrt{\frac{3RT}{M_B}}$ $\therefore \frac{8}{3\pi} = \frac{M_A}{M_B}$

For $u_{AV-A} = \sqrt{\frac{8RT_2}{\pi M_A}}; u_{AV-B} = \sqrt{\frac{8RT}{\pi M_B}}$

$$\frac{T_2}{T} = \frac{M_A}{M_B} = \frac{8}{3\pi}$$

$$\therefore \quad T_2 = \frac{8}{3\pi}.T \text{ or } T_2 < T$$

52. The root mean square velocity of a gas is expressed as $V_{r.m.s} = \sqrt{\frac{3P}{d}}$ When is doubled at constant temperature, the $V_{r.m.s}$

(a) will be doubled
(b) less will be than doubled
(c) will be less than doubled
(d) remain the same

Solution $d = \frac{PM}{RT} \Rightarrow \frac{P}{d} = \frac{RT}{M}$

When T = constant for a given gas

$$\Rightarrow \quad \frac{RT}{M} = \text{constant} = \frac{P}{d} \text{ or } \mathbf{P \propto d}$$

Hence density will proportionally increase keeping the volume of $V_{r.m.s}$ intact.

So far the PVT behaviour of a gas has been presumed to obey the ideal gas equation PV = nRT. When measurements are extended to higher pressures, or even when very accurate measurements are made at ordinary pressures, the results do not confirm this equation. The ideal gas laws are not followed.

All gases exhibit, to some extent, deviations from the ideal-gas laws. When these deviations are recognized, the gas is said to behave as a real, non ideal or imperfect gas.

53. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is, **[IIT-1996]**

(a) 4 (b) 2
(c) 1 (d) 1/4

Solution (c) The expression of root mean square speed is

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\frac{C_{rms}(H_2)}{C_{rms}(O_2)} = \left[\frac{3R\ (50K)/(2g\ mol^{-1})}{3R\ (800K)/(32g\ mol^{-1})}\right]^{1/2} = 1$$

54. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as **[IIT-2000]**

(a) d^2 (b) d
(c) $\sqrt{d}$ (d) $1/\sqrt{d}$

Solution (d) $u_{RMS} = \sqrt{\frac{3RT}{M}}$ Using ideal gas equation,

$$PV = nRT = \frac{w}{M}RTl;\ \frac{RT}{M} = \frac{PV}{w} = \frac{P}{d}$$ where d is the density of the gas

$$\therefore \quad u_{RMS} = \sqrt{\frac{3P}{d}} \text{ at constant pressure, } u_{RMS} \propto \frac{1}{\sqrt{d}}$$

55. The root mean square velocity of one mole of a monoatomic gas having molar mass M is $U_{r.m.s.}$. The relation between the average kinetic energy (E) of the gas and $U_{r.m.s.}$ is **[IIT-2004]**

(a) $u_{r.m.s.} = \sqrt{\frac{3E}{2M}}$ (b) $u_{r.m.s.} = \sqrt{\frac{2E}{3M}}$

(c) $u_{r.m.s.} = \sqrt{\frac{2E}{M}}$ (d) $u_{r.m.s.} = \sqrt{\frac{E}{3M}}$

Solution (c) Average $KE = E\frac{1}{2}M\,u_{rms}^2$

$$\therefore \quad u_{rms}^2 = \frac{2E}{M} \text{ or } u_{rms} = \sqrt{\frac{2E}{M}}$$

56. At 400K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is **[IIT-2009]**

Solution 4 $gmol^{-1}$ $U_{rms} = \sqrt{\frac{3RT}{M}}$

$$U_{rms} = \sqrt{\frac{2RT}{M}}$$

$\therefore$ From questions

$$\sqrt{\frac{3R \times 400}{40}} = \sqrt{\frac{2R \times 60}{M}}$$

$$M = 4$$

Van der Waals' Equation of State for a Real Gas

An empirical equation of state generated by Van der Waals in 1873 reproduces the observed behaviour with moderate accuracy. For n moles of gas, the Van der Waals equation is,



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

where a and b are constants characteristic of a gas. This equation can be derived by considering a real gas and 'converting ' it to an ideal gas.

Volume correction: We know that for an ideal gas P×V = nRT. Now in a real gas the molecular volume cannot be ignored and therefore let us assume that 'b' is the volume excluded (out of the volume of container) for the moving gas molecules per mole of a gas. Therefore due to n moles of a gas the volume excluded would be nb. Therefore, a real gas in a container of volume V has only available volume of (V-nb) and this can be thought of as an ideal gas in container of volume (V-nb).

Pressure correction: Let us assume that the real gas exerts a pressure P. The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are assumed not to be exerting pressure.

It can be seen that the pressure the real gas exerts would be less than the pressure an ideal gas would have exerted. The real gas experiences attractions by its molecules in the reverse direction. Therefore, if a real gas exerts a pressure P, then an ideal gas would exert a pressure equal to P + p (p is the pressure lost by the gas molecules due to attractions). This small pressure p would be directly proportional to the extent of attraction between the molecules which are hitting the container wall and the molecules which are attracting these.

Therefore, $p \propto \frac{n}{V}$ (concentration of molecules which are hitting the container's wall)

$P \propto \frac{n}{V}$ (concentration of molecules which are attracting these molecules)

$\Rightarrow \quad p \propto \frac{n^2}{V^2}$

$\therefore \quad p = \frac{an^2}{V^2}$ where a is the constant of proportionality which depends on the nature of gas. A higher value of 'a' reflects the increased attraction between gas molecules.

Note: The Van der Waals constant b (the excluded volume) is actually four times the volume of a single molecule.

$\therefore \quad b = 4 \times 6.023 \times 10^{23} \times \frac{4}{3}\pi r^3$, where r is the radius of a molecule.

The constants a and b: Van der Waals constant for attraction (a) and volume (b) are characteristic for a given gas. Some salient feature of a and b are:

(i) For a given gas Van der Waal's constant of attraction 'a' is always greater than Van der Waals constant of volume (b).
(ii) The gas having higher value of 'a' can be liquefied easily and therefore H_2 and He are not liquefied easily.
(iii) The units of a = litre^2 atm mole^{-2} and that of b = litre mole $^{-1}$
(iv) The numerical values of a and b are in the order of 10^{-1} to 10^{-2} and 10^{-2} to 10^{-4} respectively.
(v) Higher is the value of 'a' for a given gas, easier is the liquefaction.

Kinetic Theory for Real Gases: The vander Waals Equation

Almost all gases, in particular which get easily liquefied show appreciable deviations from the ideal gas behaviour. The main causes of deviations have been described above. Thus, if an effort is to be made for deriving a gas equation for a real gas, due allowance has to be made for the finite size of the molecules, and also for the forces operating between them. This is done as described below.

Correction for Volume

V_1 in the ideal gas equation represents an ideal volume where the molecules can move freely. In real gases, a part of the total volume is, however, occupied by the molecules of the gas. Hence, the free volume V_1 is the total volume V minus the volume occupied by the molecules. If b represents the effective volume occupied by the molecules of 1 mole of a gas, then for the amount n of the gas V_i is given by,

$$V_i = V - nb \qquad \ldots\ldots (1)$$

Where b is called the excluded volume or co-volume. The numerical value of b is four times the actual volume occupied by the gas molecules. This can be shown as:

If we consider only bimolecular collisions then the volume occupied by the sphere of radius 2r represent the excluded volume per pair of molecules as shown in Figure below:

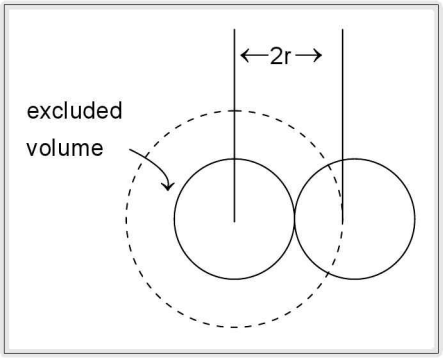


Fig. 2.4 Excluded volume per pair of molecules

Thus, excluded volume per pair of molecules,

$$= \frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right)$$

Excluded volume per molecule,

$$= \frac{1}{2}\left[8\left(\frac{4}{3}\pi r^3\right)\right] = 4\left(\frac{4}{3}\pi r^3\right) = 4 \text{ (volume occupied by a molecule)}$$

Since b represents excluded volume per mole of the gas, it is obvious that,

$$b = N_A\left[4\left(\frac{4}{3}\pi r^3\right)\right]$$

Correction for Forces of Attraction

Consider a molecule A in the bulk of a vessel as shown in fig. 2.5. This molecule is surrounded by other molecules in a symmetrical manner, with the result that this molecule on the whole experiences no net force of attraction.

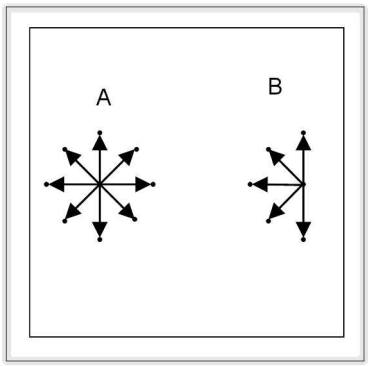


Fig. 2.5 Arrangement of molecules within and near the surface of a vessel

Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only on one side of the vessel,

i.e., towards its centre, with the result that this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas, i.e.,

$$P_i = P + \text{correction term} \quad \ldots\ldots (2)$$

This correction term depends upon two factors:

(i) The number of molecules per unit volume of the vessel: Larger this number, larger will be the net force of attraction with which the molecule B is dragged behind. This results in a greater decrease n the velocity of the molecule B and hence a greater decrease in the rate of change of momentum. Consequently, the correction term also has a large value. If n is the amount of the gas present in the volume V of the container, the number of molecules per unit volume of the container is given as,

$$N' = \frac{nN_A}{V}$$

Or $$N' \propto \frac{n}{V}$$

Thus, the correction term is given as:

$$\text{Correction term} \propto \frac{n}{V} \quad \ldots\ldots (3)$$

(ii) The number of molecules striking the side of the vessel per unit time: Larger this number, larger will be the decrease in the rate of change of momentum. Consequently, the correction term also has a larger value. Now, the number of molecules striking the side of vessel in a unit time also depends upon the number of molecules present in unit volume of the container, and hence in the present case:

$$\text{Correction term} \propto \frac{n}{V} \quad \ldots\ldots (3b)$$

Taking both these factors together, we have

$$\text{Correction term} \propto \left(\frac{n}{V}\right)\left(\frac{n}{V}\right)$$

or $$\text{Correction term} = a\frac{n^2}{V^2} \quad \ldots\ldots (4)$$

Where a is the proportionality constant and is a measure of the forces of attraction between the molecules. Thus,

$$P_i = P + a\frac{n^2}{V^2} \quad \ldots\ldots (5)$$

The unit of the term an^2/V^2 will be the same as that of the pressure. Thus, the SI unit of a will be Pa m^6 mol^{-2}. It may be conveniently expressed in kPa dm^6 mol^{-2}.

When the expressions as given by Eqs (1) and (5) are substituted in the ideal gas equation $p_iV_i = nRT$, we get,

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

This equation is applicable to real gases and is known as the van der Waals equation.

Values of van der Waals constants

The constants a and b in van der Waals equation are called van der Waals constants and their values depend upon the nature of the gas (Table below).

Gas	a / kPa dm^6 mol^{-2}	b / dm^3 mol^{-1}	Gas	a / kPa dm^6 mol^{-2}	b / dm^3 mol^{-1}
H_2	21.764	0.026 61	CH_4	228.285	0.042 78
He	3.457	0.023 70	C_2H_6	556.173	0.063 80
N_2	140.842	0.039 13	C_3H_8	877.880	0.084 45
O_2	137.802	0.031 83	$C_4H_{10}^{(n)}$	1 466.173	0.122 6
Cl_2	657.903	0.056 22	$C_4H_{10}^{(iso)}$	1 304.053	0.114 2
NO	135.776	0.027 89	$C_5H_{12}^{(n)}$	1 926.188	0.146 0
NO_2	535.401	0.044 24	CO	150.468	0.039 85
H_2O	553.639	0.030 49	CO_2	363.959	0.042 67

The value of these constants are determined by the critical constants of the gas. Actually, the so-called constants vary to some extent with temperature and this shows that the van der Waals equation is not a complete solution of the behaviour of real gases.

It should however be remarked that *a* and *b* are not totally independent of temperature and pressure.



Worked-out Example

57. Two van der Waals gases have the same value of *b* but different *a* values. Which of these would occupy greater volume under identical conditions? If the gases have the same *a* value but different values of *b* which would be more compressible?

Solution If two gases have same value of *b* but different values of *a*, then the gas having a larger value *a* will occupy lesser volume. This is because the gas with a larger value of *a* will have a larger force of attraction, and hence lesser distance between its molecules.

If two gases have the same value of *a* but different values of *b*, then the smaller the value of *b*, larger will be the compressibility because the gas with the smaller value of *b* will occupy lesser volume and hence will be more compressible.

Van der Waal's equation under different pressure condition

For one mole of a gas, the van der Waal's equation is given by $\left(P + \frac{a}{V^2}\right)(V - b) = RT$.

This may be written as $PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$

Case I At a very high pressure, $V \approx b$

Hence, $\frac{a}{V} - \frac{ab}{V^2} = 0 \quad \Rightarrow \quad P(V_m - b) = RT$

At very low pressure $V >> b$

Hence $(V - b) \approx V$

$$\left(P + \frac{a}{V_m^2}\right)(V_m) = RT$$



Worked-out Examples

58. Assuming O_2 molecule spherical in shape and occupying the radius 150 pm. Calculate
(i) the volume of single molecule of gas
(ii) the percentage of empty space in one mole of O_2 at NTP

Solution (i) Volume of 1 molecule = $\frac{4}{3}\pi r^3$

($\because$ r = 150 pm = 150×10^{-10} cm)

Volume of 1 molecule = $\frac{4}{3} \times \frac{22}{7} \times (150 \times 10^{-10})^3$

$V_1 = 1.41 \times 10^{-23}$ cc/molecule

(ii) The volume occupied by N molecules = $N \times V_1$

$= 6.023 \times 10^{23} \times 1.41 \times 10^{-23}$

= 8.49 cc per mole

$\therefore$ Volume of 1 mole of N_2 = 22400 ml of STP

Thus empty space = (22400 – 8.49) = 22391.51cc

% empty space = $\frac{22391.51}{22400} \times 100 =$ **99.96%**

59. Using Van der Waal's equation calculate the constant 'a' when two moles of gas contained in a four litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The volume of 'b' is 0.05 lit/mol^{-1}

Solution Van der Waal's equation for n moles of gas is

$$\left(P + \frac{n^2a}{V^2}\right)(V\text{-}nb) = nRT$$

given V = 4 lt, P = 11.0 atm, T = 300 K, b = 0.05 lt/mol n = 2

$\therefore$ $\left[11 + \frac{2^2a}{4^2}\right]$ [4–2×0.05] = 2 × 0.082 × 300 $\Rightarrow$ a = 6.46 atm litre^2 mol^{-2}

60. In the van der Waals' equation $\left(P + \frac{n^2a}{V^2}\right)(V\text{-}nb) = nRT$, the constant 'a' reflects the actual volume of the gas molecules. (State whether True or False) **[IIT-1993]**

Solution False: The constant 'a' reflects the intermolecular attraction between gaseous molecules. The constant 'b' reflects the actual volume of one mole of gaseous molecules.

61. Arrange the van der Waals constant for the gases: **[IIT-1995]**

I $C_6H_{6(g)}$	A 0.217
II $C_6H_5.CH_{3(g)}$	B 5.464
III $Ne_{(g)}$	C 18.000
IV. $H_2O_{(g)}$	D 24.060

(a) I-A, II-D, III-C, IV-B
(b) I-D, II-A, III-B, IV-C
(c) I-C, II-D, III-A, IV-B
(d) I-B, II-C, III-A, IV-D

Solution (c) The values provided are for the constant 'a', which indicates the magnitude of the attractive forces among the gas molecules, which increases with the size of molecules. So inert gas will have the minimum value followed by H_2O, C_6H_6 and $C_6H_5CH_3$.

62. Read the following statement and explanation and answer as per the options given below:
Assertion: The value of van der Waals' constant 'a' is larger for ammonia than for nitrogen.
Reason: Hydrogen bonding is present in ammonia. **[IIT-1998]**
(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion.
(b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion.
(c) If assertion is correct but reason is incorrect.
(d) If assertion is incorrect but reason is correct.

Solution (a) 'a' indicates the magnitude of the attractive forces among the gas molecules, which increases in NH_3 due to H-bonding.

63. A gas described by van der Waals equation **[IIT-2008]**
(a) behaves similar to an ideal gas in the limit of large molar volumes.
(b) behaves similar to an ideal gas in the limit of large pressures.
(c) is characterized by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature.
(d) has the pressure that is lower than the pressure exerted by the same gas behaving ideally.

Solution (a, c, d)

64. The term that corrects for the attractive forces present in a real gas in the van der Walls equation is **[IIT-2009]**
(a) nb (b) $\frac{an^2}{V^2}$
(c) $-\frac{an^2}{V^2}$ (d) –nb

Solution (b) Van der waals' equation for n moles of a real gas is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The pressure correction factor $\frac{an^2}{V^2}$ accounts for the loss of pressure due to inward pull. `a' is van der waals' constant for a gas and it is the measure of the strength of the vanderwaals' intermolecular attraction.

Hence, $\frac{an^2}{V^2}$

Some Other Important Definitions

Mean Free Path (λ)
It is the average distance travelled by a particle between collisions

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N}$$



Worked-out Example

65. Longest mean free path stands for: **[IIT-1995]**

(a) H_2 (b) N_2

(c) O_2 (d) Cl_2

Solution (a) The mean free path, $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N}$

or $\lambda \propto \frac{1}{a^2}$, where, a = molecular diameter

Smaller the molecular diameter, longest the mean free path. Hence, H_2 is the answer.

Collision Frequency (z)

It is the number of collisions taking place per second

$$z = \pi\sigma^2 N u_{av}$$

where, σ = collision diameter. It is the distance between the centres of two molecule without collision.

N = number of molecules per unit volume,

And u_{av} = average velocity



Worked-out Example

66. Read the following statement and explanation and answer as per the options given below:
Assertion: The pressure of a fixed amount of an ideal gas is proportional to its temperature
Reason: Frequency of collisions and their impact both increase in proportion to the square root of temperature. **[IIT-2000]**

(a) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.

(b) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.

(c) If assertion is CORRECT, but reason is INCORRECT.

(d) If assertion is INCORRECT, but reason is CORRECT.

Solution (d) Here assertion is incorrect because condition of constancy of volume is not given

Boyle's Temperature (T_b)

Temperature at which real gas obeys the gas laws over a wide range of pressure is called Boyle's Temperature. Gases which are easily liquefied have a high Boyle's temperature [$T_b(O_2)$] = 46 K] whereas, the gases which are difficult to liquefy have a low Boyle s temperature [T_b(He) = 26K].

$$\text{Boyle's temperature } T_b = \frac{a}{Rb} = \frac{1}{2}T_i$$

Where, T_i is called **Inversion Temperature** and a, b are called van der Waals constant.

Critical Constants

For one mole of a gas, the van der Waal's equation is given by $(P + \frac{a}{V^2})(V - b) = RT$.

This may be written as $PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$. Multiplying by V^2 and dividing by P and rearranging in decreasing powers of V,

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

This is a cubical equation in V. If at a constant temperature, the values of V are plotted against P then a curve similar to the one marked I in the figure should be obtained.

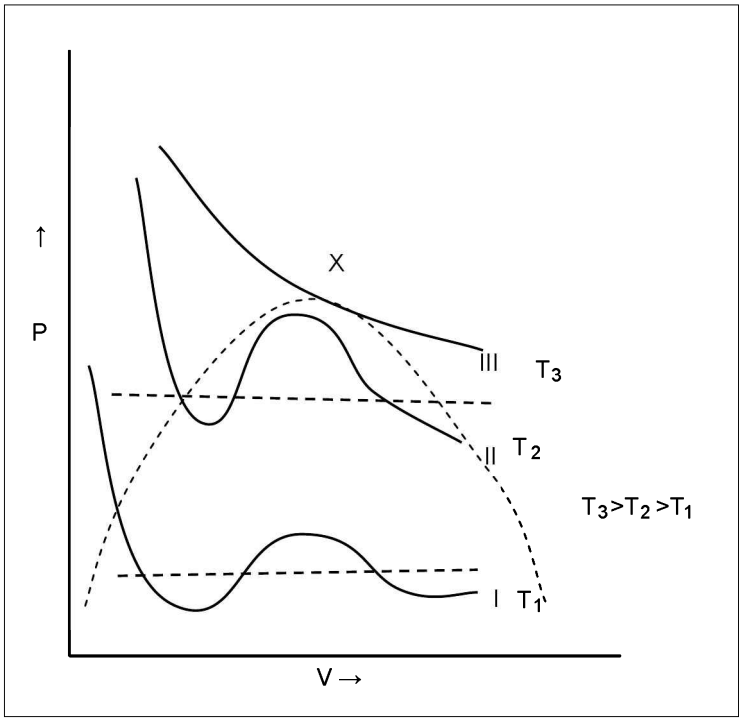


Fig. 2.6

At the point X, all the three values of V become idential. This volume corresponding to this point is called critical volume, and the pressure is called critical pressure and the temperature is called critical temperature. At this point $V = V_c$ or $(V - V_c) = 0$ or $(V - V_C)^3 = 0$

Expanding and writing in decreasing powers of V, we have,

$$V^3 - 3V^2V_C + 3V_C^2V - V_C^2 = 0 \quad \ldots(2)$$

The above equation must be identical with van der Waal's equation at the critical temperature and critical pressure, which for one mole of gas is written as

$$V^3 - \left(b + \frac{RT_C}{P_C}\right)V^2 + \frac{a}{P_C}V - \frac{ab}{P_C} = 0 \quad \ldots.(3)$$

Comparing the coefficients in (2) and (3

$$3V_C = b + \frac{RT_C}{P_C} \quad ...(4)$$

$$3V_C^2 = \frac{a}{P_C} \quad ...(5)$$

$$V_C^2 = \frac{ab}{P_C} \quad ...(6)$$

Using the above equations, we can obtain relationships between van der Waals' constants and critical constants.

(i) **Critical Temperature (T_c):** It (T_c) is the maximum temperature at which a gas can be liquefied i.e., the temperature above which a gas cannot exist as liquid.

$$T_c = \frac{8a}{27Rb}$$

(ii) **Critical Pressure (P_c):** It is the minimum pressure required to cause liquefaction at T_c.

$$P_c = \frac{a}{27b^2}$$

(iii) **Critical Volume:** It is the volume occupied by one mol of a gas at T_c and P_c

$$V_c = 3b$$

Worked-out Example

67. The critical temperature and pressure of CO_2 gas are 304.2K and 72.9 atm respectively. What is the radius of O_2 molecule assuming it to behave as van der Waal's gas?

Solution $\because V_c = 3b = 3\frac{RT_c}{8P_c}$ and also

$$V_c = 4 \times N \times \frac{4}{3}\pi r^3$$

So $4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times 3.14 \times r^3 = \frac{3 \times 0.0821 \times 304.2}{8 \times 72.9}$

$\Rightarrow r^3 = 4.25 \times 10^{-30} \Rightarrow$ **r = 1.62 A°.**

CONTINUITY OF STATE

In the given figure, the end-points of the horizontal lines have been connected with a dotted line. This portion, known as the surface of discontinuity, separates the liquid state on one side and the gas on the other. Within this curve, the liquid and the gas coexist. Because of this coexistence curve, it is possible to distinguish between the two states of matter, namely, gas and liquid. However, in practice, this is not always true because it is possible to convert matter from one state into another without any sharp discontinuity. This can be done as shown in the figure.

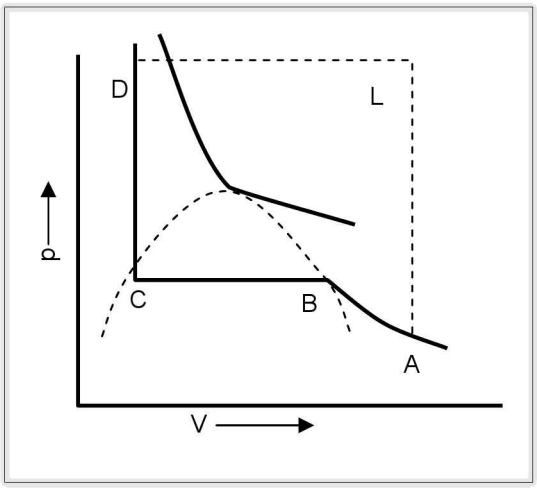


Fig. 2.7

(i) Increase the temperature of the gas keeping volume constant. The pressure rises along AL.
(ii) Having reached L, the pressure is kept constant and the gas is cooled; this decreases the volume along the line LD.

Thus, we have passed from A to D without the gradual change as it occurs along the line BC, i.e., condensation in the usual sense of the term did not occur. Point D could be said to represent a highly compressed gaseous state of the substance. Whether we refer to the state in the region of point D as liquid state or as highly compressed gaseous state, depends purely upon which of the two view points happens to be convenient at the moment. Thus, in the absence of the surface of discontinuity, there is no way of distinguishing between liquid and gas.

Reduced Equation State

Since critical constants are definite quantities for a gas, it is possible to express its P, V, T as multiples or sub-multiples of critical values let us say,

$$P = \pi P_C;\ V = \phi V_C,\ T = \theta T_C$$

where π, ϕ, θ are called reduced pressure, reduced volume and reduced temperature.
The van der Waal's equation may be changed as

$$\left(1 + \frac{a}{V^2}\right)(V - b) = RT \text{ [for 1 mole of gas]}$$

$$\left(\pi P_C + \frac{1}{\varphi^2 V_C^2}\right)(\theta\phi V_C - b) = R\theta T_C$$

$$\left(\frac{\pi a}{27b^2} + \frac{9}{9\varphi^2 b^2}\right)(3\phi b - b) = R\theta \cdot \frac{8a}{27Rb}$$

$$\left(\pi + \frac{3}{\varphi^2}\right)(3\phi + 1) = 8\theta$$

This is called law of corresponding states.

Compressibility Factor (Z) or Compression Factor

Compressibility factor is a measure of extent of deviation from the ideal behaviour of gas.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

We know,

$$P_{id}\,\overline{V}_{id} = RT$$

This equation is true for the ideal gas, real gases do no obey that equation at any temperature and pressure

$$P_{real}\,\overline{V}_{real} \neq RT$$

Compressibility factor expressed as,

$$Z = \frac{P_{real}\,\overline{V}_{real}}{P_{id}\,\overline{V}_{id}} = \frac{P_{real}\,\overline{V}_{real}}{RT} = \frac{P_{real}V_{real}}{nRT}$$ [All the parameters are of real gas]

Hence, for a real gas $P_{real}\,V_{real} = ZnRT$

Case I Z = 1:

- It represents that the real gas is behaving ideally.
- No attraction or repulsion among the molecules.

Case II Z < 1:

- Attraction predominates.
- Hence gas can be liquefied easil .

Case III Z > 1:

- Repulsion predominates.
- The liquification becomes difficul

Z for a particular gas can change with pressure and temperature.
It is very difficult to liquefy $_2$ and He.

H_2 and He cannot be liquefie

Proof $\rightarrow Z = \dfrac{P_{real}\,\overline{V}_{real}}{P_{id}\,\overline{V}_{ideal}}$

$$= \frac{P_{real}\,\overline{V}_{real}}{RT} = \frac{P_{real}V_{real}}{nRT}$$

Liquification is difficult when Z >

$$\left(P_{real} + \frac{a}{\overline{V}_{real}}\right)(\overline{V}_{real} - b) = RT$$

$$P_{real}\,(V_{real} - b) = RT$$

$$P_{real}\,V_{real} - P_{real}\,b = RT$$

$$\frac{P_{real}V_{real}}{RT} - \frac{P_{real}b}{RT} = 1$$

$$Z = 1 + \frac{P_{real}b}{RT} \qquad Z > 1$$

So it is difficult to liquif .

Real gas can be liquefied unde critical conditions

$$\textbf{Proof} \rightarrow \frac{P_C \overline{V}_C}{RT_C} = \frac{3}{8} < 1$$

Thus, gas can be liquefied
One way of writing the equation of state for real gas.

$$P\overline{V} = RT\,[1 + \frac{B}{V} + \ldots\ldots].$$

Express 'B' in terms of 'a' and 'b'

$$\frac{P\overline{V}}{RT} = RT[1 + \frac{B}{V} + \ldots.]$$

$$Z = [1 + \frac{B}{V} + \ldots.] \qquad \ldots\ldots 1$$

$$\Rightarrow \quad \left(P + \frac{a}{\overline{V}^2}\right) = \frac{RT}{(\overline{V} - b)}$$

$$Z = \left(1 - \frac{b}{\overline{V}}\right)^{-1} - \frac{a}{\overline{V}RT}$$

$$Z = \left(1 + \frac{b}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \ldots\ldots\right) - \frac{a}{\overline{V}RT}$$

$= 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \ldots\ldots$ by comparing from given equation, we get neglecting the higher terms we get,

$\therefore \quad B = b - \frac{a}{RT}$, where 1st virial coefficient is 1 and B is called the 2nd virial co-efficien

$\therefore \quad Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}}$

For Hydrogen and Helium, the value of 'a' is very small

$$\frac{a}{RT} < b$$

$$\left(b - \frac{a}{RT}\right) = +ve$$

Special Case

When temperature is decreased, $\frac{a}{RT}$ increases,

Hence, $\frac{a}{RT} > b$

$$\Rightarrow \quad \left(b - \frac{a}{RT}\right) = -ve \Rightarrow Z < 1$$

When temperature is low gas can be easily liquefied
When the temperature is decreased the value of Z decreases so liquification becomes easie .

NH_3, $SO_2 \Rightarrow$ These gases have a high value $\frac{a}{RT} > b$

$Z < 1$ Thus these can be easily liquefied.

Variation of compressibility factor (Z) with pressure

Figure shows the variation of Z with pressure for different gases at constant temperature.

We have seen that

At low pressures, the gas equation can be written as,

$$\left(P + \frac{a}{V_m^2}\right)(V_m) = RT \text{ or } Z = \frac{V_m}{RT} = 1 - \frac{a}{V_m RT} \quad \ldots\ldots\ldots (1)$$

Hence, $Z < 1$ in low pressure region

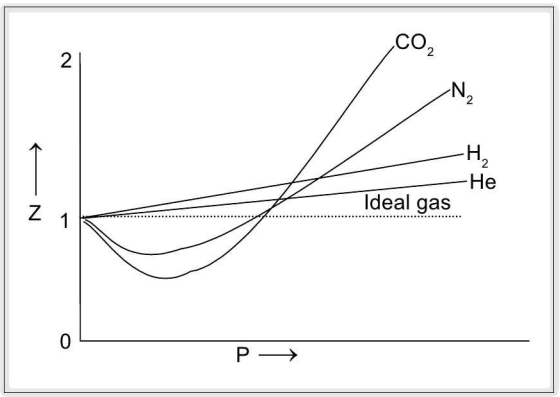


Fig. 2.8 Deviation of gases from ideal behaviour with pressure.

The greater the value of 'a' the more 'z' deviates from unity in the low pressure region At high pressures, the gas equation can be written as,

$$P(V_m - b) = RT \quad Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT} \quad \ldots\ldots (2)$$

Hence, $z > 1$ in the high pressure region.

The greater the value of 'b' the more is the deviation

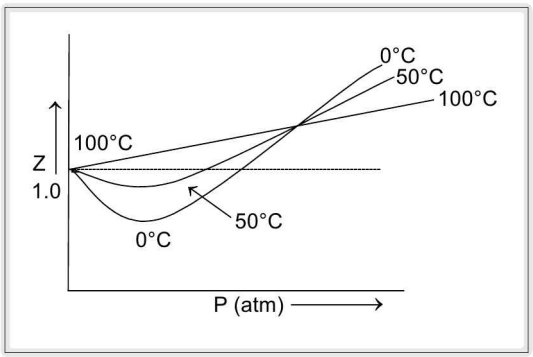


Fig. 2.9 The plot of Z vs P for N_2 gas at different temperature is shown here.

Figure represents the variation in the 'z' for the same gas at different temperature in high and low pressure region.

We can see from equation 1 and 2 that the extent of deviation of 'z' from unity decreases with the increase in temperature.

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Worked-out Examples

68. The behaviour of a real gas is usually depicted by plotting compressibility factor Z versus P at a constant temperature. At high temperature and high pressure, Z is usually more than one. This fact can be explained by van der Waals equation when

(a) the constant 'a' is negligible and not 'b'

(b) the constant 'b' is negligible and not 'a'

(c) both constant 'a' and 'b' are negligible

(d) both the constant 'a' and 'b' are not negligible.

Solution (a) $(P + n^2a/V^2)(V-nb) = nRT$

At low pressures, 'b' can be ignored as the volume of the gas is very high. At high temperature 'a' can be ignored as the pressure of the gas is high.

$\therefore \quad P(V - b) = RT$

$PV - Pb = RT$

$PV = RT + Pb$

$$\frac{PV}{RT} = Z = 1 + \frac{Pb}{RT}$$

69. One litre of a gas at 300 atm and 473 K is compressed to a pressure of 600 atm and 273 K. The compressibility factors found are 1.072 and 1.375 respectively at initial and final states. Calculate the final volume.

Solution $P_1V_1 = Z_1nRT_1$ and $P_2V_2 = Z_2nRT_2$

$$\frac{P_2V_2}{T_2} \times \frac{T_1}{P_1V_1} = \frac{Z_2}{Z_1}$$

or $$V_2 = \frac{Z_2}{Z_1} \times \frac{T_2}{T_1} \times \frac{P_1V_1}{P_2}$$

$$= \frac{1.375}{1.072} \times \frac{273}{473} \times \frac{300 \times 1}{600} = 370.1 \text{ ml}$$

70. The compressibility factor for an ideal gas is **[IIT-1997]**

(a) 1.5 (b) 1.0 (c) 2.0 (d) ∞.

Solution (b) The compressibility factor of a gas is defined as $z = \frac{\rho V_m}{RT}$

71. Positive deviation from ideal behaviour takes place because of

(a) Molecular interaction between atoms and PV/nRT > 1

(b) Molecular interaction between atoms and PV/nRT < 1

(c) Finite size of atoms and PV/nRT > 1

(d) Finite size of atoms and PV/nRT < 1

Solution (c) For positive deviation: $PV = nRT + nPb \Rightarrow PV/nRT = 1 + (PB/RT)$

Thus, the factor nPb is responsible for increasing the PV value, above ideal value, b is actually the effective volume of molecule. So, it is the finite size of molecules that leads to the origin of b and hence positive deviation at high pressure.

72. The compressibility of a gas is less than unity at STP. Therefore, **[IIT-2000]**

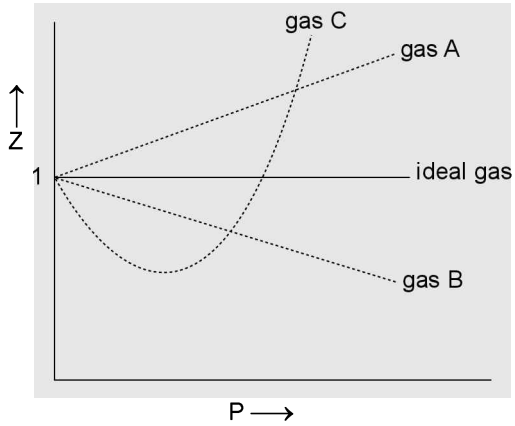
(a) $V_m > 22.4$ litres (b) $V_m < 22.4$ litres

(c) $V_m = 22.4$ litres (d) $V_m = 44.8$ litre

Solution (b) $(PV)_{Observed}/(PV)_{Ideal} < 1 \Rightarrow V_{obs} < V_{ideal}$, $V_{obs} < 22.4$ litre.

73. Refer to the figure given: **[IIT-2006]**

Which of the following statements is wrong?



(a) For gas A, a = 0 and Z will linearly depend on pressure

(b) For gas B, b = 0 and Z will linearly depend on pressure

(c) Gas C is a real gas and we can find 'a' and 'b' if intersection data is given

(d) All van der Waal gases will behave like gas C and give positive slope at high pressure

Solution (b) For gas A, a = 0, $Z = 1 + \frac{Pb}{RT}$ implies Z varies linearly with pressure.

For gas B, b = 0, $Z = 1 - \frac{a}{VRT}$. Hence, Z does not vary linearly with pressure.

Given the intersection data for gas C, it is possible to find the values of 'a' and 'b'. All van der Waal gases, like gas C, give positive slope at high pressures.

Gas Eudiometry

The relationship amongst gases, when they react with one another, is governed by two laws, namely Gay-Lussac law and Avogadro's law.

Gaseous reactions for investigation purposes are studied in a closed graduated tube open at one end and the other closed end of which is provided with platinum terminals for the passage of electricity through the mixture of gases. Such a tube is known as **Eudiometer tube** and hence the name **Eudiometry** is also used for gas analysis.

During Gas analysis, the Eudiometer tube filled with mercury is inverted over a trough containing mercury. A known volume of the gas or gaseous mixture to be studied is next introduced, which displaces an equivalent amount of mercury. Next, a known excess of oxygen is introduced and the electric spark is passed, whereby the combustible material gets oxidized. The volumes of carbon dioxide, water vapour

or other gaseous products of combustion are next determined by absorbing them in suitable reagents. For example, the volume of CO_2 is determined by absorption in KOH solution and that of excess of oxygen in an alkaline solution of pyrogallol. Water vapour produced during the reaction can be determined by noting contraction in volume caused due to cooling, as by cooling the steam formed during combustion forms liquid (water) which occupies a negligible volume as compared to the volumes of the gases considered. The excess of oxygen left after the combustion is also determined by difference if other gases formed during combustion have already been determined. From the data thus collected, a number of useful conclusions regarding reactions amongst gases can be drawn:

(a) Volume-volume relationship amongst gases or simple gaseous reactions.
(b) Composition of gaseous mixtures.
(c) Molecular formulae of gases.
(d) Molecular formulae of gaseous hydrocarbons.

The various reagents used for absorbing different gases are:

$O_3 \longrightarrow$ turpentine oil

$O_2 \longrightarrow$ alkaline pyrogallol

$NO \longrightarrow FeSO_4$ solution

$CO_2, SO_2 \longrightarrow$ alkali solution (NaOH, KOH, $Ca(OH)_2$, $HOCH_2CH_2NH_2$, etc.)

$NH_3 \longrightarrow$ acid solution or $CuSO_4$ solution

$Cl_2 \longrightarrow$ water

Equation for combustion of hydrocarbons:

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

General Assumptions

In all problems, it is assumed that the sparking occurs at room temperature. This implies that water formed would be in liquid state and that nitrogen gas is inert towards oxidation.



Worked-out Examples

74. A 20 c.c. mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The decrease in volume is found to be 13 c.c. A further contraction of 14 c.c. occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage.

Solution Let the volume of CO be 'a' c.c. and CH_4 be 'b' c.c $\quad \therefore$ volume of He = (20–a–b)
On explosion with oxygen,

$$CO\,(g) + \frac{1}{2}\,O_2(g) \longrightarrow CO_2(g)$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O\,(l)$$

'a' c.c. of CO give 'a' c.c. of CO_2 and 'b' c.c. of CH_4 gives 'b' c.c. of CO_2. Therefore, the volume decrease is due to the consumption of O_2. O_2 consumed for 'a' c.c. of CO is $\frac{a}{2}$ c.c. and O_2 consumed for 'b' c.c. of CH_4 is '2b' c.c.

$$\therefore \qquad \frac{a}{2} + 2b = 13$$

The further contraction occurs because of the absorption of CO_2 by KOH, a+b = 14

$\therefore$ b = 4 c.c.

$\therefore$ a = 10 c.c.

$\therefore$ percentage composition of CO = $\frac{10}{20}\times 100 = \mathbf{50\%}$

percentage composition of CH_4 = $\frac{4}{20}\times 100 = \mathbf{20\%}$

percentage composition of He = $\frac{(20-10-4)}{20}\times 100 = \frac{6}{20}\times 100 = \mathbf{30\%}$

Eudiometry

75. A mixture of propane and methane is contained in a vessel of unknown volume V at a temperature T and exerts a pressure of 320 mm Hg. The gas is burnt in excess O_2 and all the carbon is recovered as CO_2. The CO_2 is found to have a pressure of 448 mm Hg in a volume V_1 at the same temperature T. Calculate mole fraction of propane in mixture.

Solution Let the moles of propane (C_3H_8) = n_1

Moles of methane CH_4 = n_2

We know that PV = nRT

$\therefore$ $20 \times V = (n_1+n_2)\,RT$

after combustion,

$$\underset{n_1}{C_3H_8} + 5O_2 \rightarrow \underset{3n_1}{3O_2} + 4H_2O$$

$$\underset{n_2}{CH_4} + 2O_2 \rightarrow \underset{n_2}{CO_2} + 2H_2O$$

total moles of CO_2 formed = $(3n_1+n_2)$

Once again we have, PV = nRT

$$448 \times V = (3n_1 + n_2)\frac{RT}{V} \qquad \ldots.(2)$$

Dividing eqn (2) by (1) we have,

$$\frac{448}{320} = \frac{(3n_1 + n_1)}{(n_1 + n_2)} \Rightarrow \frac{n_1}{n_2} = 0.25$$

mol fraction of C_3H_8 = $\frac{n_1}{n_1 + n_2}$

$$= \frac{0.25n_2}{0.25n_2 + n_2} = \mathbf{0.2}$$

76. 50 ml of a mixture of NH_3 and H_2 was completely decomposed by sparking into nitrogen and hydrogen. 40 ml of oxygen was then added and the mixture was sparked again. After cooling to the room temperature, the mixture was shaken with alkaline pyro-gallol and a contraction of 6 ml was observed. Calculate the % of NH_3 in the original mixture.

Solution Let the volume of NH_3 be *x* ml

$\therefore$ volume of H_2 = (50– *x*) ml

On sparking,

$$NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$$

Since 40 ml of O_2 is added and sparked, it must have reacted with H_2 to form liquid water. Moreover, since 6 ml contraction occurs with alkaline pyrogallol, 34 ml is the volume of O_2 used up.

$\therefore$ total volume of H_2 is 68 ($\because$ $2H_2 + O_2 \longrightarrow 2H_2O$)

$\therefore$ $(50-x) + \frac{3}{2}x = 68$

$$50 + \frac{x}{2} = 68 ; \quad x = 36 \qquad \therefore \mathbf{NH_3 = 72\%}$$

77. When a certain quantity of oxygen was ozonised in suitable apparatus, the volume decreases by 4 ml. On addition of turpentine oil, the volume decreases further by 8 ml. Find the formula of ozone, assuming all measurements are made at same temperature and pressure.

Solution The reaction occurring in the ozonizer is the conversion of oxygen to ozone and the conversion is never 100%. Let the volume of oxygen in the beginning be 'a' ml.

	nO_2	$\rightleftharpoons$	$2O_n$
Initial volume	a		0

Volume after attainment of equilibrium a–n x $\quad$ 2 x

The initial volume reduction is due to reaction alone.

$\therefore$ initial volume – volume at equilibrium = 4 ml

$\therefore$ $a-(a-n\,x+2\,x) = 4$

$$n\,x - 2\,x = 4$$

$$n\,x = 4 + 2\,x \qquad \text{---------- (i)}$$

The second decrease in volume is due to absorption of ozone by turpentine oil.

$\therefore$ $2\,x = 8$ and $x = 4$

Putting the value of x in equation (i)

$\therefore$ $n\,x = 4+8 = 12 \qquad n = \frac{12}{4} = 3$

$\therefore$ **Molecular formula of ozone is O_3.**

78. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. (State whether true of false) **[IIT-1985]**

Solution **False**: The pressure exerted by the gas is the result of collisions of the molecules on the walls of the container.

79. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is **[IIT-1981]**

(a) 1.086 : 1 (b) 1 : 1.086

(c) 2 : 1.086 (d) 1.086 : 2

Solution (d) Pressure exerted by H_2 is proportional to its mole fraction.

$$\text{Mole fraction of } H_2 \frac{\frac{W}{2}}{\frac{W}{2}+\frac{W}{30}} = \frac{30}{32} = \frac{15}{16}$$

ONE CORRECT OPTION TYPE QUESTIONS

1. The composition of the equilibrium mixture for the equilibrium $Cl_2 \rightleftharpoons 2Cl$ at 1470 K may be determined by the rate of diffusion of the mixture through a pin hole. It was found that at 1470 K, the mixture diffuses 1.16 times as fast as Krypton (atomic weight = 83.8) diffuses under the same conditions. Find the degree of dissociation of Cl_2 at equilibrium.

(a) 0.14 (b) 0.7

(c) 0.3 (d) 0.4

2. A flask contains 10g of a gas (relative molecular mass 100) at a pressure of 100 KPa was evacuated to a pressure of 0.01 KPa at constant temperature. Which one of the following is the best estimate of the number of molecules left in the flask

(a) 6.02×10^{16} (b) 6.02×10^{17}

(c) 6.02×10^{18} (d) 6.02×10^{19}

3. Two gases A and B present separately in two vessels X and Y at the same temperature with molecular weights M and 2 M respectively are effused out. The orifice in vessel X is circular while that in Y is a square. If the radius of the circular orifice is equal to that of the length of the square orifice, the ration of rates of effusion of gas A to that of gas B is

(a) $\sqrt{2\pi}$ (b) $\sqrt{\frac{\pi}{2}}$

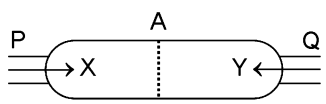
(c) 2π (d) $\sqrt{\frac{2}{\pi}}$

4. A compound exists in the gaseous state both as monomer (F) and dimer (A_2). The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in vessel of volume 33.6 L and heated to 273°C. Calculate the pressure developed, if the compound exists as a dimer to extent of 50% by weight under these conditions.

(a) 7.5 atm (b) 2.0 atm

(c) 0.9 atm (d) 5.4 atm

5. 1 mole of gas "X" and 2 moles of gas "Y" enters from the end "P" and "Q" of the cylinder respectively. The cylinder has the area of cross-section A, shown as under.



The length of the cylinder is 150 cm. The gas "X" intermixes with gas "Y" at the point A. If the molecular weight of the gases X and Y is 20 and 80 respectively, then what will be the distance of point A from Q?

(a) 75 cm (b) 50 cm

(c) 100 cm (d) 90 cm.

$\Rightarrow$ distance of A from point Q = 75 cm.

6. The density of the gaseous mixture in a vessel (CH_4 and He) at 2 atmosphere pressure and 300 K is 0.9756 g/liter. If a small pin-hole is made on the wall of the vessel, through which gases effuse, then which of the followings is the correct composition of the gases CH_4 and He effusing out initially?

(a) 1 : 1 (b) 2 : 1

(c) 3 : 1 (d) 1 : 4.

7. If the critical temperature of the gas be $T_C = \frac{8a}{27Rb}$ and T_B is the Boyle's temperature, then which of the following is the correct relation between T_C and T_B?

(a) $T_C = \frac{8}{27} T_B$ (b) $T_C = \frac{27}{8} T_B$

(c) $T_C = \frac{4}{27} T_B$ (d) $T_C = \frac{27}{4} T_B$

8. What will be the percentage of 'free volume' available in 1 mole of H_2O (g) at 760 mm and 373 K? Density of H_2O (l) at 373 K is 0.953 g/ml.

(a) 0.0613% (b) 99.9386%

(c) 0.0543 (d) 99.9457%

9. A flask containing air (open to the atmosphere) is heated from 300 K to 500 K. Then % of air escaped to the atmosphere is

(a) 20.0 (b) 40

(c) 60 (d) 80.

10. Two vessels of volume 2V and 3V contain two gases A and B separately at 1.5 and 4 atm respectively. If the vessels are connected through a tube (negligible volume) at constant temperature, the total pressure of gaseous mixture is

(a) 3 atm (b) 15/2 atm

(c) 5 atm (d) 6 atm

11. 4.0 g of argon (at. mass = 40) in a bulb at a temperature of T K had a pressure P atm. When the bulb was placed in hotter bath at a temperature 50° more than the first one, 0.8 g of gas had to be removed to get the original pressure. T is equal to

(a) 510 K (b) 200 K
(c) 100 K (d) 73 K

12. Ideal gas equation in terms of K.E. per unit volume, E, is
(a) $P = \frac{3}{2} RT$ (b) $P = \frac{2}{3} E$
(c) $P = \frac{2}{3} RT$ (d) $P = \frac{3}{2} E$

13. A quantity of gas is collected in a graduated tube over mercury. The volume of the gas at 20°C is 50.0 mL and the level of the mercury in the tube is 100 mm above the outside mercury level. The barometer reads 750 mm. Volume of the gas at STP is
(a) 40 mL (b) 42 mL
(c) 39.8 mL (d) 60 mL

14. The rate of diffusion of two gases A and B is in the ratio of 1 : 4 and that of B and C in the ratio of 1 : 3 the rate of diffusion of C with respect to A is
(a) $\frac{1}{12}$ (b) 12
(c) 6 (d) 4

15. A mixture of C_3H_8 and CH_4 exerts a pressure of 320 mm Hg at temperature T K in a V litre flask. On complete combustion, gaseous mixture contains CO_2 only and exerts a pressure of 448 mm Hg under identical conditions. Hence mole fraction of C_3H_8 in the mixture is
(a) 0.2 (b) 0.8
(c) 0.25 (d) 0.75

16. The third virial coefficient of a He gas is 4×10^{-2} $(lit/mol)^2$, then what will be volume of 2 mole He gas at NTP?
(a) 22.0 lit (b) 44.0 lit
(c) 44.8 lit (d) 45.3 lit

17. Calculate relative rate of effusion of SO_2 to CH_4, if the mixture obtained by effusing out a mixture with molar ratio $\frac{n_{SO_2}}{n_{CH_4}} = \frac{8}{1}$ for three effusing steps.
(a) 2 : 1 (b) 1 : 4
(c) 1 : 2 (d) none of these

18. 7 moles of a tetra-atomic non-linear gas 'A' at 10 atm and T K are mixed with 6 moles of T another gas B at $\frac{T}{3}$ K and 5 atm in a closed, rigid vessel without energy transfer with surroundings. If final temperature of mixture was $\frac{5T}{6}$ K, then gas B is (Assuming all modes of energy are active)
(a) monoatomic (b) diatomic
(c) triatomic (d) tetra atomic

19. Dalton's law of partial pressure is not applicable to, at normal conditions
(a) H_2 and N_2 mixture
(b) H_2 and Cl_2 mixture
(c) H_2 and CO_2 mixture
(d) H_2 and O_2 mixture

20. Two vessels of volume 2V and 3V contain two gases A and B separately at 1.5 and 4 atm respectively. If the vessels are connected through a tube (negligible volume) at constant temperature, the total pressure of gaseous mixture is
(a) 3 atm (b) 15/2 atm
(c) 5 atm (d) 6 atm

21. Arrange the van der Waals constant for the gases:

I $C_6H_{6(g)}$	A 0.217
II $C_6H_5.CH_{3(g)}$	B 5.464
III $Ne_{(g)}$	C 18.000
IV $H_2O_{(g)}$	D 24.060

(a) I-A, II-D, III-A, IV-B
(b) I-D, II-A, III-B, IV-C
(c) I-C, II-D, III-A, IV-B
(d) I-B, II-C, III-A, IV-D

22. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is
(a) 1.2 atm (b) 2.4 atm
(c) 2.0 atm (d) 1.0 atm

23. Boyle's law may be expressed as
(a) $\left(\frac{dP}{dV}\right)_T = \frac{K}{V}$ (b) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V^2}$
(c) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V}$ (d) none

24. X ml of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is
(a) 10 seconds : He (b) 20 seconds : O_2
(c) 25 seconds : CO (d) 55 seconds : CO_2

25. Under identical conditions of temperature, the density of a gas X is two times that of gas Y while molecular mass of gas Y is three times that of X. The ratio of pressure of X and Y will be
(a) 2/3 (b) 3/2
(c) 6 (d) 3

26. What per cent of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are to be changed from 220°C, 3 atm and 1.65 L to 100 °C, 0.7 atm and 1 L respectively?
(a) 41.4 % (b) 8.18 %
(c) 4.14 % (d) 81.8 %.

27. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is
(a) 1.2 atm (b) 2.4 atm
(c) 2.0 atm (d) 1.0 atm

28. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas, then
(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$
(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\ T(N_2)$

29. X ml of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is
(a) 10 seconds : He
(b) 20 seconds : O_2
(c) 25 seconds : CO
(d) 55 seconds : CO_2

30. The volume of 0-0168 mol of O_2 obtained by decomposition of $KC1O_3$ and collected by displacement of water is 428 ml at a pressure of 754 mm Hg at 25°C. The pressure of water vapour at 25°C is
(a) 18 mm Hg (b) 20 mm Hg
(c) 22 mm Hg (d) 24 mm Hg

31. At which of the four conditions, the density of nitrogen will be the largest?
(a) STP (b) 273 K and 2 atm
(c) 546 K and 1 atm (d) 546 K and 2 atm

32. 5 ml of N HCl, 20 ml of N/2 H_2SO_4 and 30 ml of N/3 HNO_3 are mixed together and volume made one litre. The normality of the resulting solution is
(a) N/5 (b) N/10
(c) N/20 (d) N/40

33. At low pressure, the van der Waals equation is reduced to
(a) $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RTV_m}$
(b) $Z = \frac{pV_m}{RT} = 1 + \frac{b}{RT}p$
(c) $pV_m = RT$
(d) $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RT}$

34. Under idential conditions of pressure and temperature, 4 L of gaseous mixture (H_2 and CH_4) effuses through a hole in 5 min whereas 4 L of a gas X of molecular mass 36 takes to 10 min to effuse through the same hole. The mole ratio of H_2 : CH_4 in the mixture is
(a) 1 : 2 (b) 2 : 1
(c) 2 : 3 (d) 1 : 1

35. The number of molecules in 4.25 g of ammonia is approximately
(a) 0.5×10^{23} (b) 1.5×10^{23}
(c) 3.5×10^{23} (d) 2.5×10^{23}

36. The volume of balloon filled with 4.0 g of He at 22°C and 720 mm of Hg is:
(a) 25.565 litre (b) 20 litre
(c) 15 litre (d) 30 litre

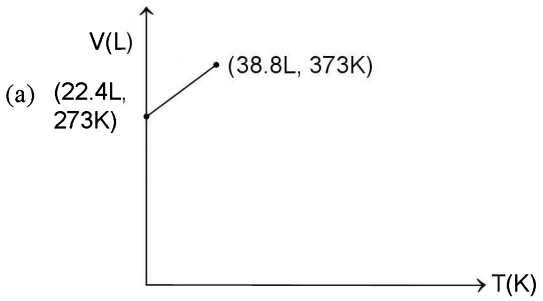
37. A mixture of H_2 and He in 1 : 1 mass ratio is allowed to diffuse through a porous pot. The mole ratio of H_2 to He in the initially effused mixture will be
(a) $2 : \sqrt{2}$ (b) $2\sqrt{2} : 1$
(c) 1 : 2 (d) 1 : 1

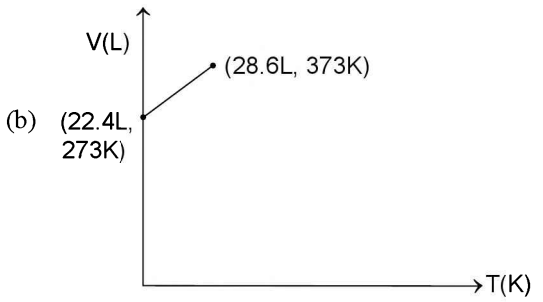
38. The rate of effusion of two gases 'a' and 'b' under identical condition of temperature and pressure are in the ratio of 2 : 1. What is the ratio of rms velocity of their molecules if T_a and T_b are in the ratio of 2 : 1?
(a) 2 : 1 (b) $\sqrt{2} : 1$
(c) $2\sqrt{2} : 1$ (d) $1 : \sqrt{2}$

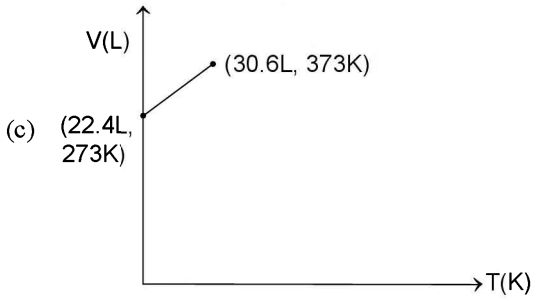
39. Hydrogen gas diffuses four times as rapidly as a mixture of C_2H_4 and CO_2. The molar ratio of C_2H_4 to CO_2 in the mixture is
(a) 1 : 1 (b) 2 : 1
(c) 3 : 1 (d) 3 : 2

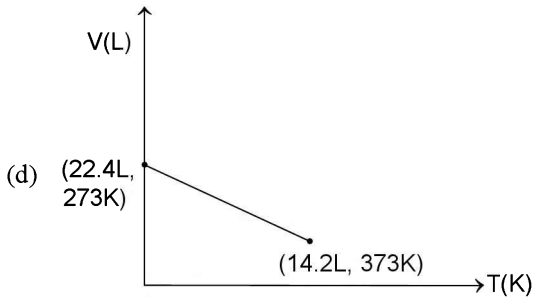
40. Positive deviation from ideal behaviour takes place because of:
(a) Molecular interaction between atoms and PV/nRT > 1
(b) Molecular interaction between atoms and PV/nRT < 1
(c) Finite size of atoms and PV/nRT > 1
(d) Finite size of atoms and PVInRT< 1

41. Which of the following volume (V) – temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?

(a)


(b)


(c)


(d)


42. The density of a gaseous substance at 1 atm pressure and 750 K is 0.30 g/lt. If the molecular weight of the substance is 27 the forces existing among gas molecules is

(a) Attractive (b) Repulsive
(c) Both (a) and (b) (d) None of these

43. Let the most probable velocity of hydrogen molecules at a temperature t°C is V_0. Suppose all the molecules dissociate into atoms when temp is raised to $(2t + 273)$°C, then the new r.m.s velocity is

(a) $\sqrt{2/3}\ V_0$ (b) $2\ V_0$
(c) $2\sqrt{3}\ V_0$ (d) $\sqrt{6}\ V_0$

44. A vessel has N_2 gas and water vapours at a total pressure of 1 atm. The partial pressure of water vapours is 0.3 atm. The contents of this vessel are transferred to another vessel having one third of the capacity of original volume, completely at *v* the same temperature the total pressure of this system in the new vessel is

(a) 3.0 atm (b) 1 atm
(c) 3.33 atm (d) 2.4 atm

ANSWER KEYS

1. (a)	**2.** (c)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (a)	**7.** (a)	**8.** (b)	**9.** (b)	**10.** (a)
11. (b)	**12.** (b)	**13.** (c)	**14.** (b)	**15.** (a)	**16.** (d)	**17.** (c)	**18.** (b)	**19.** (b)	**20.** (a)
21. (c)	**22.** (b)	**23.** (b)	**24.** (b)	**25.** (c)	**26.** (d)	**27.** (b)	**28.** (c)	**29.** (b)	**30.** (d)
31. (b)	**32.** (d)	**33.** (a)	**34.** (d)	**35.** (b)	**36.** (a)	**37.** (b)	**38.** (c)	**39.** (c)	**40.** (a)
41. (c)	**42.** (b)	**43.** (d)	**44.** (d)						

HINTS AND EXPLANATIONS

1. For the equilibrium $Cl_2 \rightleftharpoons 2Cl$

	Cl_2		2Cl
Initial moles	1		0
At equilibrium	1-x		2x

(x is the degree of dissociation) Molecular weight of the mixture of Cl_2 and Cl at equilibrium , i.e., M_{mix} is calculated as

$$M_{mix} = \frac{(1-x)71 + (2x)35.5}{(1-x) + 2x} = \frac{71}{1+x}$$

Now we have, $\frac{r_{mix}}{r_{Kr}} = \sqrt{\frac{M_{Kr}}{M_{mix}}}$

$$\Rightarrow \sqrt{\frac{83.3}{71/(1+x)}} = 1.16 \qquad x = 0.14$$

2. $PV = \frac{w}{M}RT$

$PV = \frac{10}{100}RT$ $P = 100$ kPa

$100 \times V = \frac{RT}{10}$ $V = \frac{RT}{1000}$

At constant T, $P_1 = 0.1$ kPa

$100 \times V = 0.1\ RT$

$0.01 \times V = n_1RT$

$\frac{n_1}{0.1} = \frac{.01}{100}$

$n_1 = 10^{-5}$

1 mole will contain 6.023×10^{23} molecules

$\therefore$ 10^{-5} mole will contain $\frac{6.023 \times 10^{23}}{10^{-5}}$

6.023×10^{18} moles

3. (a) $\frac{r_x}{r_y} = \sqrt{\frac{2M}{M}} \times \frac{A_x}{A_y}$ where A_x and A_y are the area of cross section of orifice

$\therefore$ $\frac{r_x}{r_y} = \sqrt{2} \times \frac{\pi r^2}{\ell^2}$ r = radius of a radius orifice

ℓ = length of square orific

$\frac{r_x}{r_y} = \sqrt{2} \times \pi$

4. Volume = 33.6 L

Temperature = 273 + 273 = 546 K

Molar mass of monomer = 48

Dimer = 96

Mole of monomer = 1

Mole of dimer = 1/2

$PV = N_{mix} \times R \times T$

$P \times 33.6 = 1\ ½ \times 0.0821 \times 546$

$P = \frac{3}{2} \times \frac{0.0821 \times 146}{33.6} = 2.00$ atm

5. (a) $\frac{r_X}{r_Y} = \frac{W_X}{n_Y}\sqrt{\frac{M_Y}{M_X}} = \frac{1}{2}\sqrt{\frac{80}{20}} = 1:1$

$\Rightarrow$ $\frac{\text{distance travelled by gas X}}{\text{distance travelled by gas Y}} = 1:1$

$\Rightarrow$ distance of A from point Q = 75 cms.

6. (a) $\because PM_{mix} = dRT$

$M_{mix}\ \frac{dRT}{P} = \frac{0.9756 \times 0.082 \times 300}{2} \approx 12$

$\therefore$ Let x, y are the moles of He and CH_4 respectively.

$M_{mix} = \frac{x \times 4 + y \times 16}{x + y} = 12$

$\therefore$ $\frac{x}{y} = \frac{1}{2}$ $\because \frac{r_{He}}{r_{CH_4}} = \frac{r_{He}}{r_{CH_4}}\sqrt{\frac{M_{CH_4}}{M_{He}}} = \frac{1}{2}\sqrt{\frac{16}{4}}$

$\therefore$ $\frac{r_{H_e}}{r_{CH_4}} = 1:1$

$\Rightarrow$ $\frac{\text{Vol. of He effused}}{\text{Vol. of } CH_4 \text{ effused}} = 1:1$

7. (a) $\because T_B = \frac{a}{Rb}$ and $T_C = \frac{8a}{27Rb}$ $\therefore \frac{T_C}{T_B} = \frac{8}{27}$

8. (b) Volume occupied by 1 mole of H_2O (g) at 373 K = nRT/P

$= \frac{1 \times 0.0821 \times 373}{1} = 30.62$ L

Volume of 1 mole of H_2O (l)

$= \frac{M}{d} = \frac{18}{0.958} = 18.789$ ml

$\simeq 18.79 \times 10^{-3}$ L

% of volume occupied by liquid water

$= \frac{18.79 \times 10^{-3}}{30.64} \times 100 = 0.0613\%$

% of free volume = 100–0.0613 = 99.9386%

9. (b) $P_1V_1 = n_1RT_1$ and $P_2V_2 = n_2RT_2$

($\because$ P and V are constant)

$\therefore$ $n_1RT_1 = n_2RT_2$

or $n_1T_1 = n_2T_2$

$n_1 \times 300 = n_2 \times 500$

$\therefore$ $n_2 = 3/5\ n_1$

Number of moles escaped = $n_1 - 3/5\ n_1 = 2/5\ n_1$

$\therefore$ % escaped = $2/5 \times 100 = 40\%$

10. (a) $P'V' = P_1V_1 + P_2V_2$

$P \times 5V = 1.5 \times 2V + 4 \times 3V$

$P = 3$ atm.

11. (b) $PV = nRT$ or $PV = \frac{W}{M}RT$ or $WT = \frac{PV.M}{R}$

or $W_1T_1 = W_2T_2$ ($\because$ P and V are constant)

Hence $4 \times T = 3.2 (T + 50)$ or $T = 200$ K

12. (b) $PV = \frac{1}{3} Mu^2$

$PV = \frac{2}{3}.\frac{1}{2} Mu^2$

$PV = \frac{2}{3}$ (K.E.)

$P = \frac{2}{3}\left(\frac{K.E.}{V}\right)$

$P = \frac{2}{3}$ E.

13. (c) $T_1 = 20 + 273 = 293$ K, $T_2 = 273$ K

$V_1 = 50$ mL $V_2 = ?$

$P_1 = 750–100 = 650$ mm Hg; $P_2 = 760$ mm Hg

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{50 \times 650 \times 273}{293 \times 760} = 39.8$ mL

14. (b) $r_A/r_B = \frac{1}{4}$, $r_B/r_C = \frac{1}{3}$

Multiplying the two,

$r_A/r_C = \frac{1}{4} \times \frac{1}{3} = \frac{1}{12}$ or $r_C/r_A = 12$

15. (a) Let V at T K and 320 mm Hg represents 1 mol then V L at T K and 448 mm Hg represents

$= \frac{448}{320}$ mol $= 1.4$ mol

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2(l)$

x mol 3x mol

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 4H_2O(l)$

(1–x) mol (1–x) mol

Let moles of $C_3H_8 = x$

$\therefore$ Moles of $CH_4 = 1 - x$

Moles of CO_2 produced $= 3x + 1–x = 1 + 2x$

$1 + 2x = 1.4$

$2x = 0.4$

$x = 0.2$

Mole fraction of $C_3H_8 = \frac{x}{1} = 0.2$

16. (d) $b^2 = 4 \times 10^{-2}$ (lit/mol)^2

$\Rightarrow$ $b = 2 \times 10^{-1}$ lit/mol

$\therefore$ extended volume for 2 mole real gas

$= 2b = 2 \times 0.2 = 0.4$ lit

$\therefore$ $V_{real} = V_i + nb$

$= 44.8 + 0.4 = 45.3$ lit

17. (c) $\frac{n^3_{SO_2}}{n^3_{CH_4}} = \left(\frac{16}{64}\right)^{3/2} = \frac{1}{1}$; $\frac{r_{SO_2}}{r_{CH_4}} = \frac{1}{1}.\sqrt{\frac{16}{64}} = \frac{1}{2}$

18. (b) C_v of gas A $= \frac{3}{2}R + \frac{3}{2}R + 6R = 9R$

Let C_v of gas B $= X$

Heat lost by gas A $= 7 \times 9R \times \left(T - \frac{5T}{6}\right)$

Heat gained by gas B $= 6X\left(\frac{5T}{6} - \frac{T}{3}\right)$

$\Rightarrow$ $63R\left(\frac{T}{6}\right) = 6X\left(\frac{T}{2}\right) = X = \frac{7}{2}$ R;

$\therefore$ Gas is diaatomic

19. (b) H_2 and Cl_2 reacts to form HCl; Dalton's law of partial pressure is valid only for the gases which don't react at ordinary conditions.

20. $P'V' = P_1V_1 + P_2V_2$

$P \times 5V = 1.5 \times 2V + 4 \times 3V$

$P = 3$ atm.

21. (c)

22. (b)

23. (b) from Boyle's law

$PV =$ constant

$PdV + VdP = 0$

$\left(\frac{dP}{dV}\right) = -\frac{P}{V} = -\frac{K}{V^2}$ ($PV = K$)

24. (b)

25. (c) $P = \frac{dRT}{M}$ $P_x = \frac{d_x RT}{M_x}$ $P_y = \frac{d_y RT}{M_y}$

$\frac{Px}{Py} = \frac{d_x}{d_y} \times \frac{M_y}{M_x} = 6$

26. (d) $n_1 = \frac{3 \times 1.65}{R \times 493}; n_2 = \frac{0.7 \times 1}{R \times 383} \Rightarrow = \frac{n_2}{n_1} = \frac{0.7 \times 1}{R \times 383} \times$

$\frac{R \times 493}{3 \times 1.65} = 0.182$ Fraction remaining

Fraction escaped = $1 - 0.182 = 0.818$

$\Rightarrow$ Percentage escaped = 81.8 %

27. (b)

	$N_2O_4(g)$	$2NO_2(g)$
At start	100/92 mol = 1.08 mol	0
At equilibrium	80/92 mol = 0.86	20/46 mol = 0.43 mol

According to ideal gas equation, at two condition

At 300 K $P_0V = n_0RT_0$

$1 \times V = 1.08 \times R \times 300$ ...(i)

At 600 K $P_1V = n_1RT_1$

$P_1 \times V = (0.86 + 0.43) \times R \times 600$ ...(ii)

Divide (ii) by (i)

$\frac{P_1}{1} = \frac{1.29 \times 600}{1.08 \times 300}; P_1 = \frac{1.29 \times 2}{1.08} = 2.38 \text{atm.}$

28. (c) $\sqrt{\frac{3RT_{H_2}}{2}} = \sqrt{7}\sqrt{\frac{3RT_{N_2}}{28}}$; $\therefore \quad T_{N_2} = 2T_{H_2}$

29. (b) Under identical conditions, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

As rate of diffusion is also inversely proportional to time, we will have, $\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

Thus, For He, $t_2 = \sqrt{\frac{4}{2}}(5s) = 5\sqrt{2}s \neq 10s;$

For $O_2, t_2 = \sqrt{\frac{32}{2}}(5s) = 20s$

For CO, $t_2 = \sqrt{\frac{28}{2}}(5s) \neq 25s;$

For $CO_2, t_2 = \sqrt{\frac{44}{2}}(5s) \neq 55s$

30. (d)

31. (b)

32. (d) Meq. of HCl = 5 × 1 = 5; Meq. Of H_2SO_4 = 20 × (1/2) = 10;

Meq. of HNO_3 = 30 × (1/3) = 10;

Thus, total Meq. of acid = 5 + 10 + 10 = 25

Total volume = 100 mL. Also Meq. = N × V,

$\therefore \quad N = \frac{25}{1000} = \frac{1}{40}$

33. (a) Van der Waals equation is $\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$ = RT

Where $V_m = \frac{V}{n}$ = molar volume. At low pressure

V_m is high and b can be igonered

$\therefore \quad \left(p + \frac{a}{V_m^2}\right)V_m = RT$ or $pV_m + \frac{a}{V_m} = RT$

$\therefore \quad pV_m = RT - \frac{a}{V_m}$ or $\frac{pV_m}{RT} = 1 = \frac{a}{RTV_m}$

or $Z = 1 - \frac{a}{RTV_m}$

34. (d) $\frac{r_{mix}}{r_x} = \frac{4/5}{4/10} = 2 = \sqrt{\frac{M_x}{M_{Mix}}} \Rightarrow M_{mix} = 9\,M_{mix}$

$= M_{H_2}X_{H2} + M_{CH_4}X_{CH_4}$

$= 2X_{H_2} + 16(1 - X_{H_2}) = 9 \Rightarrow X_{H_2} = 0.5$

35. (b) 17 g NH_3 has NB molecules.

36. (a) Use $PV = \frac{w}{m}RT$

37. (b) $\frac{n_{H_2}}{n_{He}} = \frac{1 \times 4}{2 \times 1}\sqrt{\frac{4}{2}} = 2\sqrt{2}$

38. (c) $\frac{r_a}{r_b} = \frac{2}{1} = \sqrt{\frac{M_b}{M_a}}$

$V_{rms} \propto \sqrt{\frac{T}{M}}$ (As $V_{rms} = \sqrt{\frac{3RT}{M}}$)

$\frac{V_{rms(a)}}{V_{rms(b)}} = \sqrt{\frac{T_a}{T_b} \times \frac{M_b}{M_a}} = \frac{2}{1} \times \frac{\sqrt{2}}{1} = \frac{2\sqrt{2}}{1}$

$\therefore \quad 2\sqrt{2} : 1$

39. (c) Effective molar mass of C_2H_2 and CO_2 is given by

$$\frac{r_{H_2}}{r_{mix}} = \sqrt{\frac{M_{eff}}{M_{H_2}}}$$

$$4 = \sqrt{\frac{M_{eff}}{2}}$$

$$M_{eff} = 32$$

$$M_{eff} = X_{C_2H_4}M_{C_2H_4} + X_{CO_2}M_{CO_2}$$

$$= (1 - X_{CO_2})\, M_{C_2H_4} + X_{CO_2}M_{CO_2}$$

$$32 = M_{C_2H_4} + (M_{CO_2} - M_{C_2H_4})\, x_{CO_2}$$

$$= 28 + (44 - 28)\, X_{CO_2}$$

$$X_{CO_2} = \frac{1}{4}$$

$$\therefore \quad X_{C_2H_4} = \frac{3}{4}\frac{X_{C_2H_4}}{X_{CO_2}} = \frac{3}{1}$$

40. (a) For positive deviation Z > 1, i.e., the condition when repulsive forces predominates.

41. (c) Volume of 1 mole of an ideal gas at 273 K and 1 atm is 22.4 L and that at 373 K and 1 atm pressure is calculated as; $V = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.58\,L$

42. $Z = \frac{PV}{nRT} = \frac{PM}{dRT}$

$$= \frac{1 \times 27}{0.30 \times 0.082 \times 750} = 1.46$$

43. $V_0 = \sqrt{\frac{2R(t + 273)}{2}}$

$$V_1 = \sqrt{\frac{3R(2t + 2 \times 273)}{1}}$$

44. (d) $P'_{N_2} + P'_{H_2O} = 1\,atm$

$P'_{H_2O} = 0.3\,atm$

$P'_{N_2} = 0.7\,atm$

Now new pressure of N_2 in another vessel of volume V/3 at same temperature T is given by

$$P''_{N_2} \times \frac{V_1}{3} = 0.7\,V$$

$$\therefore \quad P''_{N_2} = 2.1\ atm$$

since aqueous tension remains constant, and thus total pressure in new vessel

$= P''_{N_2} + P'_{H_2O} = 2.1 + 0.3 = 2.4$ atm

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. According to kinetic theory of gases,
- (a) pressure of the gas molecule is proportional to most probable velocity of the gas molecules.
- (b) The pressure exerted by the gas molecule is proportional to root mean square velocity of the gas molecules.
- (c) The root mean square velocity is directly proportional to square root of the kelvin temperature.
- (d) Kinetic energy of the gas molecule does not depend upon, P, V and molar mass of the gas molecules.

2. Which of the following is correct for diffusion?
- (a) ΔG must be positive
- (b) ΔH must be negative
- (c) ΔS must be positive
- (d) ΔS must be negative

3. At constant volume, for a fixed number of moles of a gas, the pressure of the gas increases with increase in temperature due to
- (a) increase in the average molecular velocity.
- (b) increase rate of collision among molecules.
- (c) increase in molecular attraction.
- (d) decrease in mean free path.

4. Which of the following relationship is/are not true?
- (a) most probable velocity, $V_{mp} = \sqrt{\frac{2RT}{M}}$
- (b) mean velocity, $V_{mean} = \sqrt{\frac{3RT}{M}}$
- (c) compressibility factor, $Z = \frac{RT}{PV}$
- (d) average kinetic energy of a gas = $\frac{1}{2}$ kT.

5. Which of the following statements are correct?

(a) At absolute zero, thermal motion of the molecules of gas ceases to exist.

(b) As temperature increases, the fractions of the molecules having average kinetic energy decreases.

(c) At very high temperature, all real gases show +ve deviation as pressure increases and intermolecular forces of attraction decrease.

i.e., $\left(P+\frac{a}{V^2}\right)(V-b) = RT$ gets converted to $P(V-b) = RT$.

6. Ratio of the rate of diffusion of He and H_2 at 0°C is same to the case:

(a) when temperature is changed to 100°C

(b) when O_2 and CH_4 are taken instead of He and H_2

(c) when volume of the flask is doubled

(d) when CH_4 and O_2 are taken instead of He and H_2

7. The root mean square velocity of an ideal gas in a closed container of fixed volume is increased from 5×10^4 cm s^{-1} to 10×10^4 cm s^{-1}. Which of the following statement correctly explains how the change is accomplished?

(a) By heating the gas, the temperature is doubled

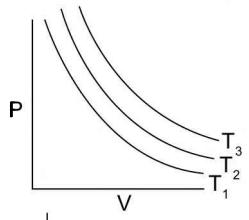
(b) By heating the gas, the pressure is quandrupled (i.e., made four times)

(c) By heating the gas, the temperature is quadrupled

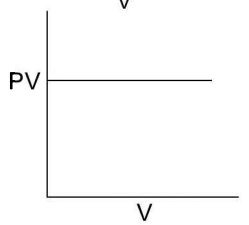
(d) By heating the gas, the pressure is doubled.

8. Which of the following graphs represent Boyle's law?

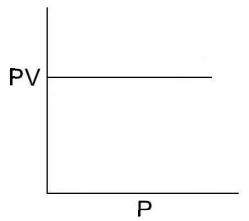
(a)



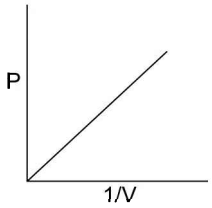
(b)



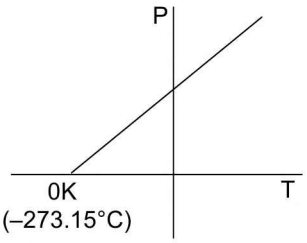
(c)

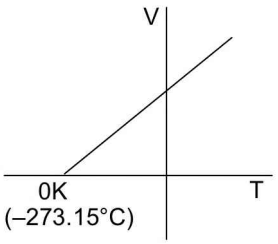


(d)



9. What type of conclusion, you draw from the following graphs?





(a) As the temperature is reduced, the volume as well the pressure is increased.

(b) As the temperature is reduced, the volume becomes zero and the pressure reaches infinit .

(c) As the temperature reduces, both the volume and the pressure decreases.

(d) At 0K temperature, theoretically the volume as well the pressure become zero.

10. Which of the following is the correct for critical temperature?

(a) It is the highest temperature at which liquid and vapour can coexist.

(b) Beyond the critical temperature, there is no distinction between two phases and gas cannot be liquefied by compression.

(c) At critical temperature, the surface tension of the system is zero.

(d) At critical temperature, the gas and the liquid phases have the different critical densities.

ANSWER KEYS

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

HINTS AND EXPLANATIONS

1. (c, d) $P = \frac{1}{3}\frac{M}{V}C^2$; $C = \sqrt{\frac{3RT}{M}}$; $KE = \frac{3}{2}RT$

2. Diffusion being spontaneous process, randomness of the gas molecules increases, thereby ΔS increases.

3. (a, b) With increase in temperature, average velocity of the molecule as well as rate of collision increase.

4. (b, c, d) Compressibility factor, $Z = \frac{PV}{K^{-1}}$

Average K.E. of gas = $\frac{3}{2}$ RT

7. (c) $u = \sqrt{\frac{3RT}{M}}$. u will be doubled when T is made 4 times (at constant volume).

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

Van der Waal's equation of state: Due to following two faulty assumptions of kinetic theory of gases, van der Waal's equation of state for real gases had taken into account. According to kinetic theory of gases:

(a) Volume occupied by a gas molecule is negligible with respect to the volume occupied by the gases or volume of the container.

(b) There does not exist force of attraction among the gas molecules. Thereby, the gas molecules make elastic collision with the wall of the container without loosing the momentum or energy of the gas molecules.

He modified the ideal gas equation by suggesting that the gas molecules are not point mass, but behave like rigid sphere having a certain diameter and a certain intermolecular force of attraction between them. Thereby, he introduced correction term in volume and pressure, are known as volume correction and pressure correction respectively in PV = nRT.

(i) **Pressure correction:** There will be force of attraction between gas molecules due to which gas molecule will collide with the wall of the container with reduced correction in pressure be p. Their ideal pressure.

$P_i = P_0 + P$

$\therefore P \propto \frac{n^2}{V^2}$, where n = number of moles of real gas

V = volume of container

$\Rightarrow P = a\frac{n^2}{V^2}$

$\therefore P_i = P_0 + P = P_0 + \frac{an^2}{V^2}$

Where *a* is known as van der Waal's constant, it measures the amount of force of attraction among the gas molecules. Higher the value of "*a*", higher the force of attraction among the gas molecules, higher will be the ease of liquefication

Gases (in dm^6 atm/mol^2)	Value of "a"
SO_2	6.71
NH_3	4.17
CO	1.49
CO_3	3.59

(ii) **Volume correction:** The volume of the gas molecule which will undergo compression and expansion effect, is known as ideal volume.

$$V_i = V_{real} - nb$$

b is known as excluded volume per mole or, co-volume per mole of gas i.e., volume of the gas molecules when gas molecules are supposed to be a rigid sphere i.e., impenetrable and incompressible sphere.

Therefor, the excluded volume for *n* mole of gas = *nb*,

b signifies the finite size of the gas molecules. So, van der Waal's equation of state for *n* moles real gas will be

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Answer the following questions on the basis of the above write up:

1. If the graph is drawn for 1 mole real gas in such a way, PV is drawn in Y-axis and P in X-axis, then which of the following will be correct value for the intercept of the graph for real gas?

(a) RT (b) $RT + Pb + a$

(c) $RT - Pb + a$ (d) $RT + Pb + ab + a$

2. Berthelot proposed the following empirical relation to explain the real behaviour of the real gases:

$$\left(P + \frac{a^2}{TV^2}\right)(V - b) = RT$$

If the Berthelot equation of state be one of the forms of virial equation for 1 mole real gas is as under:

$$PV = RT\left[1 + \frac{A}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \ldots\ldots\ldots \text{ to higher power of } n\right]$$

where A, B and C are constants which are known as second, third and fourth virial coefficients respectively. Then what will be the correct value of Boyle's temperature i.e., T_B i.e., the temperature at which PV = RT i.e., ideal gas equation is obeyed?

(a) $\frac{a}{Rb}$ (b) $\frac{b}{Ra}$

(c) $\sqrt{\frac{a}{Rb}}$ (d) $\frac{aR}{b}$

3. What will be the value of compressibility factor for real gas at low pressure and high temperature?

(a) $Z \approx 1$ (b) $Z > 1$

(c) $Z < 1$ (d) None.

COMPREHENSION-II

Compressibility factor (Z): Real gases deviate from ideal behaviour due to the following two faulty assumptions of kinetic theory of gases.

(i) Actual volume occupied by the gas molecule is negligible as compared to the total volume of the gases.

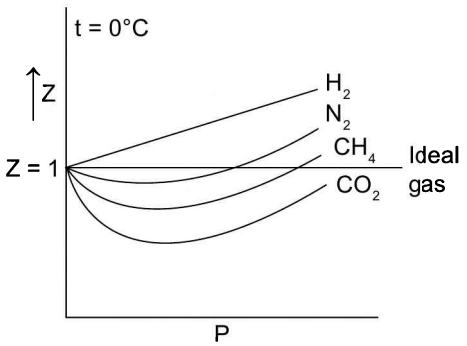
(ii) Forces of attraction and repulsion among the gas molecules are negligible. To explain, the extent of deviation of the real gas from ideal behaviour in terms of compressibility or, compression factor (Z), which is function of pressure and temperature for real gases.

$$Z = \frac{P_0V_0}{nRT} \qquad \text{For ideal gases } Z = 1$$

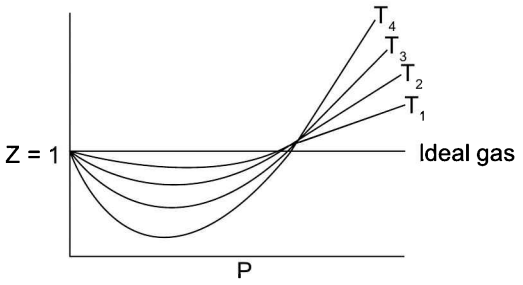
For real gases either $Z > 1$ or $Z < 1$

When $Z > 1$, then it is less compressible because force of repulsion dominates over force of attraction when $Z < 1$, force of attraction dominates over the repulsion and it is more compressible.

Graph in between Z and P is shown as under:



On increasing temperature, Z increases and approaches to unity. Graph between Z and P at different temperature for the same gases are as under:



Answer the following questions on the basis of the write up:

4. What is the correct increasing order of liquefiability of the gases shown as in the above graph?
(a) $H_2 < N_2 < CH_4 < CO_2$
(b) $CO_2 < CH_4 < N_2 < H_2$
(c) $H_2 < CH_4 < N_2 < CO_2$
(d) $CH_4 < H_2 < N_2 < CO_2$.

5. Which of the following is the correct order of temperature shown in the above graph Z vs P for the same gases?
(a) $T_4 > T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3 > T_4$
(c) $T_1 > T_2 > T_4 > T_3$ (d) $T_3 > T_4 > T_2 > T_1$.

6. Which of the following statements is correct for gas A having molar mass 16 g and density 0.75 g/litre at 2 atmospheric pressure and 27° C temperature?
(a) Force of attraction are dominating than force of repulsion among the gas molecules.
(b) Force of repulsion are dominating than force of attraction among the gas molecules.
(c) Gas molecules are behaving ideally.
(d) None of these

COMPREHENSION-III

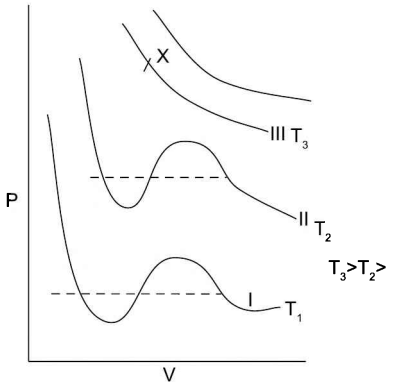
For one mole of a gas, the van der Waal's equation is given by $(P + \frac{a}{V^2})(V - b) = RT$.

This may be written as $PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$.

Multiplying by V^2 and dividing by P and rearranging in decreasing powers of V,

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0$$

This is a cubical equation in V. If at a constant temperature, the values of V are plotted against P then a curve similar to the one marked I in the figure should be obtained.



At the point X, all the three values of V become idential. This volume corresponding to this point is called critical volume, and the pressure is called critical pressure and the temperature is called critical temperature. At this point $V = V_c$ or $(V - V_c) = 0$ or $(V - V_C)^3 = 0$

Expanding and writing in decreasing powers of V, we have,

$$V^3 - 3V^2V_C + 3V_C^2 V - V_C^2 = 0 \quad ...(2)$$

The above equation must be identical with van der Waal's equation at the critical temperature and critical pressure, which for one mole of gas is written as

$$V^3 - \left(b + \frac{RT_C}{P_C}\right)V^2 + \frac{a}{P_C}V - \frac{ab}{P_C} = 0 \quad ....(3)$$

Comparing the coefficients in (2) and (3)

$$3V_C = b + \frac{RT_C}{P_C} \quad ...(4)$$

$$3V_C^2 = \frac{a}{P_C} \quad ...(5)$$

$$V_C^2 = \frac{ab}{P_C} \quad ...(6)$$

Using the above equations, we can obtain relationships between van der Waals' constants and critical constants.

7. The van der Waals' constants of a gas are: a = 0.751 dm^6 atm mol^{-2} and b = 0.0226 $dm^3 mol^{-1}$. Which of the following is correct?
(a) Its critical volume is 0.0678 dm^3 mol^{-1}
(b) Its critical temperature is 160 K
(c) Its critical pressure is 50 atm
(d) All of the above

8. The critical compressibility factor has the value
(a) 1 (b) 1.375
(c) 0.375 (d) 0.5

9. The van der Waals' constant 'b' for gas is 0.0329 dm^3 mol^{-1}. The radius of one molecule is

(a) $\left(\frac{4.096\times10^{-29}}{4\pi}m^3\right)^{1/3}$

(b) $\left(\frac{5.46\times3\times10^{23}}{4\pi}m^3\right)^{1/3}$

(c) $\left(\frac{3\times5.46\times10^{23}}{4}m^3\right)^{1/3}$

(d) $\left(\frac{5.46\times10^{23}}{4\pi}m^3\right)^{3}$

ANSWER KEYS

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

HINTS AND EXPLANATIONS

COMPREHENSION-I

1. (a) For 1 mole of real gas

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

Put $PV = y$ and $P = x$

$\Rightarrow$ $V=\frac{y}{x}$ in eqn. (1), then

So, eqn. (1) reduces into

$y^3 + axy - bxy^2 - abx = RT_{y_2}$

Put $x = 0$,

$\therefore$ $y = RT$

$\therefore$ Intercept on y-axis = RT

2. (c) For 1 mole real gas,

$$\Rightarrow \left(P+\frac{a}{TV_2}\right)(V-b)=RT$$

$$\Rightarrow \left(P+\frac{a}{TV_2}\right)V\left(1-\frac{b}{V}\right)=RT$$

$$\Rightarrow PV+\frac{a}{TV}=\frac{RT}{1-\frac{b}{V}}=RT\left[1-\frac{b}{V}\right]^{-1}$$

$$\Rightarrow PV+\frac{a}{TV}=RT\left[1+\frac{b}{V}+\frac{b^2}{V^2}+\frac{b^3}{V^3}+....\right]$$

$$\Rightarrow PV=RT\left[1+\frac{(b-a/RT^2)}{V}+\frac{b^2}{V^2}+\frac{b^3}{V^3}+....\right]$$

Now $PV = RT\left[1+\frac{A}{V}+\frac{B}{V^2}+\frac{C}{V^3}+....\right]$ ...(1)

$$PV=RT\left[1+\frac{\left(a-\frac{b}{RT^2}\right)}{V}+\frac{b^2}{V^2}+\frac{b^3}{V^3}+....\right] ..(2)$$

Comparing equation (1) and (2), we get

$$A=a-\frac{b}{RT^2}$$

$\therefore$ at Boyle's temperature,

i.e., $T \to T_B$, $A = 0$

$$b-\frac{a}{RT_B^2}=A=0$$

$$\therefore T_B=\sqrt{\frac{a}{Rb}}$$

3. (a) At low pressure and at high temperature $PV \approx RT$

$$\therefore Z\approx\frac{PV}{RT}\approx 1$$

COMPREHENSION-III

7. (a) $V_c = 3b = 3 \times 0.0226 = 0.0678\ dm^3\ mol^{-1}$

$$P_c=\frac{a}{27b^2}=\frac{0.751}{27\times(0.226)^2}=54.5\text{atm}$$

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 0.751}{27 \times 0.082 \times 0.0226} = 120 \text{ K}$$

8. (c) $Z_c = \dfrac{P_c V_c}{RT_c} = \dfrac{\left(\dfrac{a}{27b^2}\right)3(b)}{R\left[\dfrac{8a}{27Rb}\right]} = \dfrac{3}{8} = 0.375$

9. (a) $b = 0.0329 \text{ dm}^3 \text{ mol}^{-1}$

$$b = 4 \times \frac{4}{3}\pi r^3 \times N \quad r = \left(\frac{3b}{N \times 16\pi}\right)^{\frac{1}{3}}$$

$$= \left[\frac{3 \times 0.0329 \times 10^{-3}}{6.023 \times 10^{23} \times 4(4\pi)}\right]^{\frac{1}{3}}$$

$$= \left[\frac{3 \times 3.29 \times 10^{-26}}{6.023 \times 4(4\pi)}\right]^{\frac{1}{3}}$$

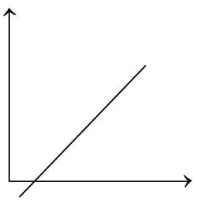
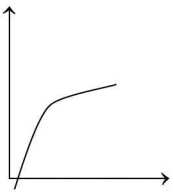
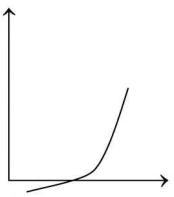
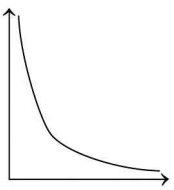
$$= \left[\frac{4.096 \times 10^{-29}}{4\pi}\right]^{\frac{1}{3}} \text{m}$$

MATCH THE COLUMN TYPE QUESTIONS

1. Match gases under specified conditions listed in Column–I with their properties/laws in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

Column-I	**Column–II**
(a) Hydrogen gas (P = 200 atm, T = 273K	(p) Compressibility factor ≠ 1
(b) Hydrogen gas (P~0, T = 273 K)	(q) Attractive forces are dominant
(c) CO_2(P = 1 atm, T = 273 K)	(r) PV = nRT
(d) Real gas with very large molar volume	(s) P(V – nb) = nRT

2.

Column-I	**Column–II**
(a) $\frac{1}{V^2}$ vs P for ideal gas at constant T and n.	(p) 
(b) V vs $\frac{1}{T}$ for ideal gas at constant P and n	(q) 
(c) PT vs T^2 for ideal gas at constant T and n.	(r) 
(d) V vs $\frac{1}{P^2}$ for ideal gas at constant T and n.	(s) 

ANSWER KEYS

1. (a); (p, s) (b); (r) (c); (p, q) (d); (r) **2.** (a); (r) (b); (s) (c); (p) (d); (q)

TRUE/FALSE TYPE QUESTIONS

1. At constant pressure, the mean free path of a molecule of a gas increases with increasing temperature.
2. Kinetic energy of a molecule is zero at 0°C
3. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top.
4. If the root mean square speed of a gas at 300 K is 3 $\sqrt{R}$. The molar mass of gas will be 100 kg/mol.
5. Compressibility factor is constant for a given gas at constant temperature.

ANSWER KEYS

1. T 2. F 3. F 4. T 5. F.

ASSERTION/REASON TYPE QUESTIONS

1. **Assertion:** The diffusion is the spontaneous process of intermixing of the gases against law of gravitation.
   Reason: ΔG for diffusion has positive value.
2. **Assertion:** Most probable velocity is the velocity possessed by maximum fraction of molecules at the same temperature.
3. **Assertion:** CH_4, CO_2 has value of Z (compressibility factor) less than one.
   Reason: $Z < 1$ is due to the attractive forces dominate among the molecules.
4. **Assertion:** Helium shows only positive deviation from ideal behaviour at room temperature.
   Reason: Helium is an inert gas.
5. **Assertion:** A lighter gas diffuses more rapidly than a heavier gas.
   Reason: At a given temperature, the rate of diffusion of a gas is inversely proportional to the density.
6. **Assertion:** The gases He and H_2 are very different in their behaviour at any temperature and pressure but their compressibility factors are nearly the same at the critical point.
   Reason: They have nearly the same critical constant.
7. **Assertion:** The compressibility factor for ideal gas is independent of P and T.
   Reason: Z for ideal gas is one at any pressure and at any temperature.
8. **Assertion:** On increasing the temperature, the height of the peak of the Maxwell distribution curve decreases.
   Reason: The fraction of molecules is very less at the higher velocities.
9. **Assertion:** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
   Reason: The volume occupied by the molecules of an ideal gas is zero.
10. **Assertion:** The value of the van der Waals' constant' a' is larger for ammonia than for nitrogen.
    Reason: Hydrogen bonding is present in ammonia.

ANSWER KEYS

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

SUBJECTIVE QUESTIONS

1. An iron pipe 3 m long closed at one end is lowered vertically into water until the close end is flushed with water. Calculate the height of the water level in the pipe. Given diameter of the pipe = 2 inches.
   density of water = 1×10^3 k.g.m^{-3}
   pressure = 1×10^5 Pa = 10 m (hydrostatic head of water), Temperature is kept constant.
2. 0.22 g of a sample of a volatile compound containing C, H and Cl only yielded on combustion in O_2 0.195 g of CO_2 and 0.0804 g of H_2O. 0.12 g of the compound occupied a volume of 37.24 ml at 105°C and 768 mm Hg pressure. Calculate the molecular formula of the compound.
3. The solubility of oxygen, nitrogen and CO at 15°C, 760 mm pressure are 0.048, 0.022 and 0.03 per litre of water respectively. A mixture containing 10% O_2, 70% N_2 and 20% CO at a pressure of 740 mm is bubbled through 200 ml water at 15°C. What weight of each gas is dissolved?
4. Inside the spherical glass flask A of radius 1 m containing 300 g of H_2 there was a rubber balloon B containing some N_2. Inside the balloon B was another rubber balloon C containing some O_2. At 27°C it was found that the balloon B had a radius of 60 cm and balloon C had a radius of 30 cm. Calculate total weight of gases inside the flask. If another 50 g of H_2 was not introduced in flask A, what would be the volume of B and C. If the flask is now dipped in a bath containing acetone and dry ice (–78°C) for sufficient time, the temperature of the entire contents would react at this temperature. Assuming that at this temperature rubber cracks up and both the balloons burst what would be pressure inside flask
5. Find out the percentage of molecule in a gas at 1 atm and 27°C whose kinetic energy lines in the range of E and E + 0.01E.
   [Where, $E = \frac{3}{2}KT$]

HINTS AND EXPLANATIONS

1. Since temperature is constant.
   $P_f V_f = P_{in} V_i$
   $$P_f = P_{in} \frac{3 \times \text{area of the pipe}}{h \times \text{area of the pipe}} = \frac{3P_{in}}{h}$$
   But by the problem, $P_f = P_{in} + 10$ m
   $$\therefore \quad h + 10 = \frac{3 \times 10}{h}$$
   i.e., $h^2 + 10h - 30 = 0 \quad \therefore \quad h = \frac{-10 + \sqrt{10^2 + 120}}{2}$
   = 2.4161985 m = 2.4 m
   The pipe is 3 m long. Hence water level would rise up 0.6 m in the pipe (3–24) = 0.6)
2. On combustion in O_2 all carbon and hydrogen atms of the compound are converted into CO_2 and H_2O respectively.
   44 g CO_2 having 12 g C
   $\therefore$ 0.195 g CO_2 having 0.0531 g C
   Similarly, 0.0804 g H_2O contain 0.0089 g H_2.
   Hence, 0.22 g compound contain 0.0531 g C, 0.0089 g H_2 and 0.158 g H_2
   $\therefore$ % of C = 24.13%; H = 4.04% Cl = 71.8%
   $$\frac{V \times 760}{273} = \frac{37.2 \times 768}{378}$$
   or V weights = 12 g
   22400 ml weights 98.5 g
   The empirical formula is CH_2Cl
   Molecular formula $(CH_2Cl)_n$
   Let volume of 0.12 g compound occupies V ml at N.T.P. then
   Molecular weight = 98.5
   $\therefore$ 12 n + 2n + 35.5 n = 49.5n = 98 or n = 2
   $\therefore$ molecular formula = $C_2H_4Cl_2$
3. Applying $PV = nRT = \frac{m}{M}RT$
   or $P = \left(\frac{m}{V}\right)\frac{RT}{M} = \frac{SRT}{M}$ where S = solubility
   $\therefore \quad \frac{P}{S} = \frac{RT}{M}$ = constant for a gas at a given temperature

$\therefore \quad \frac{P_1}{S_1} = \frac{P_2}{S_2}$

Given that $P_1 = 760$ mm, $P_2 = 740$ mm

$$S_2 = \frac{S_1 \times 740}{760} = 0.97S_1$$

For oxygen solubility at 740 mm = $0.97 \times 0.048 = 0.0465$ g ml^{-1}

$= 0.0465$ g ml^{-1}

For nitrogen solubility at 740 mm = $0.97 \times (0.02)^2 = 0.0213$ g ml^{-1}

For CO solubility at 740 mm = $0.97 \times 0.03 = 0.029$ g ml^{-1}

$\therefore$ Amount of O_2 dissolved in 200 ml of water $= (0.0465 \times 0.2) = 0.0093$ g ml^{-1}

Amount of N_2 dissolved in 200 ml of water = $0.0213 \times 0.2 = 0.00426$ g ml^{-1}

Amount of CO dissolved in 200 ml of water = $0.029 \times 0.2 = 0.0058$ g ml^{-1}

4. Volume of flask A = $\frac{4}{3}\pi(1)^3 = \frac{4}{3}\pi$

Volume of balloon B = $\frac{4}{3}\pi\left(\frac{60}{100}\right)^3 = 0.216 \times \frac{4}{3}\pi$

Volume occupied by H_2 in A = $\frac{4}{3}\pi - \frac{4}{3} \times 0.216\pi$

$= 3.284$ m^3 $= 3284$ lit

Pressure in A = $\frac{150 \times 0.082 \times 300}{3284} = 1.123$ atm

Pressure in B = 1.123 atm

Volume of N_2 in B = $\frac{4}{3}\pi\left(\frac{60}{100}\right)^3 - \frac{4}{3}\pi\left(\frac{30}{100}\right)^3$

$= 0.7917$ m^3 $= 791.7$ lit

Moles of N_2 = $\frac{1.123 \times 791.7}{0.082 \times 300} = 36.14$

Mass of N_2 = $(36.14 \times 28) = 1011.92$ g

Mass of O_2 in C = $\frac{1.123 \times 113.09 \times 32}{0.082 \times 300} = 165.12$ g

Total weight of all the gases $(165.2 + 300 + 1011.92)$ g $= 1477.12$ g

Total pressure inside the flask of –78°C after the balloon cracks up

$$= \frac{(150 + 36.14 + 5.16) \times 0.082 \times 195}{\frac{4}{3}\pi \times 1000} = 0.73 \text{ atm}$$

5. We have,

$$E = \frac{3}{2}KT = \frac{3}{2} \times 1.38 \times 10^{-16} \times 300$$

$= 6.2 \times 10^{-14}$ ergs

$dE = 0.01\ E = 6.2 \times 10^{-16}$ ergs

$$\frac{dnE}{n} = 2\pi\left(\frac{1}{\pi kt}\right)^{3/2} E^{1/2} e^{-EK/T} dE$$

$$= 2 \times 3.4 \times \left(\frac{1}{3.14 \times 1.38 \times 10^{-16} \times 300}\right)^{3/2}$$

$$\times (6.2 \times 10^{-14})^{1/2} \times e^{-3/2} \times (6.2 \times 10^{-16})$$

$= 0.0046 \therefore 46\%$

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

1. Flask A of volume 10 liter containing 20 gram of H_2 and flask B of volume 10 litre containing 88 gram CO_2 are connected by a connector having negligible volume. When valve of the connector is opened what is the composition of H_2 gas in flask B after openening the valve.

(a) 10% (b) 13%
(c) 15% (d) 20%

2. Consider the reaction, $2X(g) + 3Y(g) \rightarrow Z(g)$
Where gases X and Y are insoluble and inert to water and Z form a basic solution. In an experiment 3 mole each of X and Y are allowed to react in 15 litre flask at 500 K. When the reaction is complete, 5 litre of water is added to the flask and temperature is reduced to 300 K. The pressure in the flask is (neglect aqueous tension)

(a) 1.64 atm (b) 2.46 atm
(c) 4.92 atm (d) 3.28 atm

3. Three gases A, B and C are at same temperature. If their r.m.s speed are in the ratio $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ then their molar masses will be in the ratio

(a) 1 : 2 : 3 (b) 3 : 2 : 1
(c) $1 : \sqrt{2} : \sqrt{3}$ (d) $\sqrt{3} : \sqrt{2} : 1$

4. There are n containers having volumes V, 2V, ……, nV. A fixed mass of a gas is filled in all containers connected with stopcock. All containers are at the same temperature. If pressure of first container is P then final pressure when all stopcocks are opened is:

(a) $\frac{np}{n(n+1)}$ (b) $\frac{2np}{n(n+1)}$

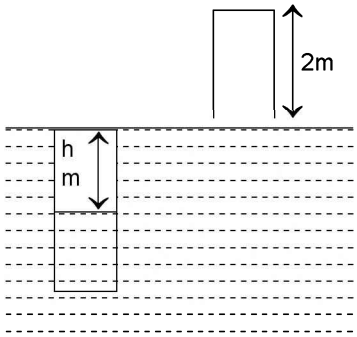
(c) $\frac{3np}{n(n+1)}$ (d) $\frac{np}{2n(n+1)}$

5. A mixture of two gases A and B in the mole ratio 2 : 3 is kept in a 2 litre vessel. A second 3 litre vessel has the same two gases in the mole ratio 3 : 5. Both gas mixtures have the same temperature and same total pressure. They are allowed to intermix the final temperature and total pressure are the same as the initial values, the final volume being 5 litres. Given that the molar masses are M_A and M_B, what is the mean molar mass of the final mixture?

(a) $\frac{77M_A + 123M_B}{200}$ (b) $\frac{123M_A + 77M_B}{200}$

(c) $\frac{77M_A + 123M_B}{250}$ (d) $\frac{123M_A + 77M_B}{250}$

6. A 2 m long tube closed at one end is lowered vertically into water until the closed end is flush with the water surface, see figure below. Calculate the water level height in the tube. (Barometric pressure –1 atm = 10 m of hydrostatic water head, Temperature = 25°C, Density of water = 1.00 g/ml. Neglect water vapour pressure).



(a) 1.01 m (b) 0.29 m
(c) 1.71–m (d) 0.92 m

7. At a certain temperature for which RT = 25 lit. atm. mot^{-1}, the density of a gas, in gm lit^{-1}, is $d = 2.00\ P + 0.020\ P^2$, where P is the pressure in atmosphere. The molecular weight of the gas in gm mot^{-1} is

(a) 25 (b) 50
(c) 75 (d) 100

8. Given the value of their Van der Wails' constant 'a', arrange the following gases in the order of their expected liquifi ation pressure at a temperature T. T is below the critical point of all the gases.

Gas	CH_4	Kr	N_2	Cl_2
'a' ($atmL^2.\ Mol^{-2}$)	2.283	2.439	1.408	6.579

(a) $CH_4 < Kr < N_2 < Cl_2$
(b) $N_2 < CH_4 < Kr < Cl_2$
(c) $Cl_2 < Kr < CH_4 < N_2$
(d) $Cl_2 < N_2 < Kr < CH_4$

9. The Van der Waal's constant 'b' for N_2 and H_2 has the values 0.039 lit $moil^{-1}$ and 0.0266 lit $mo1^{-1}$. The density of solid N_2 is 1 g cm^{-3}. Assuming the molecules in the solids to be close packed with the same percentage void, the density of solid H_2 would be (in g cm^{-3})
(a) 0.114 (b) 0.682
(c) 1.466 (d) 0.071

10. Which of the following statements is not true?
(a) The ratio of the mean speed to the rms speed is independent of the temperature.
(b) The square of the mean speed of the molecules is equal to the mean squared speed at a certain temperature.
(c) Mean kinetic energy of the gas molecules at any given temperature is independent of the mean speed.
(d) The difference between rms speed and mean speed at any temperature for different gases diminishes as larger if larger molar masses are considered.

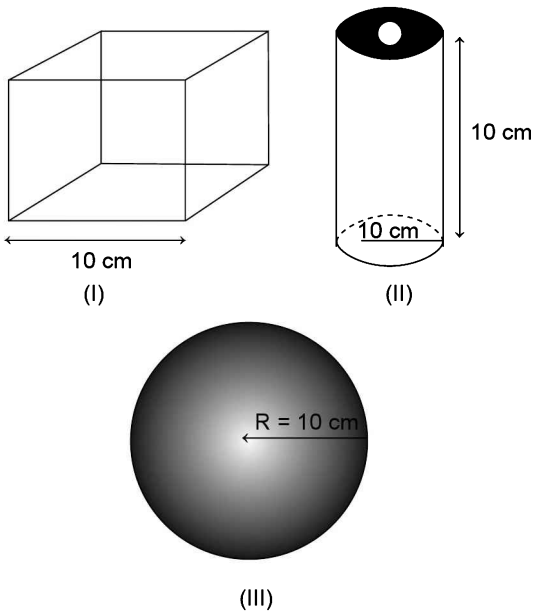
11. If the number of molecules of SO_2 (molecular weight = 64) effusing through an orifice of unit area of cross-section in unit time at 0°C and 1 atm pressure is n, the number of He molecules (atomic weight = 4) effusing under similar conditions at 273°C and 0.25 atm is
(a) $\frac{n}{\sqrt{2}}$ (b) $n\sqrt{2}$
(c) 2n (d) $\frac{n}{2}$

12. A capillary tube of uniform diameter contains gas samples A and B, separated by a short column of Hg, ℓ mm in length. The ends are sealed. In horizontal position, the confined gases occupy 'a' mm and 'b' mm in length with a common unknown pressure (P). In vertical position, the lengths become respectively a' mm and b' mm. Then P is equal to
(a) $\frac{1}{\left(\frac{b}{b'}-\frac{a}{a'}\right)}$ (b) $\frac{1}{\left(\frac{a}{a'}-\frac{b}{b'}\right)}$
(c) $\ell\left(\frac{a}{a'}-\frac{b}{b'}\right)$ (d) $\ell\left(\frac{b}{b'}-\frac{a}{a'}\right)$

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

13. Which of the following statements are correct
(a) Average velocity of molecules of a gas in a container is zero.
(b) All molecules in a gas are moving with the same speed.
(c) If an open container is heated from 300 K to 400 K the fraction of air which goes out with respect to originally present is $\frac{1}{4}$.
(d) If compressibility factor of a gas at STP is less than unity then its molar volume is less thin 22.4 L at STP.

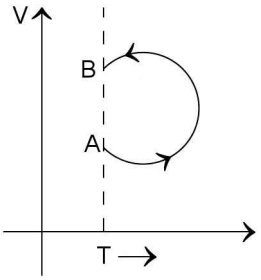
14. There are three closed containers in which equal amounts of the gas are filled



If the containers are placed at the same temperatures then find the correct options:

(a) Pressure of the gas is minimum in (III) container
(b) Pressure of the gas is equal in (I) and (II) containers
(c) Pressure of the gas is maximum in (I)
(d) The ratio of pressure in II and III containers is 3: 4

15.



With reference to the above graph, choose the correct alternatives

(a) $P_B > P_A$
(b) $P_A > P_B$
(c) Pressure first increases then decreases
(d) Pressure first decreases then increases

16. **Statement-1:** At constant temperature of pressure on the gas is doubled, density is also doubled.
Statement-2: At constant temperature, molecular mass of a gas is directly proportional to the density and inversely proportional to the pressure.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

17. **Statement-1:** At Boyle's temperature a real gas behaves as ideal gas for wide range of temperature and pressure.
Statement-2: At Boyle's temperature vanderwaal constants 'a' and 'b' compensate each other.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statment-1 is False, Statement-2 is True.

18. **Statement-1:** The greater is critical temperature the more easily a gas can be liquified
Statement-2: Critical temperature depends on the magnitude of intermolecular forces of attraction between the gas.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

TRUE AND FALSE TYPE QUESTIONS

19. The correct order of True/False of the following statements is:
S_1: Rate of diffusion and effusion of a gas increases by increasing the pressure and decreasing the temperature.
S_2: An ideal gas has Vander Wail's constant a and b equal to zero.
S_3: If an ideal gas is expanded adiabatically against a constant pressure, then $TV^{\gamma-1}$ = constant

(a) TTF
(b) FFT
(c) TTT
(d) FFF

COMPREHENSION BASED QUESTIONS

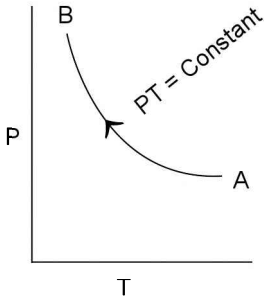
COMPREHENSION-3

When a sample of ideal gas is changed from an initial state to a final state, various curves can be plotted for the process like P – V curve, V – T curve, P – T curve etc.

For example, P – V curve for a fixed amount of an ideal gas at constant temperature is a rectangular hyperbola, V – T curve for a fixed amount of an ideal gas at constant pressure is a straight line and P – T curve for a fixed amount

of an ideal gas at constant volume is again a straight line. However, the shapes may vary if the constant parameters are also changed.

Now, answer the following questions:



20. Which of the following statements is correct regarding a fixed amount of ideal gas undergoing the following process:

(a) Root mean square (RMS) speed of gas molecules increases during the process A → B.

(b) Density of the gas increases during the process A → B.

(c) Such a graph is not possible.

(d) If $P_{BS} = PA$, then $V_A = 4V_B$ (where P_A, V_A, P_{BS} and V_B represent pressure and volume values at states A and B).

21. Two moles of an ideal gas are changed from its initial state (16 atm, 6L) to final state (4 atm, 15L) in such a way that this change can be represented by a straight line in P – V curve. The maximum temperature attained by the gas during the above change is: (Take $R = \frac{1}{12}$ L atm K^{-1} mol^{-1})

(a) 324 K

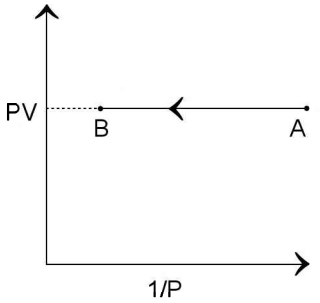
(b) 648 K

(c) 1296 K

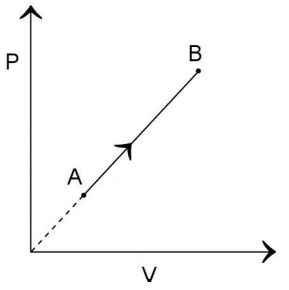
(d) 972 K

22. Which of the following graphs is not possible for a fixed amount of ideal gas upon moving from initial state A to final state B:

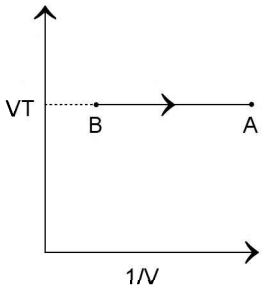
(a)



(b)



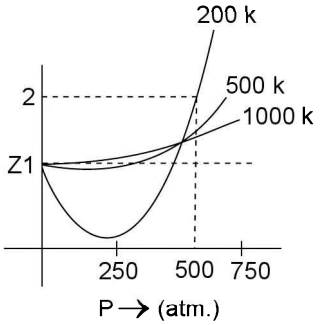
(c)

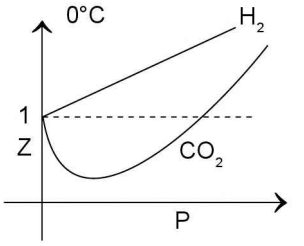


(d) None of these

COMPREHENSION-5

Sketch shows the plot of Z v/s P for of a hypothetical gas for one mole at three distinct temperatures.





Boyle's temperature is the temperature at which a gas shows ideal behaviour over a pressure range in the low pressure region. Boyle's temperature $(T_b) = \frac{a}{Rb}$. If a plot is obtained at temperatures well below Boyle's temperature then the curve will show negative deviation, in low pressure region and positive deviation in high pressure

region. Near critical temperature the curve is more likely as CO_2 and the temperature well above critical temperature curve is more like H_2 at 0°C as shown above. At high pressure suppose all the constant temperature curve varies linearly with pressure according to the following equation:

$$Z = 1 + \frac{pb}{RT} \quad (R = 2 \text{ cal mol}^{-1} \text{K}^{-1}).$$

23. Which of the following is correct:

(a) $\frac{a}{b} < 0.4$ k cal mol^{-1}

(b) 0.4 k cal mol$^{-1} < \frac{a}{b} < 2$ k cal mol^{-1}

(c) $\frac{a}{b} < 0.4$ k cal mol^{-1}

(d) $\frac{a}{b} = 1$ K Cal mol^{-1}

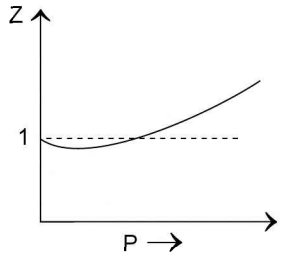
24. For 500 K, plot value of Z changes from 2 to 2.2, if pressure is varied from 1000 atm to 1200 atm (high pressure) then, the value of $\frac{b}{RT}$ will be

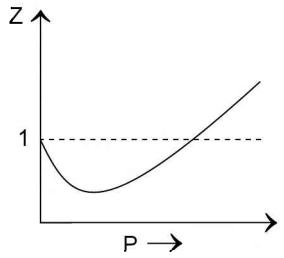
(a) 10^{-3} atm^{-1}
(b) 2×10^{-3} atm^{-1}
(c) 5×10^{-4} atm^{-1}
(d) 10^{-4} atm^{1}

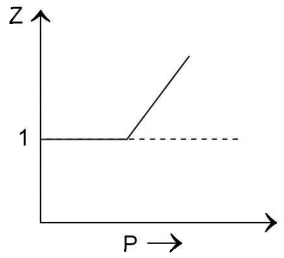
25. As shown in the figure, at 200 K and 500 atm, the value of compressibility factor is 2 (approx). Then the volume of the gas at this point will be

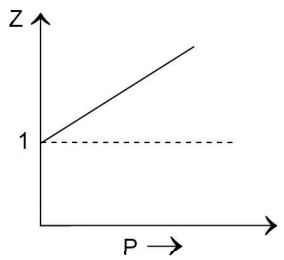
(a) 0.01 L
(b) 0.09 L
(c) 0.065 L
(d) 0.657 L

26. Plot at Boyle's temperature for the gas will be

(a)


(b)


(c)


(d)


MATCH THE COLUMN TYPE QUESTIONS

27. Match the following:

Column-I	**Column-II**
(a) H_2 (a = 0.244 litre^2-atm mole^{-2}; b = 0.02 litre mole^{-1})	(p) Maximum boiling point
(b) He (a = 0.03412 litre^2-atm mole^{-2}; b = 0.02370 litre mole^{-1})	(q) Minimum boiling point
(c) CO_2 (a = 3.592 litre^2-atm mol^{-2}; b = 0.0426 litre mole^{-1})	(r) Critical temperature < Boyle temp.
(d) H_2O (a = 5.464 litre^2-atm mol^{-2}; b = 0.03049 litre mole^{-1})	(s) Minimum critical temperature

28.

Column I	Column II
(a) An unknown gas at STP having	(p) Behaves as an ideal gas Boyle's temperature 0°C
(b) He gas at NTP having density less molecules than $\frac{1}{5.6}$ g/L.	(q) Attractive tendencies are dominant between
(c) H_2 gas at NTP	(r) Gas is less compressible with respect to an ideal gas
(d) O_2 gas at NTP having density $\frac{10}{7}$ g/L.	(s) For gas, Critical temperature < Boyle's temperature
	(t) Molar volume of gas is greater than 22.4 L

29. Match the column:
Assume the gas to be ideal and match the following:

Column-I	Column-II
(a) K.E. of 4 gram of Helium molecule	(p) $\frac{5}{2}$ R
(b) Increase in the energy of 32 gram of oxygen Molecule on raising temperature	(q) 3 R
(c) Increase in energy of 1 mole of NO_2 on raising Temperature by 1°C at constant volume	(r) 4 R
(d) Increases in energy of 1 mole of NO_2 on raising Temperature	(s) 1.5 RT

SUBJECTIVE TYPE QUESTIONS

SHORT SUBJECTIVE

30. Calculate the change in pressure (in atm) when 2 mole of NO and 16 g O_2 in a 6.25, litre originally at 27°C, react to produce the maximum quantity of NO_2 possible according to the equation.
(Take R = $\frac{1}{12}$ ltr. Atm/mol K)

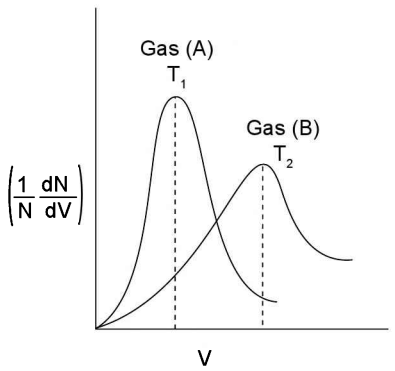
$2NO(g) + O_2(g) \rightarrow 2NO(g)$

31. 2 moles of Ne gas and 5 moles of He gas, both samples having average velocity 7×10^2 mIs, are mixed. Find the average translational kinetic energy per mole of the given gas mixture (in joules). Report your answer as 'X' where X = (Average translational KE in joules) X 0.002. The reported answer should be upto nearest integer.

32. A 1L gas mixture of CO, CO_2 and N_2 was mixed with 1L O_2 and allowed to burn completely. The product gas mixture, when passed subsequently through KOH solution and alkalline pyragallol solution, suffered a total contraction of 1.6 L. On the other hand, if the product gas mixture was mixed with excess of CO gas and again allowed to burn, the new product mixture suffered a contraction of 2.3 L on passing through KOH solution. Find the volume per cent of CO in the initial mixture. Report your answer as 'Y' where Y = (Volume per cent of CO)/10.

33. A flask of 8.96 litre capacity contains a mixture of N_2 and H_2 at 273 K and 1 atm pressure. If the mixture is made to react to form NH_3 gas at the same temperature, the pressure in the flask reduces to 0.85 atm. Find the partial pressure of NH_3 gas in the final mixture in atm. Report your answer as 'y' where y = (Partial pressure of NH_3) × 20.

34. According to Maxwell's distribution of molecular speeds, the following graph has been drawn for two different samples of gases A and B at temperature T_1 and T_2 respectively. Then, give the correct set of incorrect statements: Report your answer as sum of the numbers of incorrect statements.
For example, if statements (1) and (2) are incorrect, then report answer as (1 + 2) = 3.



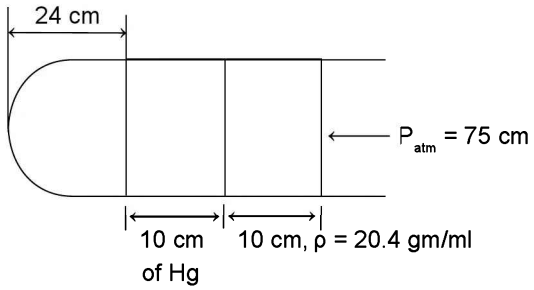
(1) If $T_1 = T_2$, then gas B can be SO_2 and gas A can be CO_2.
(2) If gases A and B are CO_2 and N_2O, then $T_1 > T_2$.
(3) If $T_1 < T_2$, then gases A and B cannot be CO_2 and SO_2 respectively.
(4) None of these

35. A vessel contains two gases A and B in the mass ratio 2 : 1 respectively. If the above gas mixture is allowed to diffuse through a hole, the molar composition of the mixture coming initially out of the hole is 1 : 4. Find the simplest whole number ratio of the mole fractions of gases A and B present in the vessel in the beginning respectively. If the simplest whole number ratio is a : b, then report your answer as 'X' where

$$X = \left(\frac{a}{b}\right) \times 6$$

LONG SUBJECTIVE

36.



If above tube is placed vertically with the open end upward, then find the length of the air column.

37. The pressure exerted by 12 g of an ideal gas at temperature t° C in a vessel of volume V litre is one atm . When the temperature is increased by 10 degree at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Molecular weight of the gas = 120)

38. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 Kg m^{-3}.The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same conditions.

Determine (i) molecular weight (ii) molar volume (iii) compression factor(z) of the vapours and (iv) which forces among gas molecules are dominating the attractive or repulsive.

If the vapours behave ideally at 1000 K determine the average translational kinetic energy of a molecule

ANSWER KEYS

1. (b)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (c)	**9.** (a)	**10.** (b)
11. (a)	**12.** (a)	**13.** (a, c, d)	**14.** (a, c, d)	**15.** (b, c)	**16.** (d)	**17.** (a)	**18.** (a)	**19.** (a)	**20.** (b)
21. (b)	**22.** (d)	**23.** (b)	**24.** (a)	**25.** (c)	**26.** (c)	**27.** (a – r), (b – q, r, s), (c – r, s, t), (d – p, s)			
28. (a –p, s), (b – r, s, t), (c – r, s, t), (d – p, s)			**29.**(a – s), (b – p), (c –q), (d – r)			**37.** 100K, 0.82 litre		**38.** (a, b)	

HINTS AND SOLUTIONS

1. (b) Thermo state at 500 K Thermo state at 200 K

Number of mole of H_2 in flask A = $\frac{20}{2}$ = 10 mole

Number of mole of CO_2 in flask B = $\frac{88}{2}$ = 2 mole

Now pressure of Gas in flask A

$PV = nRT$

$P_A \times 10 = 10 \times R \times 500$

$P_A = 500\ R$

Now pressure of Gas in flask

$P_B \times 10 = 2 \times R \times 200$

$P_B \times 40R$

Because flask A is on higher pressure that is why H_2 is flown from flas A to flask B

Let us suppose x mole of H_2 move from flask A to B.

So mole of H_2 remain in A = (10 – x) and total mole in B = (2 + x)

Now after opening stop cock pressure of both flasks become equal.

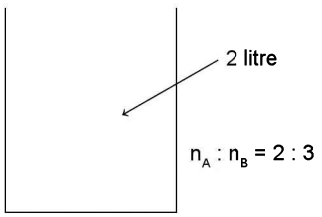
$n_A T_A = n_B T_B$

$(10 - x) \times 500 = (2 + x) \times 200$

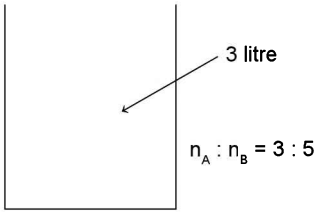
$x = 6.57$

Composition of H_2 in B = $\frac{6.57 \times 2}{101.14} \times 100 = 13\%$.

3. (a)



4. (b)



5. (a)

$\frac{n_A}{n_B} = \frac{2}{3}$ $\qquad$ $\frac{n_{A'}}{n_{B'}} = \frac{3}{5}$

$n_A = 2/3\ n_B$ $\qquad$ $n_{A'} = 3/5\ n_{B'}$

Put the value of $n_{A'}$, $n_{B''}$, $n_{A'}$, and $b_{B'}$, and get.

Mean molar mass $= \frac{(n_A + n_{A'})m_A + (n_B + n_{B'})m_B}{(n_A + n_B + n_{A'} + n_{B'})}$

6. (c) Applying Boil's law.

$P_1V_1 = P_2V_2$

$10P_w.2 = (10 + h)\ p_w$ $\qquad$ $h = 1.7$ m

Height of water level in the tube $= 2 - h = 2 - 1.71 = 0.29$ m

7. (b) $PV = nRT$

$V = \frac{nR}{P}.T$ $\qquad \Rightarrow V = KT$

$\therefore$ $\log P = \log T + \log K$

Linear dependence with positive slope

At the Y-intercept $P/_{T\to 0}$ and $p \to 0$ implying $p \to 0$, under such conditions all gases show ideal behavour.

9. (a) For equal weights, N2 will have more number of moles and hence more molecules.

15. (b, c) At constant temperature $V \propto 1/p$

19. (a) 1. Rate of diffusion $\propto \frac{P}{\sqrt{TM}}A$

$P \to$ Pressure
$A \to$ Area of hole
$T \to$ Temperature
$M \to$ Molecular weight
$\Rightarrow$ True

2. For ideal gas $PV = nRT$ [$a = 0, b = 0 \Rightarrow$ True

3. The process is irreversible adiabatic $\therefore PV^{\gamma-1} \neq$ constant

20. (b) (a) Temperature decreases A to B, so RMS speed decreases ($\because V_{RMS} \propto \sqrt{T}$)

(b) $d_{gas} = \frac{PM}{RT}$. On moving from A to B, K increases and temperature decreases. So, density of gas increases.

(c) This graph is possible if during the process: $P \propto \frac{1}{V^{1/2}}$.

$\because$ $PT = \text{Constant}$ $\quad \therefore P\left(\frac{PV}{nR}\right) = \text{Constant}$

$\therefore$ $P^2V = \text{Constant}$ or $PV^{1/2} = \text{Constant}$

(d) If $P_B = 4P_A$, then $V_A = 16V_B$ (according $P_2V =$ Constant for process).

21. (b) Equation of straight line

$(y - y_1) = \left(\frac{y_2 - y_1}{x_2 - x_1}\right)(x - x_1)$

$\therefore$ $(P - 16) = \left(\frac{4-16}{15-6}\right)(V - 6)$

$\therefore$ $3P + 4V = 72$

$T_{max} = \frac{(PV)_{max}}{nR}$

For $(PV_{max}$, $3P = \frac{72}{2}$ and $4V = \frac{72}{2}$

$\therefore$ $P = 12, V = 9$

$\therefore$ $T_{max} = \frac{12 \times 9}{1 \times (1/12)} = 648K$

22. (d) (a) This graphs is possible if the temperature of the gas is kept constant and pressure is increased from A to B.

(b) This graphs is possible if the temperature of the gas is increased continuously during the process A to B.

(c) This graphs is possible if during the process: $P \propto \frac{1}{V^2}$

$\because$ $VT = \text{constant}$

$\therefore$ $V\left(\frac{PV}{nR}\right) = \text{Constant or PV2 = constant.}$

23. (b) $200 < T_B < 1000$

$\Rightarrow \quad 200 < \frac{a}{Rb} < 1000$

$\Rightarrow \quad 400 \text{ cal} < \frac{a}{b} < 2000 \text{ cal}$

24. (a) In the high pressure region

$$z = +\frac{Rb}{RT}$$

solve for the two points.

25. (c) Use $z = \frac{P_{VM}}{RT} \Rightarrow Um = \frac{z.RT}{P}$

26. (c) At Boyle's temperature, a real gas shows ideal behaviour in the low pressure region.

27. (A – r), (B – q, r, s), (C – r), (D – p, r).

28. (A – p, s), (B – r, s, t), (C – r, s, t), (D – p, s)

29. (A – s), (B – p), (C – q), (D – r)

(a) 4 g of the He $\frac{4}{4}$ = 1 mole

$$KE = \frac{3}{2} \times nRT = \frac{3}{2} \times R \times T = 1.5RT$$

(b) 32 gram of O2 = $\frac{32}{32}$ = 1 mole

KE = KE (Translational) + KE rotational

$$\frac{3}{2}RT + \frac{2 \times RT}{2}$$ (Two rotational degree of freedom)

(c) NO_2 is triatomic and non linear molecule and thus possesses three translational and three rotational degree of freedom. Vibrational degree of freedom does not contribute at ordinary temperature

(d) At constant pressure increase in energy = $\Delta E + P\Delta V = 3R + R = 4R$

30.

	$2NO(g)$ +	$O_2(g)$	$2NO_2(g)$
Moles	2	0.5	0
	$2 - 2 \times 0.5$	0	2×0.5
	1	0	1
	$N_f = 1 + 1$		$n_f = 2 + 0.5$

∴ $\Delta n = (2.5 - 2) = 0.5$ moles

∴ Change in pressure

$$\Delta p = \frac{\Delta nRT}{V} = 0.5 \times \frac{1}{12} \times \frac{300}{6.25} = 2\text{atm}.$$

31. Average Translational kinetic energy (per mole of gas)

$$= \frac{3}{2}RT = \frac{3M}{2} \times \frac{RT}{M} = \frac{3\pi M}{16} \times \frac{8RT}{\pi M}$$

$$= \frac{3\pi M}{16} \times \left(\sqrt{\frac{8RT}{\pi M}}\right)^2 = \frac{3\pi M}{16} \times (V_{av})^2$$

∴ For one mole of gas mixture,

Average translational kinetic energy

$$= \frac{3\pi M_{mix}}{16} \times (V_{av})^2$$

$$= \frac{3}{16} \times \frac{22}{7} \times \left[\frac{(2 \times 20 + 5 \times 4)/7}{1000}\right] \times (7 \times 10^2)^2$$

[∵ M_{mix} is in Kg/mole]

= 2475 Joules.

Reported answer = 2475 × 0.002 = 4.95 ≈ 5.

32. Let volume of CO, CO_2 and N_2 in the initial mixture be xL, yL and (1 – x – y)L respectively.

On mixing 1L O_2 and burning, CO will combine with O_2 to form CO_2O

$$CO + \frac{1}{2}O2 \rightarrow CO_2$$

$$xL \quad \frac{x}{2} \quad xL$$

∴ Product gas mixture will be composed of CO_2 produced, CO_2 initial, unreacted N_2 and left O_2 having volume xL, yL, (1 – x – y)L and $\left(1 - \frac{x}{2}\right)$L.

On passing subsequently through KOH solution and alkalline pyragallol, all CO_2 and O_2 will be absorbed.

∴ $x + y + 1 - \frac{x}{2} = 1.6$

∴ $x + 2y = 1.2$ ... (1)

On mixing the product mixture with excess CO, whole of unreacted O_2 is converted to CO_2

$$CO + \frac{1}{2}O2 \rightarrow CO_2$$

$$\left(1 - \frac{x}{2}\right)L \quad 2\left(1 - \frac{x}{2}\right) \quad (2 - x)L$$

∴ Total CO_2 in the final gas mixture = (x + y) + (2 – x) = 2.3

∴ y = 0.3

Put y = 0.3 in equation (1)

∴ x = 0.6

∴ Vol % of CO in original mixture = $\frac{0.6}{1}$ × 100 = 60%.

∴ Reported answer = 60/10 = 6.

33.

	N_2 +	$3H_2$ →	$2NH_3$	
t = 0	a_{atm}	b_{atm}	0	(At constant V & T, n ∝ P)
t = f	$(a - x)_{atm}$	$(b - 3x)_{atm}$	$(2x)_{atm}$	

∴ a + b = 1 and (a – x) + (b – 3x) + 2x = a + b – 2x = 0.85

$\therefore$ $2x = 0.15$

$\therefore$ y = Partial pressure of $NH_3 = 2x = 0.15$ atm

$\therefore$ y = (Partial pressure of NH_3) $\times$ 20 = 0.15 $\times$ 20 = 3.

34. At constant temperature, decrease in molecular masses causes flattening of the graph. For the same molecular mass of gas, increase in temperature causes flattening of the graph.

From the above graph.

$$(V_{mp})_{T_1} < (V_{mp})_{T_2}$$

$$\therefore \quad \frac{T_1}{M_A} < \frac{T_2}{M_B} \therefore \frac{T_2}{T_1} > \frac{M_B}{M_A}$$

But $\frac{M_B}{M_A}$ may be less than or greater than 1.

$\therefore$ Statements (1), (2) & (3) are wrong

$\therefore$ Reported answer = 1 + 2 + 3 = 6.

35. $$\frac{r_A}{r_B} = \frac{n_A}{n_B} \times \sqrt{\frac{M_B}{M_A}}$$

$$\therefore \frac{\text{(Moles of A coming out initially) } \Delta t}{\text{Moles of B coming out initially}/\Delta t}$$

$$= \frac{\frac{2x}{M_A}}{\frac{1x}{M_B}} \times \sqrt{\frac{M_B}{M_A}}$$

$$\therefore \frac{1}{4} = \frac{2}{1}\left(\frac{M_B}{M_A}\right)^{3/2} \qquad \therefore \frac{M_B}{M_A} = \frac{1}{4}$$

$\therefore$ Ratio of Mole fractions

$$= \frac{X_A}{X_B} = \left(\frac{\frac{n_A}{n_A + n_B}}{\frac{n_B}{n_A + n_B}}\right) = \frac{n_A}{n_B} = \left(\frac{\frac{2x}{M_A}}{\frac{1x}{M_B}}\right) = \frac{2M_B}{M_A}$$

$$= 2 \times \frac{1}{4} = \frac{1}{2}$$

$\therefore$ Reported answer = $\left(\frac{1}{2}\right) \times 6 = 3$

36. P_1 = 75 cm of Hg, V1 = 30 $\times$ A

$$P_1 = 75 + 10 + \frac{20.4 \times 10}{13.6} = 100 \text{ cm of Hg}$$

$\Rightarrow$ $75 \times 24 = 100 \times x$

x = 18 cm

37. PV = nRT

$$1 \times V = \frac{1}{10} \times R \times (t + 273)$$

The pressure now is 1.1 atm.

$$\therefore \quad 1.1 \times U \ \frac{1}{10} \times R(t + 283)$$

Solve for 'v' and 't'

38. (a) 18.1, 50.25 $\times$ 10^{-3} m^{-3}, 1.225

(b) 2.07 $\times$ 10–20 J

P = 1 atm T = 500 K, d = 0.36 kg nr^3

$$\frac{r_{vapour}}{r_{o_2}} = 1.33$$

(i) Molecular weight = $\frac{r_{vapour}}{r_{o_2}} = \sqrt{\frac{m_{o_2}}{m_{vapour}}}$

$$\Rightarrow 1.33 = \sqrt{\frac{32}{m_{vapour}}}$$

(ii) Molar volume $(\overline{V}) = \frac{\text{molecular weight}}{\text{density of vapour}}$

(iii) Compression factor $z = \frac{\overline{pv}}{RT}$

(iv) Here, z > 1, then repulsion force is more dominating

(v) Translational kinetic energy = 3/2 KT
= 3/2 $\times$ 1.23 $\times$ 10^{-23} $\times$ 1000

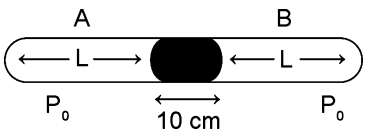
SUBJECTIVE ANSWER TYPE QUESTIONS

1. A column of Hg of 10 cm in length is contained in the middle of a narrow 1 m long tube which is closed at both ends. Both the halves of the tube contain air at a pressure 76 cm of Hg. By what distance will the column of Hg be displaced if the tube is held vertical?

Sol. Let initially the length of air Column on each side be L, then

2L + 10 = 100

$\therefore$ L = 45 cm



If the tube is held vertically, let the Hg column be displaced downwards by y to attain same pressure above and below the column of Hg. Then

$$P_B + 10 = P_A \quad ...(1)$$

Pressure is taken in terms of length of Hg.

For end A: Since mole remains same on two sides

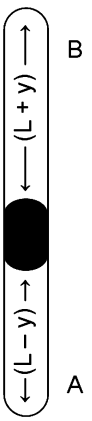
$$\frac{P_0 \times L \times a}{RT} = \frac{P_A \times (L-y) \times a}{RT} \quad ...(2)$$

$$\therefore \quad P_A = \frac{LP_0}{(L-y)} \quad ...(3)$$

For end B:

$$\frac{P_0 \times L \times a}{RT} = \frac{P_B \times (L+y) \times a}{RT} \quad ...(4)$$

$$\therefore \quad P_B = \frac{LP_0}{(L+y)} \quad ...(5)$$



By Eqs. (1), (3) and (5)

$$\left[\frac{LP_0}{(L+y)}\right] + 10 = \frac{LP_0}{(L-y)}$$

Putting L = 45 cm and P_0 = 76 cm

$$y^2 + 684y - (45)^2 = 0$$

$\therefore$ y = **3 cm**

2. A compound exists in the gaseous phase both as monomer (A) and dimmer (A_2). The molecular weight of A is 48. In an experiment 96 g of the compound was confined in a vessel of volume 33.6 litre and heated to 273°C. Calculate the pressure developed if the compound exists as dimmer to the extent of 50% by weight under these conditions.

Sol. Since A and A_2 are two states in gaseous phase having their weight ratio 50% i.e., 1 : 1

$$\therefore \quad \text{Mole of A} = \frac{96}{2} \times \frac{1}{48} = 1 \quad \left(n = \frac{w}{m}\right)$$

$$\text{Mole of } A_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$$

$$\text{Total mole of A and } A_2 \text{ are} = 1 + \frac{1}{2} = \frac{3}{2}$$

Thus, PV = nRT

$$P \times 33.6 = \frac{3}{2} \times 0.0821 \times 546$$

$\therefore$ P = **2 atm**

3. The mass of molecule A is twice the mass of molecule B. The rms speed of A is twice the rms speed of B. If two samples of A and B contain same number of molecules, what will be the ratio of P of two samples in separate containers of equal volume?

Sol. Given, $m_A = 2m_B$

$\therefore$ Mol. wt. of A = 2 × Mol. wt. of B ...(1)

Given u_{rms} of A = 2 × u_{rms} of B ...(2)

Also number of molecules of A = number of molecules of B ...(3)

For gas A $\quad P_A V_A = \frac{1}{3} M_A u^2_{rms\ A}$

For gas B $\quad P_B V_B = \frac{1}{3} M_B u^2_{rms\ B}$

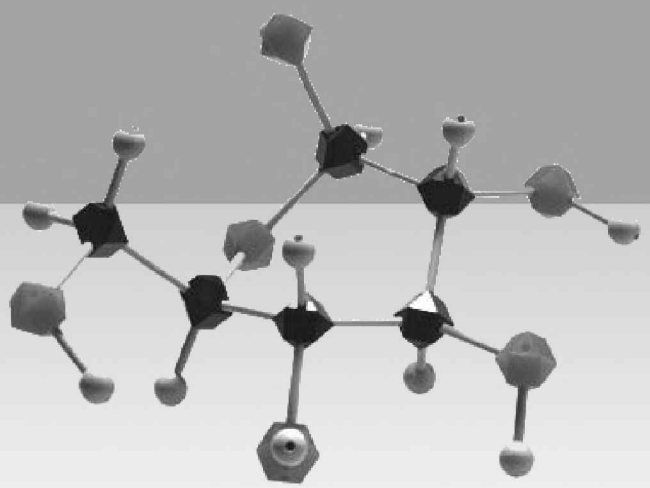
$$\therefore \quad \frac{P_A V_A}{P_B V_B} = \frac{M_A}{M_B} \times \frac{u_A^2}{u_B^2} \quad ...(4)$$

Given $V_A = V_B$ ...(5)

$\therefore$ By Eqs. (1), (2), (4) and (5)

$$\frac{P_A}{P_B} = 2 \times (2)^2 = 8$$

$\therefore$ $\mathbf{P_A = 8P_B}$



CHAPTER 3

Stoichiometry

INTRODUCTION

It is the branch of chemistry that involves chemical calculations based on chemical reaction.

The chemical calculations can be performed through the use of two different concepts:

(a) **The 'Mole' concept**
and
(b) **The equivalent concept**

It is important to know that the same problem on numerical chemistry can be solved either through the use of 'Mole' concept or equivalent concept and we will get the same answer through each of the methods. Which method is the easier way out depends upon the nature of reaction and the nature of the numerical problems.

We can classify the reaction mainly into two classes:

(i) **Redox reaction**

Those reactions which involve the exchange of electrons are called redox reactions.
It involves the change in oxidation state of the species considered.

$$\overset{0}{Mg} + \overset{0}{O_2} \longrightarrow \overset{+2\ -2}{2MgO}$$

Example: 2 Mg + O_2 ⟶ 2MgO

(In this reaction, we can consider as if magnesium has lost electrons and oxygen has gained electrons)

(ii) **Non-redox reaction**

Those reactions do not involve the exchange of electrons or, the change in oxidation state. These are mainly of the following types:

(a) **Acid-Base Reactions/Neutralization Reactions**

$$\overset{+1-1}{HCl} + NaOH \longrightarrow \overset{-1}{NaCl} + \overset{+1}{H_2O}$$

(Note that there is no change in oxidation state.)

(b) **Precipitation Reactions/Double Decomposition Reactions (exchange of ions)**

$$\underset{+1}{AgNO_3} + \underset{-1}{NaCl} \longrightarrow \underset{+1-1}{AgCl\downarrow} + NaNO_3$$

(Again note that there is no change in oxidation state.)

Actually, mole concept requires a balanced chemical reaction but application of mole concept is easier. On the other hand, equivalent concept does not need a balanced equation but application of equivalent concept requires the knowledge of a special parameter known as 'n-factor'.

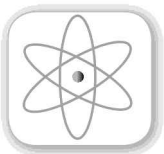
You will see that redox reactions are difficult to balance (we'll have a separate section in which we will learn how to balance redox reactions) but non-redox reactions are quite easily balanced.

Hence, we'll prefer to use 'mole concept' for non-redox reactions and 'equivalent concept' for redox reactions (in very few cases we might contradict this statement). There are very few problems for which we have to use both the concept simultaneously to get the answer.

We will gradually make a progress as follows:

- We will know about the following:
  (i) Laws of chemical combinations (elementary ideas about stoichiometry)
  (ii) Atomic mass, atomic weight, molar mass etc.
  (iii) How to calculate molar mass
  (iv) The 'Mole'
  (v) Calculation of number of moles of different substances
  (vi) Application of 'mole concept' in reactions
- We will know:
  (i) Equivalent mass
  (ii) The 'n-factor'
  (iii) How to calculate equivalent mass
  (iv) Calculation of number of equivalents of different substances
  (v) Balancing of redox reactions
  (vi) Application of 'equivalent concept' in reactions

LAWS OF CHEMICAL COMBINATIONS



Law of Conservation of Mass

It states that matter can neither be created nor destroyed.

The total mass of all products of a chemical reaction is equal to the total mass of all reactants of that reaction. These statements are summaries of many observations, which required a tremendous amount of experimentation to achieve and even more creative thinking to systematize as we have written them here. By making these assumptions, we can proceed directly with the experiments which led to the development of the atomic-molecular theory. Its also called hard law theory. Dalton believed in this theory. Goals: The statements above, though correct, are actually more vague than they might first appear. For example, exactly what do we mean when we say that all materials are made from elements? Why is it that the elements cannot be decomposed? What does it mean to combine elements into a compound? We want to understand more about the nature of elements and compounds so we can describe the processes by which elements combine to form compounds, by which compounds are decomposed into elements, and by which compounds are converted from one to another during chemical reactions. One possibility for answering these questions is to assume that a compound is formed when indestructible elements are simply mixed together, as for example, if we imagine stirring together a mixture of sugar and sand. Neither the sand nor the sugar is decomposed in the process. And the mixture can be decomposed back into the original

components. In this case, though, the resultant mixture exhibits the properties of both components: for example, the mixture would taste sweet, owing to the sugar component, but gritty, characteristic of the sand component. In contrast, the compound we call iron rust bears little resemblance to elemental iron: iron rust does not exhibit elemental iron's color, density, hardness, magnetism, etc. Since the properties of the elements are not maintained by the compound, then the compound must not be a simple mixture of the elements.

We could, of course, jump directly to the answers to these questions by stating that the elements themselves are composed of atoms: indivisible, identical particles distinctive of that element. Then a compound is formed by combining the atoms of the composite elements. Certainly, the Law of Conservation of Mass would be easily explained by the existence of immutable atoms of fixed mass. However, if we do decide to jump to conclusions and assume the existence of atoms without further evidence (as did the leading chemists of the seventeenth and eighteenth centuries), it does not lead us anywhere. What happens to iron when, after prolonged heating in air, it converts to iron rust? Why is it that the resultant combination of iron and air does not maintain the properties of either, as we would expect if the atoms of each are mixed together? An atomic view of nature would not yet provide any understanding of how the air and the iron have interacted or combined to form the new compound, and we cannot make any predictions about how much iron will produce how much iron rust. There is no basis for making any statements about the properties of these atoms. We need further observations.

Law of definite proportions

This law was given by, a French chemist, Joseph Proust.

The **law of definite proportions and also the elements** states that a chemical compound always contains exactly the same proportion of elements by mass.

An equivalent statement is the **law of constant composition**, which states that all samples of a given chemical compound have the same elemental composition.

For example, oxygen makes up $^{8}/_{9}$ of the mass of any sample of pure water, while hydrogen makes up the remaining $^{1}/_{9}$ of the mass. Along with the law of multiple proportions, the law of definite proportions forms the basis of stoichiometry.

It may be noted that although very useful in the foundation of modern chemistry, the laws of definite proportions is not universally true. There exist non-stoichiometric compounds whose elemental composition can vary from sample to sample. An example is the iron oxide wüstite, which can contain between 0.83 and 0.95 iron atoms for every oxygen atom, and thus contain anywhere between 23% and 25% oxygen. In general, Proust's measurements were not accurate enough to detect such variations.

In addition, the isotopic composition of an element can vary depending on its source, hence its weight in a pure stoichiometric compound may vary.

Law of multiple proportions

When two elements are forced together to form more than one compound, the mass of element A that combines in the first compound with a specific amount of element B has a simple whole number ratio with the mass of element A that combines in the second compound with the same given mass of element B.

In other words, when two elements can combine to form more than one compound and the same amount of the first element is used in each, then the ratio of the amounts of the other element will be a whole number.

This sounds confusing, but an example clarifies this statement. Consider the carbon oxides, and let carbon be element B and oxygen be element A. Take a fixed given mass of carbon (element B), say 1 gram. The mass of oxygen which combines with 1 gram of carbon to form the first oxide is 1.33 grams. The mass of oxygen which combines with 1 gram of carbon to form the second oxide is 2.66. These masses are in ratio 2.66:1.33=2:1, a simple whole number ratio. In explaining our observations of the Law of Multiple Proportions for the carbon oxides and the nitrogen oxides, we have concluded that the simple mass ratio arises from the simple ratio of atoms contained in the individual molecules. Thus, we have established the following postulates of the Atomic Molecular Theory.

In short, the law of multiple proportions states:

"When two elements form more than one compound, the different masses of one element that are combined with the same mass of the other element are in a ratio of small whole numbers."

Significant insight into the above problem is found by studying different compounds formed from the same elements. For example, there are actually three oxides of nitrogen, that is, compounds composed only of nitrogen and oxygen. For now, we will call them oxide A, oxide B, and oxide C. Oxide A has oxygen to nitrogen mass ratio 2.28 : 1. Oxide B has oxygen to nitrogen mass ratio 1.14 : 1, and oxide C has oxygen to nitrogen mass ratio 0.57 : 1. The fact that there are three mass ratios might seem to contradict the Law of Definite Proportions, which on the surface seems to say that there should be just one ratio. However, each mass combination gives rise to a completely unique chemical compound with very different chemical properties. For example, oxide A is very toxic, whereas oxide C is used as an anesthetic. It is also true that the mass ratio is not arbitrary or continuously variable: we cannot pick just any combination of masses in combining oxygen and nitrogen, rather we must obey one of only three. So there is no contradiction: we simply need to be careful with the Law of Definite Proportions to say that each unique compound has a definite mass ratio of combining elements. These new mass ratio numbers are highly suggestive in the following way. Notice that, in each case, we took the ratio of oxygen mass to a nitrogen mass of 1, and that the resultant ratios have a very simple relationship: 2.28:1.14:0.57 = 2:1:0.5 = 4:2:1

The masses of oxygen appearing in these compounds are in simple whole number ratios when we take a fixed amount of nitrogen. The appearance of these simple whole numbers is very significant. These integers imply that the compounds contain a multiple of a fixed unit of mass of oxygen. The simplest explanation for this fixed unit of mass is that oxygen is particulate. We call the fixed unit of mass an atom. We now assume that the compounds have been formed from combinations of atoms with fixed masses, and that different compounds have differing numbers of atoms. The mass ratios make it clear that oxide B contains twice as many oxygen atoms (per nitrogen atom) as does oxide C and half as many oxygen atoms (per nitrogen atom) as does oxide A. The simple mass ratios must be the result of the simple ratios in which atoms combine into molecules. If, for example, oxide C has the molecular formula NO, then oxide B has the formula NO_2, and oxide A has the formula NO_4. There are other possibilities: if oxide B has molecular formula NO, then oxide A has formula NO_2, and oxide C has formula N_2O. Or if oxide A has formula NO, then oxide B has formula N_2O and oxide C has formula N_4O. These three possibilities are listed in Table .

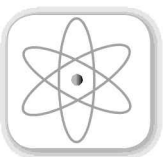
Assuming that: Oxide C is NO Oxide B is NO Oxide A is NO

Possible Molecular Formulas for Nitrogen Oxides

Oxide A	NO_4	NO_2	NO
Oxide B	NO_2	NO	N_2O
Oxide C	NO	N_2O	N_4O

We do not have a way to know which of these sets of molecular formula are right. But we can assert that either one of them or one analogous to them is right. Similar data are found for any set of compounds formed from common elements. For example, there are two oxides of carbon, one with oxygen-to-carbon mass ratio 1.33 : 1 and the other with mass ratio 2.66 : 1. The second oxide must have twice as many oxygen atoms, per carbon atom, as does the first. The general statement of this observation is the Law of Multiple Proportions.

ATOMIC MASS



The atomic mass may be considered to be the total mass of protons, neutrons and electrons in a single atom (when the atom is motionless).

The atomic mass is defined as the mass of an atom, which can only be one isotope at a time and is not an abundance-weighted average.

The present system of atomic masses is based on carbon-12 as the standard. Carbon-12 is one of the *isotopes* of carbon and can be represented as ^{12}C. In this system, ^{12}C is assigned a mass of exactly 12 atomic mass unit(**amu**) and masses of all other atoms are given relative to this standard. One **atomic mas sunit** is defined as a mass exactly equal to one twelft the mass of one carbon-12 atom.

And 1 amu = 1.66056×10^{-24} g

Mass of an atom of hydrogen = 1.6736×10^{-24} g

Thus, in terms of amu, the massof hydrogen atom = $\frac{1.6736 \times 10^{-24}\ \text{g}}{1.66056 \times 10^{-24}\ \text{g}}$

= 1.0078 amu

= 1.0080 amu

Similarly, the mass of oxygen –16 ($_{16}O$) atom would be 15.995 amu.

Today, **'amu'** has been replaced by **'u'** which is known as **unified mas** .

Atomic Weight (Symbol: A_r)

The IUPAC definitio of atomic weight is:

An atomic weight (relative atomic mass) of an element from a specified source is the ratio of the average mass per atom of the element to 1/12 of the mass of an atom of ^{12}C.

It is a dimensionless physical quantity, the ratio of the average mass of atoms of an element (from a given source) to 1/12 of the mass of an atom of carbon-12. The term is usually used, without further qualification, to refer to the **standard atomic weights** published at regular intervals by the International Union of Pure and Applied Chemistry (IUPAC) and which are intended to be applicable to normal laboratory materials.

Relative isotopic mass is the relative mass of a given isotope (more specificall , any single nuclide), scaled with carbon-12 as exactly 12. No other nuclides other than carbon-12 have exactly whole-number masses in this scale. This is due to two factors:

1. The different mass of neutrons and protons acting to change the total mass in nuclides with proton/neutron ratios other than the 1:1 ratio of carbon-12; and
2. An exact whole-number will not be located if there exists a loss/gain of mass to difference in mean binding energy relative to the mean binding energy for carbon-12. However, since any mass defect due to binding energy is a small fraction (less than 1%) compared to the mass of a nucleon, and even less compared to the average mass per nucleon in carbon-12, which is moderately-strongly bound. Since protons and neutrons differ in mass from each by an even smaller fraction (about 0.0014 u), the practice of rounding the atomic mass of any given nuclide or isotope to the nearest whole number, always gives the simple whole number total nucleon count. Neutron count can then be derived by subtracting the atomic number.

The atomic mass is sometimes incorrectly used as a synonym of **relative atomic mass**, **average atomic mass** and **atomic weight**; these differ subtly from the atomic mass. In the case of many elements that have one dominant isotope, the actual numerical similarity/difference between the atomic mass of the most common isotope and the relative atomic mass or standard atomic weights can be very small such that it does not affect most bulk calculations—but such an error can be critical when considering individual atoms. For elements with more than one common isotope the difference even to the most common atomic mass can be half a mass unit or more (e.g., chlorine). The atomic mass of an uncommon isotope can differ from the relative atomic mass or standard atomic weight by several mass units.

When we use atomic masses of elements in calculations, we actually use *average atomic masses* of elements which are explained ahead.

Determination of atomic weight

The calculation is exemplified for silicon, whose atomic weight is especially important in metrology. Silicon exists in nature as a mixture of three isotopes: ^{28}Si, ^{29}Si and ^{30}Si. The atomic masses of these nuclides are known to a precision of one part in 14 billion for ^{28}Si and about one part in one billion for the others. However, the range of natural abundance for the isotopes is such that the standard abundance can only be given to about ±0.001%. The calculation is,

$$A_r(\mathrm{Si}) = (27.97693 \times 0.922297) + (28.97649 \times 0.046832) + (29.97377 \times 0.030872) = 28.0854$$

Isotope	*Atomic mass*	*Abundance*	
		Standard	*Range*
^{28}Si	27.976 926 532 46(194)	92.2297(7)%	92.21–92.25%
^{29}Si	28.976 494 700(22)	4.6832(5)%	4.69–4.67%
^{30}Si	29.973 770 171(32)	3.0872(5)%	3.10–3.08%

The estimation of the uncertainty is complicated especially as the sample distribution is not necessarily symmetrical: the IUPAC standard atomic weights are quoted with estimated symmetrical uncertainties, and the value for silicon is 28.0855(3). The relative standard uncertainty in this value is 1×10^{-5} or 10 ppm.

The **molecular mass** (abbreviated **M**) of a substance, frequently referred to by the older term **molecular weight** and abbreviated as **MW**, is the mass of one molecule of that substance, relative to the unified atomic mass unit u (equal to 1/12 the mass of one isotope of carbon-12).

This is distinct from the **relative molecular mass** of a molecule, which is the ratio of the mass of that molecule to 1/12 of the mass of carbon 12 and is a dimensionless number. Relative molecular mass is abbreviated to $\mathbf{M_r}$.

Molecular mass differs from more common measurements of the mass of chemicals, such as **molar mass**, by taking into account the isotopic composition of a molecule rather than the average isotopic distribution of many molecules. As a result, molecular mass is a more precise number than molar mass; however, it is more accurate to use molar mass on bulk samples. This means that molar mass is appropriate most of the time except when deal **Definitio** .

Average Mass

The *average molecular mass* (sometimes abbreviated as *average mass*) is another variation on the use of the term molecular mass. The average molecular mass is the abundance weighted mean (average) of the molecular masses in a sample. This is often closer to what is meant when "molecular mass" and "molar mass" are used synonymously and may have derived from shortening of this term. The average molecular mass and the molar mass *of a particular substance in a particular sample* are in fact numerically identical and may be interconverted by Avogadro's constant. It should be noted, however, that the molar mass is almost always a computed figur derived from the standard atomic weights, whereas the average molecular mass, in fields that need the term, is often a measured figure specific to a sample. Therefore, they often vary since one is theoretical and the other is experimental. Specific samples may vary significantly from the expected isotopic composition due to real deviations from earth's average isotopic abundances.

Formula Mass

Some substances such as sodium chloride donot contain discrete molecules as their constituent units. In such compounds, positive (sodium) and negative (chloride) entities are arranged in a three-dimensional structure. It may be noted that in sodium chloride,one Na^+ is surrounded by six Cl^- and vice versa. The formula such as NaCl is used to calculate the **formula mass** instead of molecular mass as in the solid state sodiumchloride does not exist as a single entity. Thus, formula mass of sodium chloride = atomic mass of sodium + atomic mass ofchlorine = 23.0 u + 35.5 u = 58.5 u

The 'Mole'

The **mole** (symbol: **mol**) is a unit of amount of substance: it is an SI base unit, and one of the few units used to measure this physical quantity. The term 'mole' is a Latin word which means heap or pile. A mole (symbol mol) is defined as the amount of substance that contains as many atoms, molecules, ions electrons or any other elementary entities as there are carbon atoms in exactly 12 g of ^{12}C. This 'definite number' is called Avogadro number which is equal to 6.023×10^{23} ($N_A = 6.023 \times 10^{23}$). **Hence, it is used to represent microparticles**.

In chemistry, the **Avogadro constant** (symbols: L, N_A) is the number of "elementary entities" (usually atoms or molecules) in one mole, that is (from the definition of the mole), the number of atoms in exactly 12 grams of carbon-12. It was originally called **Avogadro's number**.

The names **gram-atom** and **gram-molecule** have also been used in the same sense as "mole", but these names are now obsolete. Current usage tends to apply the term "mole" to an amount containing **Avogadro's** number of whatever units are being considered. Thus, it is possible to have a mole of atoms, ions, radicals, electrons, or quanta.

All stoichiometry essentially is based on the evaluation of the number of moles of substance.

Unit type variation

The molar mass of a substance is the mass of 1 mol (the SI unit for the basis SI quantity **amount of substance**, having the symbol ***n***) of the substance. This has a numerical value which is the average molecular mass of the molecules in the substance multiplied by Avogadro's constant approximately 6.022×10^{23}. The most common units of molar mass are *g/mol* because in those units the numerical value equals the average molecular mass in units of u.

molar mass in g/mol = average molecular mass in u

(Note that these relations are true for theoretical and experimental values, but not between experimental and theoretical values. Molar mass is most often theoretical and average molecular mass is most often experimental)

The average atomic mass of natural hydrogen is 1.00794 u and that of natural oxygen is 15.9994 u; therefore, the molecular mass of natural water with formula H_2O is (2 × 1.00794 u) + 15.9994 u = 18.01528 u.

Therefore, one mole of water has a mass of 18.01528 grams. However, the exact mass of hydrogen-1 (the most common hydrogen isotope) is 1.00783, and the exact mass of oxygen-16 (the most common oxygen isotope) is 15.9949, so the mass of the most common molecule of water is 18.01056 u.

The difference of 0.00472 u or 0.03% comes from the fact that natural water contain traces of water molecules containing, oxygen-17, oxygen-18 or hydrogen-2 (Deuterium) atoms. Although this difference is trivial in bulk chemistry calculations, it can result in complete failure in situations where the behaviour of individual molecules matters, such as in mass spectrometry and particle physics (where the mixture of isotopes does not act as an average).

There are also situations where the isotopic distributions are not typical such as with heavy water used in some nuclear reactors which is artificially enriched with Deuterium. In these cases, the computed values of molar mass and average molecular mass, which are ultimately derived from the standard atomic weights, will not be the same as the actual molar mass or average molecular mass of the sample. In this case, the mass of deuterium is 2.0136 u and the average molecular mass of this water (assuming 100% deuterium enrichment) is,

(2 × 2.0136 u) + 15.9994 u = 20.0266 u.

This is a very large difference of ~11% error from the expected average molecular mass based on the standard atomic weights. Furthermore, the most abundant molecular mass is actually slightly less than the average molecular mass since oxygen-16 is still the most common.

(2 × 2.0136 u) + 15.9949 u = 20.0221 u.

Although this is an extreme artificial example, natural variation in isotopic distributions do occur and are measurable. For example, the atomic weight of lithium as found by isotopic analysis of 39 lithium reagents from several manufacturers varied from 6.939 to 6.996.

At. No.	Name of Element	Symbol of Element	Atomic Weight	At. No.	Name of Element	Symbol of Element	Atomic Weight
89.	Actinium	Ac	227.0278	80.	Mercury	Hg	200.5
13.	Aluminium	Al	26.981	42.	Molybdenum	Mo	95.9
95.	Americium	Am	234.0614	60.	Neodymium	Nd	144.2
51.	Antimony	Sb	121.7	10.	Neon	Ne	20.17
18.	Argon	Ar	39.94	93.	Neptunium	Np	237.048
33.	Arsenic	As	74.922	28.	Nickel	Ni	58.7
85.	Astatine	At	209.9871	41.	Niobium	Nb	92.906
56.	Barium	Ba	137.3	7.	Nitrogen	N	14.007
97.	Berkelium	Bk	247.07	102.	Nobelium	No	259.1
4.	Beryllium	Be	9.012	76.	Osmium	Os	190.2
83.	Bismuth	Bi	208.981	8.	Oxygen	O	15.999
5.	Boron	B	10.81	46.	Palladium	Pd	106.4
35.	Bromine	Br	79.904	15.	Phosphorus	P	30.974
48.	Cadmium	Cd	112.40	78.	Platinum	Pt	195.0
55.	Cesium	Cs	132.905	94.	Plutonium	Pu	244.06
20.	Calcium	Ca	40.08	84.	Polonium	Po	208.98
98.	Californium	Cf	251.079	19.	Potassium	K	39.10
6.	Carbon	C	12.011	59.	Praseodymium	Pr	140.908
58.	Cerium	Ce	140.12	61.	Promethium	Pm	144.91
17.	Chlorine	Cl	35.453	91.	Protactinium	Pa	231.036
24.	Chromium	Cr	51.996	88.	Radium	Ra	226.025
27.	Cobalt	Co	58.933	86.	Radon	Rn	222.017
29.	Copper	Cu	63.54	75.	Rhenium	Re	186.2
96.	Curium	Cm	247.07	45.	Rhodium	Rh	102.905
66.	Dysprosium	Dy	162.5	37.	Rubidum	Rb	85.467
99.	Einsteinium	Es	252.08	44.	Ruthenium	Ru	101.07
68.	Erbium	Er	167.27	104.	Rutherfordium	Rf	261.11
63.	Europium	Eu	151.96	62.	Samarium	Sm	150.4
100.	Fermium	Fm	257.09	21.	Scandium	Sc	44.956
9.	Fluorine	F	18.998	34.	Selenium	Se	78.9
87.	Francium	Fr	223.019	14.	Silicon	Si	28.08
64.	Gadolinium	Gd	157.2	47.	Silver	Ag	107.868
31.	Gallium	Ga	69.72	11.	Sodium	Na	22.990
32.	Germanium	Ge	72.61	38.	Strontium	Sr	87.62
79.	Gold	Au	196.966	16.	Sulphur	S	32.06
72.	Hafnium	Hf	178.49	73.	Tantalum	Ta	180.947
2.	Helium	He	4.003	43.	Technetium	Tc	98.906
67.	Holmium	Ho	164.930	52.	Tellurium	Te	127.6
1.	Hydrogen	H	1.008	65.	Terbium	Tb	158.925
49.	Indium	In	114.82	81.	Thallium	Tl	204.3
53.	Iodine	I	126.904	90.	Thorium	Th	232.038
77.	Iridium	Ir	192.2	69.	Thulium	Tm	168.934

(Contd)

At. No.	Name of Element	Symbol of Element	Atomic Weight	At. No.	Name of Element	Symbol of Element	Atomic Weight
26.	Iron	Fe	55.84	50.	Tin	Sn	118.6
36.	Krypton	Kr	83.80	22.	Titanium	Ti	47.9
57.	Lanthanum	La	138.905	74.	Tungsten	W	183.8
103.	Lawrencium	Lr	262.11	92.	Uranium	U	238.036
82.	Lead	Pb	207.2	23.	Vanadium	V	50.941
3.	Lithium	Li	6.94	54.	Xenon	Xe	131.30
71.	Lutetium	Lu	174.97	70.	Ytterbium	Yb	173.04
12.	Magnesium	Mg	24.305	39.	Yttrium	Y	88.906
25.	Manganese	Mn	54.938	30.	Zinc	Zn	65.3
101.	Mendelevium	Md	258.1	40.	Zirconium	Zr	91.22



Worked-out Examples

1. Carbon occurs in nature as a mixture of atoms of which 98.89% have a mass of 12.0000 u and 1.11% have a mass of 13.0035 u. Calculate the atomic weight of carbon.

Solution AW = (12.0000 u × 0.9889) + (13.00335 u × 0.0111) = 12.011 u

2. To account for nitrogen's atomic weight of 14.0067, what must be the ratio of ^{15}N to ^{14}N atoms in natural nitrogen?

Solution Let x = fraction ^{14}N; then 1.000 – x = fraction ^{15}N

$x(14.00307) + (1.000 - x)(15.0001) = 14.0067$

$x = 0.9964 \qquad 1 - x = 0.0036$

$$\text{Ratio} = \frac{0.0036}{0.9964} = 0.0036$$

3. At one time there was a chemical atomic weight scale based on the assignment of the value 16.0000 to naturally occurring oxygen. What would have been the atomic weight, on such a table, of silver, if current information had been available? The atomic weights of oxygen and silver on the present table are 15.9994 and 107.868.

Solution Since the old atomic weight of oxygen was 16.0000/15.9994 times as large as the new value, the old atomic weight of silver must be,

$$(107.868)\left(\frac{16.0000}{15.9994}\right) = 107.872$$

4. P and Q are two elements which forms P_2Q_3 and PQ_2. If 0.15 mole of P_2Q_3 weighs 15.9 g and 0.15 mole of PQ_2 weighs 9.3g, what are atomic weights of P and Q?

Solution Let atomic weight of P and Q are a and b respectively

$\therefore$ Molecular weight of $P_2Q_3 = 2a + 3b$

and Molecular weight of $PQ_2 = a + 2b$

Now given that 0.15 mole of P_2Q_3 weigh 15.9g

$$(2a+3b) = \frac{15.9}{0.15} \quad \left(\therefore \frac{\text{wt.}}{\text{mol. wt.}} = \text{mole}\right) \text{ Similarly, } (a+2b) = \frac{9.3}{0.15}$$

Solving these two equations

b = 18

Calculation of Number of Moles

The number of moles can be calculated by a number of formulae depending upon the data given:

$$\text{Number of moles of molecules} = \frac{\text{Wt. of substance in g}}{\text{Mol. wt. of substance}}$$

$$\text{Number of moles of atoms} = \frac{\text{Wt. of element in g}}{\text{At. wt. of the element}}$$

$$\text{Number of moles of gas} = \frac{PV}{RT} = \frac{\text{Volume of the gas at N.T.P}}{\text{Standard molar volume (i.e., 22.4L)}}$$

$$\text{Number of moles of particles e.g., atoms, molecules ions etc.,} = \frac{\text{Number of particles}}{\text{Avogardro number}}$$



Worked-out Examples

5. One mole of P_4 molecules contain:

(a) 1 molecule
(b) 4 molecules
(c) $\frac{1}{4} \times 6.022 \times 10^{23}$ atoms
(d) 24.088×10^{23} atoms

Solution (d) 1 mole P_4 = N molecules of P_4 = 4 N atoms of P_4.

6. The number of molecules in 3.2 g of oxygen gas are:

(a) 6.02×10^{22}
(b) 6.02×10^{23}
(c) 12.04×10^{22}
(d) 12.04×10^{23}

Solution (a) Mole of $O_2 = \frac{3.2}{32} = \frac{1}{10}$

$\therefore$ molecules of O = N $\times \frac{1}{10} = 6.02 \times 10^{22}$

Case 1: Number of moles of compound and mass

7. How many moles of NaCl is 2.735 g of NaCl?

Solution The problem gives the number of grams of NaCl and asks for the number of moles of NaCl. We must find the formula mass for NaCl and use it to write a conversion factor for changing grams NaCl to moles NaCl.

To save time and let you concentrate on new skills, a table of frequently used formula masses is printed inside the back cover. From the table inside the back cover, the formula mass for NaCl is 58.4425 u.

Because the formula mass for NaCl is 58.4425 u,

1 mol NaCl ≈ 58.4425 g NaCl

The conversion factor for converting g NaCl to mol NaCl is 1 mol NaCl/58.44 g NaCl. (The mass of 1 mol NaCl is rounded to four digits because there are four significant figures in 2.735 g NaCl, the quantity given in the problem.)

$$2.735 \cancel{\text{ g NaCl}} \left(\frac{1 \text{ mol NaCl}}{58.44 \cancel{\text{ g NaCl}}} \right) = 0.046\,80 \text{ mol NaCl}$$

8. What is the mass in grams of 3.47 moles of NaCl?

Solution The problem gives the number of moles of NaCl and asks for the number of grams of NaCl, the conversion factor is obtained from the relationship,

$$1 \text{ mol NaCl} \approx 58.4425 \text{ g NaCl}$$

This time there are three significant figures in the number given in the problem, 3.4

$$3.47 \text{ mol NaCl}\left(\frac{58.4 \text{ g NaCl}}{1 \text{ mol NaCl}}\right) = 203 \text{ g NaCl}$$

Check: The answer is reasonable because 203 g is between 3 and 4 times 60, the approximate mass of 1 mol NaCl, and 3.47 moles is between 3 and 4 moles.

9. Calculate the number of atoms in 2.00 g of N_2.

Solution The problem asks for the number of atoms in 2.00 g of N_2. From the table inside the back cover, the formula mass of nitrogen gas, N_2, is 28.01348 u. Therefore, one mole of nitrogen gas has a mass of 28.01348 g. The relationships needed to solve this problem are,

$$1 \text{ mol } N_2 \approx 28.0 \text{ g } N_2 \qquad 1 \text{ } N_2 \text{ molecule} \approx 2 \text{ N atoms}$$

$$1 \text{ mol } N_2 \text{ molecules} \approx 6.02 \times 10^{23} \text{ } N_2 \text{ molecules}$$

Using these relationships to write conversion factors gives,

$$2.00 \text{ g } N_2\left(\frac{1 \text{ mol } N_2}{28.0 \text{ g } N_2}\right)\left(\frac{6.02\times10^{23} \text{ } N_2 \text{ molecules}}{1 \text{ mol } N_2}\right)\left(\frac{2 \text{ N atoms}}{1 \text{ } N_2 \text{ molecule}}\right)$$

$$= 8.60 \times 10^{22} \text{ N atoms}$$

10. Calculate the mass in grams of a single nitrogen atom to three significant figures

Solution The problem asks for the mass of a single N atom to three significant figures. From the table inside the front cover, the atomic mass of nitrogen is 14.006 74 u. Therefore, the mass of one mole of N atoms is 14.006 74 g. The relationships needed to calculate the mass of a single N atom to three significant figures are:

$$1 \text{ mol N atoms} \approx 14.0 \text{ g N} \qquad 1 \text{ mol N atoms} \approx 6.02 \times 10^{23} \text{ N atoms}$$

Using these relationships to write conversion factors gives,

$$1 \text{ N atom}\left(\frac{1 \text{ mol N atoms}}{6.02\times10^{23} \text{ N atoms}}\right)\left(\frac{14.0 \text{ g N}}{1 \text{ mol N atoms}}\right) = 2.33\times10^{-23} \text{ g N}$$

The mass of one N atom is 2.33×10^{-23} g, which is a very small mass indeed.

Case 2: Number of moles of pure liquid and its volume

11. The number of molecules in 27 mL of water is:

(a) 9.033×10^{23} (b) 6.022×10^{23}

(c) 27 (d) 3.011×10^{22}

Solution (a) 18 mL H_2O = 18 g H_2O = 1 mole H_2O = N molecules H_2O.

12. The number of moles of water present in 90 mL of a water is:

(a) 2 (b) 3

(c) 4 (d) 5

Solution (d) 1 mole of water = 18 g = 18 mL water.

Case 3: Number of moles of pure gas and its volume

13. Compute the weight (mass) of 6.00 L of ammonia gas, NH_3, at STP.

Solution $$n = \frac{6.00\ \text{L}}{22.4\ \text{L/mol (STP)}} = (0.268\ \text{mol})\left(\frac{17.0\ \text{g}}{\text{mol}}\right) = 4.55\ \text{g}$$

14. Determine the volume occupied by 4.0 g oxygen at STP.

Solution Volume of 4.0 g O_2 at STP = number of moles in 4.0 g O_2 x standard molar volume

$$= \left(\frac{4.0\ \text{g}}{32\ \text{g/mol}}\right)(22.4\ \text{L/mol}) = 2.8\ \text{L}$$

Concentration

It represents the amount of solute in the solution.

The concentration can be expressed in different units.

We are going to discuss some commonly used units.

Mass versus volume

Units of concentration—particularly the most popular one, molarity—require knowledge of a substance's volume, which unlike mass is variable depending on ambient temperature and pressure.

Molarity

Molarity (in units of mol/L, molar, or M) or molar concentration denotes the number of moles of a given substance per liter of solution. A capital letter M is used to abbreviate units of mol/L.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

$$\text{or Molartiy} = \frac{\text{Weight of solute/Molecular weight of solute}}{\text{Volume of solution in litre}}$$

So, number of moles of solute = Volume of solution (in litre) × Molarity of solution

number of milli moles(mm) of solute = Volume of solution (in milliliter (mL)) × Molarity of solution

$$\text{or, Molarity} = \frac{\text{Number of mm of solute}}{\text{Volume of solution in ml}}$$

For instance:

$$\frac{2.0\ \text{moles of dissolved particles}}{4.0\ \text{liters of liquid}} = \text{solutions of } 0.5\ \text{mol/L}.$$

The actual formula for **molarity** is:

$$\frac{\text{Moles of solute}}{\text{Liters of solution}} = \text{Molarity of solution}.$$

Remember:

- Such a solution may be described as "0.50 molar." It must be emphasized a 0.5 molar solution contains 0.5 moles of solute in 1.0 liter of solution. This is not equivalent to 1.0 liter of **solvent**. A 0.5 mol/L solution will contain either slightly more or slightly less than 1 liter of solvent because the process of dissolution causes volume of liquid to increase or decrease.
- Normally, the solute is the reactive component when the solution is made to react with other reagents. Hence, the number of moles of solute is important for chemical calculation.



Worked-out Examples

15. What volume of 3.0 M NaOH (formula weight = 40 g/mol) can be prepared with 84.0 g NaOH?

Solution

$$V\ (\text{litre})\ M\ (\text{molartiy}) = n_B\ (\text{Number of moles of solute})$$

$$= \frac{W_B}{M_B}$$

$$V\ (3\ \text{Moles litre}^{-1}) = \frac{84\ \text{g}}{40\ \text{g/mole}} = 0.7\ \text{L}$$

16. What is the molarity of NaOH in a solution which contains 24.0 g NaOH dissolved in 300 mL solution?

Solution

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\dfrac{24\ \text{g}}{40\ \text{g/mole}}}{0.3\ \text{L}} = 2\,\text{M}$$

Dilution

- It is the process of addition of solvent to the solution keeping the same amount of solute.
- On dilution the volume of solution increases, so molarity of solution decreases.

NO of moles (or mm) of solute $= n_B = \text{constant} = V_iM_i = V_fM_f$

Where, V_i = initial volume of solution

V_f = final volume of sol tion

M_i = Initial molarity

M_i = Final molarity



Worked-out Example

17. How many mL of water must be added to 200 mL of 0.65 M HCl to dilute the solution to 0.20 M?

Solution Number of moles (or mm) of solute = n_B = constant = $V_iM_i = V_fM_f$

$$(200 \text{ ml})(0.65 \text{ M}) = V_f(0.20 \text{ M})$$

$$\Rightarrow \quad V_f = 650 \text{ mL}$$

Approximately, (650 mL) – (200 mL) = 450 mL must be added.

Mixing of solution

- When solutions are mixed their concentration cannot be added.
- Concentration is an intensive property ⇒ not additive.
- Number of moles of solute can be added provided they do not react with each other.
- The volume of the solution can be added provided there is no significant volume change on mixing (normally, we assume that there is no significant change)



Worked-out Example

18. How much 1.00 M HCl should be mixed with what volume of 0.250 M HCl in order to prepare 1.00 L of 0.500 M HCl?

Solution Let x = Vol of 0.25 M HCl in L; then (1.00 – x) = Vol of 1.00 M HCl in L,

Hence, the total number of moles of HCl after mixing = x(0.25) + (1.0 – x)(1.00) = (1.00)(0.500)

Thus, x = 0.667

L = 667 mL of 0.25 M HCl and 1.00 – x = 0.333 L = 333 mL of 1.00 M HCl.

Molality

Molality (mol/kg, molal, or m) denotes the number of moles of solute per kilogram of solvent (not solution). For instance, adding 1.0 mole of solute to 2.0 kilograms of solvent constitutes a solution with a molality of 0.50 mol/kg. Such a solution may be described as "0.50 molal". The term molal solution is used as a shorthand for a "one molal solution", i.e., a solution which contains one mole of the solute per 1000 grams of the solvent.

In a dilute aqueous solution near room temperature and standard atmospheric pressure, molarity and molality will be very similar in value. This is because 1 kg of water roughly corresponds to a volume of 1 L at these conditions, and because the solution is dilute, the addition of the solute makes a negligible impact on the volume of the solution.

However, in all other conditions, this is usually not the case.



Worked-out Example

19. The density of a 2.03 M solution of acetic acid in water is 1.017 g/mL. Calculate the molality of the solution.

Solution One liter of the solution, containing 2.03 mol solute, has a mass of 1017 g. Thus the solution contains 2.03 mol x 60.0 g/mol = 122 g acetic acid and also 1017 – 122 = 895 g water. The molality is 2.03 mol solute/0.895 kg water = 2.27 m

Mole fraction

The mole fraction X, (also called molar fraction) denotes the number of moles of solute as a proportion of the total number of moles in a solution. For instance, 1 mole of solute dissolved in 9 moles of solvent has a mole fraction of 1/10 or 0.1. Mole fractions are dimensionless quantities. (The mole percentage or molar percentage, denoted "mol %" and equal to 100% times the mole fraction, is sometimes quoted instead of the mole fraction.)



Worked-out Examples

20. A solution contains 18.0 g glucose (MW = 180), 24 g acetic acid (MW = 60), and 81 g water (MW = 18). What is the mole fraction of acetic acid in the solution?

Solution

$$\frac{18.0\text{ g glucose}}{180\text{ g/mol}} = 0.100\text{ mol glucose}\quad \frac{24\text{ g acetic acid}}{60\text{ g/mol}} = 0.40\text{ mol acetic acid}$$

$$\frac{81\text{ g water}}{18\text{ g/mol}} = 4.5\text{ mol water}\quad \text{x(acetic acid)} = \frac{0.40}{4.5+0.4+0.1} = 0.080$$

21. A solution contains 10.0 g acetic acid, CH_3COOH, in 125 g water. What is the concentration of the solution expressed as

(a) mole fractions of CH_3COOH and H_2O (b) molality?

Solution

(a) $$(10.0\text{ g } HC_2H_3O_2)\left(\frac{1\text{ mol } HC_2H_3O_2}{60.0\text{ g } HC_2H_3O_2}\right) = 0.167\text{ mol } HC_2H_3O_2$$

$$(125\text{ g } H_2O)\left(\frac{1\text{ mol } H_2O}{18.0\text{ g } H_2O}\right) = 6.94\text{ mol } H_2O$$

$$\text{x(acid)} = \frac{0.167}{0.167+6.94} = 0.0235\quad \text{x(water)} = 1.0000 - 0.0235 = 0.9765$$

(b) $$\frac{0.167\text{ mol } HC_2H_3O_2}{0.125\text{ kg } H_2O} = 1.34\text{ m}$$

Mass Percentage (Fraction)

Mass percentage denotes the mass of a substance in a mixture as a percentage of the mass of the entire mixture. (Mass fraction x_m can be used instead of mass percentage by dividing mass percentage to 100.) Commercial concentrated aqueous reagents such as acids and bases are often labeled in concentrations of weight percentage with the specific gravity also listed. In older texts and references this is sometimes referred to as weight-weight percentage (abbreviated as w/w% or wt%). In water pollution chemistry, a common term of measuring total mass percentage of dissolved solids in an aqueous medium is total dissolved solids.

For instance, if a bottle contains 40 grams of ethanol and 60 grams of water, then it contains 40% ethanol by mass or 0.4 mass fraction ethanol. Note that the total weight of the solution will be 100 grams, but the total volume of the solution will be more than 100 milliliters because ethanol is less dense than water.

Mass-volume percentage

Mass-volume percentage, (sometimes referred to as weight-volume percentage or per cent weight per volume and often abbreviated as % m/v or % w/v) describes the mass of the solute in g per 100 mL of the resulting solution. Mass-volume percentage is often used for solutions made from a solid solute dissolved in a liquid. For example, a 40% w/v sugar solution contains 40 g of sugar per 100 mL of resulting solution.

Volume-volume percentage

Volume-volume percentage (sometimes referred to as per cent volume per volume and abbreviated as % v/v) describes the volume of the solute in mL per 100 mL of the resulting solution. This is most useful when a liquid-liquid solution is being prepared, although it is used for mixtures of gases as well. For example, a 40% v/v ethanol solution contains 40 mL ethanol per 100 mL total volume. The percentages are only additive in the case of mixtures of ideal gases.



Worked-out Examples

22. For a solute of molecular weight W, show that the molar concentration M and molality m of the solution are related by,

$$M = \left(\frac{W}{1000} + \frac{1}{m}\right) = d$$

where d is the solution density in g/mL. (Hint: Show that each mL of solution contains MW/1000 g of solute am M/m g of solvent.)

Solution The number of g solute per mL solution is given by

$$\left(\frac{M \text{ mol}}{L}\right)\left(\frac{1 L}{10^3 \text{ mL}}\right)\left(\frac{W \text{ g}}{\text{mol}}\right) = \frac{MW}{1000} \text{ g solute/mL soln}$$

The number of g solvent per mL solution is given by

$$\left(\frac{M \text{ mol solute}}{L}\right)\left(\frac{\text{kg solvent}}{m \text{ mol solute}}\right)\left(\frac{L}{10^3 \text{ mL}}\right)\left(\frac{10^3 \text{ g}}{\text{kg}}\right) = \frac{M}{m} \text{ g solvent/mL soln}$$

$$\text{Density} = \frac{\text{total g}}{\text{mL}} = \frac{MW}{1000} + \frac{M}{m} = M\left(\frac{W}{1000} + \frac{1}{m}\right)$$

23. A sample of H_2SO_4 (density 1.787 g mL^{-1}) is labeled as 86% by weight. What is molarity of acid? What volume of acid has to be used to make 1 litre of 0.2m H_2SO_4?

Solution H_2SO_4 is 86% by weight

$\therefore$ Weight of H_2SO_4 = 86 g Weight of solution = 100 g

$\therefore$ Volume of solution = $\frac{100}{1.787}$ mL = $\frac{100}{1.787 \times 1000}$ litre

$\therefore$ $M_{H_2SO_4} = \frac{86}{98 \times \frac{100}{1.787 \times 1000}} = 15.68$

Let V mL of this H_2SO_4 are used to prepare 1 litre of 0.2 M H_2SO_4

$\therefore$ mM of concentrated H_2SO_4 = mM of dilute H_2SO_4

$V \times 15.68 = 1000 \times 0.2$

$\therefore$ V = **12.75 mL**

What are the quantitative information we get from a 'Chemical Equations'?

- In Stiochiometry, we normally assume that the reaction proceeds to completion(unless something else is mentioned in the question).
- A balanced equation only provides the molar ratio (**not the actual number of moles**) in which the reactants react or the products are formed.
- It does not tell you anything about the the initial number of moles of the reactants taken.

Let us consider a balanced chemical equation,

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

This equation will provide us various quantitative informations:

1. The molar ratio of reactants, i.e., PbS and H_2O_2 in which they react together is 1:4.
2. The molar ratio of the two products i.e., $PbSO_4$ and H_2O being formed in the reaction is also 1:4.
3. The initial moles of PbS and H_2O_2 for the reaction to take place not necessarily be 1 and 4 respectively or also should not be in the molar ratio of 1:4.
4. One can start the reaction with PbS and H_2O_2 in any molar ratio, but the ratio of PbS and H_2O_2 which are reacting will always be in the ratio of 1:4.
5. One mole of $PbSO_4$ and 4 moles of H_2O will be formed for each mole of PbS being consumed.

The stoichiometric coefficients of a balanced chemical equation is the molar ratio and not the mass ratio.

Limiting Reactants

When chemical reactions take place in a laboratory, manufacturing plant, or in the environment, the reactants are not usually present in the proportions shown by the equation for the reaction. The quantity of one reactant controls the amount of products that can be formed. This reactant is called the limiting reactant or limiting reagent. In the cupcake example at the beginning of this chapter, the egg is the limiting reactant. The recipe calls for two eggs and 2 and 1/4 cups of flour to make 30 cupcakes. If you have only one egg you can only make half a recipe. You will get 15 cupcakes. The egg controls the amount of product (cupcakes). An excess of the other reactant or reactants is present. To make half a recipe of cupcakes you will need 1 and 1/8 cups of flou . If there are three cups of flour in the bag, you will have 1 and 7/8 cups of flour left. An excess of flour is present

When you are making cupcakes, you leave the excess of flour in the bag (unless you like very dry cupcakes). However, when a reaction is carried out in a laboratory, manufacturing plant, or in the atmosphere, an excess of one reactant is often present in the reaction mixture. For example, hydrogen gas made by using the sun's energy, instead of electricity, to decompose water has been suggested as a non-polluting fuel because the only product of burning hydrogen gas in air is water. Remember that when a fuel burns in air, it reacts with the oxygen gas in the air. The equation for the burning of hydrogen gas in air is

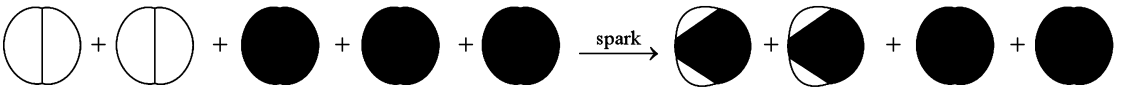
$$2H_2(g) + O_2(g) \xrightarrow{\text{spark}} 2H_2O(l)$$

or, using models to show the reaction on a molecular scale,



2 hydrogen molecules + 1 oxygen molecule ⟶ 2 water molecules

When hydrogen gas burns in air, many more oxygen molecules than hydrogen molecules are usually present. But no more than two water molecules can be formed from two molecules of hydrogen gas even if extra oxygen molecules are present.



2 hydrogen molecules + 3 oxygen molecules ⟶ 2 water molecules + 2 leftover oxygen molecules

Hydrogen gas is the limiting reactant and is all used up in the reaction. An excess of oxygen molecules is present. Oxygen molecules are left over.

Sample Problem below shows how to work problems that involve a limiting reactant. You can recognize a limiting reactant problem by the fact that quantities are given for more than one reactant.

- If quantities are given for more than one reactant, a problem may be a limiting reactant problem.
- Always begin solving problems about quantitative relationships in reactions by writing an equation for the reaction.
- The fraction 0.865 is a pure number, that is, it has no units.



Worked-out Examples

Sample Problem

24. A mixture of 3.50 g of hydrogen and 26.0 g of oxygen is made to react to form water. (a) Which reactant is limiting? (b) How many grams of water will be formed? (c) Which reactant will be left over? (d) How many grams of this reactant will be left over?

Solution As usual, begin by writing the equation for the reaction and making a table of information. The table of information for this problem is

Problem	3.50 g	26.0 g	? g
Equation	$2H_2(g) + O_2(g)$	$\xrightarrow{\text{spark}}$	$2H_2O(l)$
Formula masses, u	2.02	32.0	18.0
Recipe, mol	2	1	2

(a) and (c) To find out which reactant is limiting and which will be left over, reason exactly as you would if you were baking cupcakes. You would say to yourself: "One egg, that is half a recipe. I have three cups of flour but that's more than a recipe of flou . I will only be able to make half a recipe of cupcakes; I will have some flour left over." Because the "recipe" for a chemical reaction is in moles, you must convert the quantities of reactants to moles before finding the fraction or multiple of a recipe available.

$$3.50\ \text{g}\ H_2\left(\frac{1\ \text{mol}\ H_2}{2.02\ \text{g}\ H_2}\right) = 1.73\ \text{mol}\ H_2$$

and

$$26.0\ \text{g}\ O_2\left(\frac{1\ \text{mol}\ O_2}{32.0\ \text{g}\ O_2}\right) = 0.813\ \text{mol}\ O_2$$

Now, 1.73 mol H_2 is $\dfrac{1.73\ \text{mol}\ H_2}{2\ \text{mol}\ H_2} = 0.865$

of a recipe of H_2 and 0.813 mol O_2 is $\dfrac{0.813\ \text{mol}\ O_2}{1\ \text{mol}\ O_2} = 0.813$

of a recipe of O_2. Because the fraction of a recipe of oxygen used (0.813) is less than the fraction of a recipe of hydrogen used (0.865), O_2 is limiting and hydrogen will be left over. The amount of the limiting reactant, O_2, that is available determines how much hydrogen can react and how much water can be formed.

(b) Calculation of the amount of water that can be formed.

$$26.\ \text{g}\ O_2\left(\frac{1\ \text{mol}\ O_2}{32.0\ \text{g}\ O_2}\right)\left(\frac{2\ \text{mol}\ H_2O}{1\ \text{mol}\ O_2}\right)\left(\frac{18.0\ \text{g}\ H_2O)}{1\ \text{mol}\ H_2O}\right) = 29.3\ \text{g}\ H_2O$$

(d) The problem states that 3.50 g of hydrogen were present at the beginning of the reaction. To find out how much hydrogen will be left over, we need to determine how much hydrogen will be used up by reaction with 26.0 g of oxygen.

$$26.0\ \text{g}\ O_2\left(\frac{1\ \text{mol}\ O_2}{32.0\ \text{g}\ O_2}\right)\left(\frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2}\right)\left(\frac{2.02\ \text{g}\ H_2}{1\ \text{mol}\ H_2}\right) = 3.28\ \text{g}\ H_2$$

Subtract the mass of H_2 needed to react with 26.0 g O_2 from the mass of H_2 that was present at the beginning of the reaction to find out how much hydrogen is left over

(3.50 g H_2 present) – (3.28 g H_2 reacted) = 0.22 g H_2 left.

None of the limiting reactant is left over; all of the limiting reactant is used up in the reaction.

25. If 0.5 mole of $BaCl_2$ is mixed with 0.2 mole of Na_3PO_4 the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is

(a) 0.7 (b) 0.5

(c) 0.3 (d) 0.1

Solution $3\ BaCl_2 + 2Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + 6NaCl$

From the molar ratio we see,

$BaCl_2 : Na_3PO_4 : Ba_3(PO_4)_2 : NaCl$

3 : 2 : 1 : 6

$\therefore$ (d)

Gravimetric Analysis

Gravimetric analysis relation between the mass or volume of the substances through the number of moles. The analysis can be divided into three kinds:

(i) Mass-Mass relationship
(ii) Mass-Volume relationship
(iii) Volume-Volume relationship

Calculation involving in mass–mass relationship

In general, the following steps are adopted in making necessary calculations:

1. Write down balanced molecular equation for the chemical change.
2. Write down the relative masses of the reactants and the products with the help of formula below the respective formula. These shall be the theoretical amounts of reactants and product.
3. Calculate the number of moles below the formula of each of the reactant and product.
4. By the applications of mole concept, mass co-relation through unitary method or proportionality method, principle of atomic conservation the unknown quantity can be determined.

Let us consider a question in which all possible methods have been applied to solve the same problem.



Worked-out Example

26. Caustic soda, NaOH, can be prepared commercially by the reaction of Na_2CO_3 with slaked lime, $Ca(OH)_2$. How many g of NaOH can be obtained by treating 1.000 kg of Na_2CO_3 with $Ca(OH)_2$?

Solution First write the balanced equation for the reaction.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

(1 mol = 106.0 g) (2 mol = 2(40.0 g) = 80.0 g)

The mass ratio 106.0/80.0 is all that is needed to solve the problem. We show four methods, all equivalent, of handling the arithmetic.

- **First method (Unitary Co-relation of Mass)**

$$106.0 \text{ g } Na_2CO_3 \text{ gives } 80.0 \text{ g NaOH}$$

$$\text{So, } 1 \text{ g } Na_2CO_3 \text{ gives } \frac{80.0}{106.0} \text{ g NaOH}$$

$$1000 \text{ g } Na_2CO_3 \text{ gives } 1000 \times \frac{80.0}{106.0} = 755 \text{ g NaOH}$$

- **Second method (Mole Method)**

The symbol n(X) will be used to refer to the number of moles of a substance whose formula is X, and m(X) will denote the mass of substance X. Consider 1000 g Na_2CO_3.

$$n(Na_2CO_3) = \frac{1000 \text{ g}}{106.0 \text{ g/mol}} = 9.433 \text{ mol } Na_2CO_3$$

From the coefficients in the balanced equation, n(NaOH) = 2n(Na_2CO_3) = 2(9.433) = 18.87 mol NaOH. m(NaOH) = (18.87 mol NaOH)(40.0 g NaOH/mol NaOH) = 755 g NaOH

- **Third method (Proportion Method for mass co-relation)**
  Let x = number of g of NaOH obtained from 1000 g of Na_2CO_3. It is known that 106.0 g of Na_2CO_3 gives 80 g of NaOH; then, by proportion,

$$\frac{106.0\text{ g } Na_2CO_3}{80.0\text{ g NaOH}} = \frac{1000\text{ g } Na_2CO_3}{x} \quad x = (1000\text{ g } Na_2CO_3)\left(\frac{80.0\text{ g NaOH}}{106.0\text{ g } Na_2CO_3}\right) = 755\text{ g NaOH}$$

  Note It should be evident that 1000 g of Na_2CO_3 will give 755 g of NaOH, and that 1000 tons of Na_2CO_3 will give 755 tons of NaOH.

- **Fourth method (Factor-Label Method)**
  As in the previous method, x = mass of NaOH obtained. Now x is equated to the 1000 g Na_2CO_3, and the right side of the equation is multiplied by successive conversion factors until it has the desired units g NaOH.

$$x = (1000\text{ g } Na_2CO_3)\left(\frac{1\text{ mol } Na_2CO_3}{106.0\text{ g } Na_2CO_3}\right)\left(\frac{2\text{ mol NaOH}}{1\text{ mol } Na_2CO_3}\right)\left(\frac{40.0\text{ g NaOH}}{1\text{ mol NaOH}}\right) = 755\text{ g NaOH}$$

  The equation for the reaction of sucrose (sugar) with oxygen is,

$$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$$

- **Fifth method (Principle of Atom Conservation)**

$$n(Na_2CO_3) = \frac{1000\text{ g}}{106.0\text{ g/mol}} = 9.433\text{ mol } Na_2CO_3$$

  From the principle of conservation of Na atom, n(NaOH) = n(Na) = 2(9.433) = 18.87 mol NaOH.

  m(NaOH) = (18.87 mol NaOH)(40.0 g NaOH/mol NaOH) = 755 g NaOH

Calculation involving per cent yield

In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical amount of the product. The amount of the product that is actually obtained is called the actual yield. Knowing the actual yield and theoretical yield the percentage yield can be calculated as,

$$\%\text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$



Worked-out Examples

27. The per cent loss in weight after heating a pure sample of potassium chlorate (Molecular weight = 122.5) will be

(a) 12.25 (b) 24.50
(c) 39.18 (d) 49

Solution $2KClO_3 \rightarrow 2KCl + 3O_2$

245 g $KClO_3$ on heating shows a weight loss of 96 g,

$\therefore$ 100 g $KClO_3$ on heating shows a weight loss of $= \frac{96 \times 100}{245} = 39.18\%$

$\therefore$ (c)

28. 13.4 g of a sample of unstable hydrated salt: $Na_2SO_4 \times nH_2O$ was found to contain 6.3 g of water. Determine the number of water of crystallization.

(a) 6 (b) 5

(c) 7 (d) 8

Solution $\dfrac{\text{weight of water}}{\text{weight of sample}} = \dfrac{\text{weight of water in the compound}}{\text{molecular weight of the compound}}$

$$\frac{6.3}{13.4} = \frac{x \times 18}{142 + 18x} = 7$$

$\therefore$ (c)

29. A sample of $CaCO_3$ and $MgCO_3$ weighed 2.21 g is ignited to constant weight of 1.152 g. What is the composition of the mixture.

Solution $CaCO_3 \rightarrow CaO + CO_2$

x g

$MgCO_3 \rightarrow MgO + CO_2$

y g

$\therefore$ $(x + y) = 2.21$ g

$\because$ 100 g of $CaCO_3$ gives 56 g of CaO

$\therefore$ x g of $CaCO_3 \equiv \dfrac{56}{100} \times (x)$gm CaO

Similarly, 84 g of $MgCO_3$ gives 40 g of MgO

$\therefore$ y g of $MgCO_3 = \dfrac{40 \times (y)}{84}$ g

$\therefore$ Weight of residue $= \dfrac{56x}{100} + \dfrac{40y}{84} = 1.152$ ...(2)

Solving equations (1) and (2)

x = 1.19 g

y = 1.02 g

30. A mixture of FeO and Fe_2O_3 when heated in air to constant weight gains 5% in weight. Find out composition of mixture.

Solution $2FeO + \dfrac{1}{2}O_2 \rightarrow Fe_2O_3$

$2Fe_3O_4 + \dfrac{1}{2}O_2 \rightarrow 3Fe_2O_3$

Let, weight of FeO = x

Weight of Fe_3O_4 = y

$\therefore$ $x + y = 100$ ...(1)

$\because$ 2×72 g of FeO give Fe_2O_3 $= 160$ g

$\therefore$ x g FeO gives Fe_2O_3 $= \dfrac{160 \times (x)}{144}$ g

2×232 g of Fe_3O_4 gives Fe_2O_3 $= 3 \times 160$ g

$\therefore$ y g Fe_3O_4 gives Fe_2O_3 $= \dfrac{3 \times 160 \times y}{2 \times 232}$ g

$$\therefore \quad \frac{160x}{144}+\frac{3\times16\times y}{464}=105 \qquad \ldots(2)$$

Solving equation (1) and (2)

$x = 20.25$ g

$y = 79.95$ g

31. Pyrolusite is an ore of manganese and it contains 80% by mass MnO_2, 15% inert impurities and the rest is water. When MnO_2 is heated it converts to Mn_3O_4. A sample of pyrolusite was heated till constant weight is obtained. Calculate the percentage of Manganese in the residue.

Solution First of all think what is being asked. We have to calculate the % of Mn in the residue. This means that we must have the mass of manganese in the residue and the total mass of residue. Since the problem does not mention the mass of pyrolusite that was heated, then probably it was redundant. So, let us assume the mass of the sample to be x g.

Mass of MnO_2 in pyrolusite $= 0.8\,x$ g.

$\Rightarrow$ Mass of inert impurities $= 0.15\,x$ g.

Now, think about what is meant by 'heated till constant weight is obtained'. Well, the only thing it can mean is that the sample is heated due to which some changes took place in its weight and the sample is being heated till all the changes that were to occur have occurred. This certainly implies that all the water in the sample must have gone away.

When MnO_2 is heated it converts to Mn_3O_4.

$$\therefore \quad 3MnO_2 \rightarrow Mn_3O_4 + O_2 \qquad \ldots(1)$$

We can see that to produce 1 mole of Mn_3O_4, one would need to heat 3 moles of MnO_2.

$$\text{Moles of } MnO_2 \text{ in the sample} = \frac{0.8x}{87}$$

$$\text{Moles of } Mn_3O_4 \text{ produced} = \frac{0.8x}{87}\times\frac{1}{3}$$

$$\text{Mass of } Mn_3O_4 \text{ produced} = \left(\frac{0.8x}{87}\times\frac{1}{3}\times229\right)\text{g.}$$

$$\text{Mass of inert impurities} = 0.15\,x \text{ g. (unchanged)}$$

$$\therefore \quad \text{Total mass of residue} = \left(\frac{0.8x}{87}\times\frac{1}{3}\times229+0.15x\right)\text{g.}$$

Now let us find the mass of Mn in the residue

$$\text{Moles of } MnO_2 \text{ in pyrolusite} = \frac{0.8x}{87}$$

$$\text{Moles of Mn in } \frac{0.8x}{87} = \text{moles of } MnO_2 = \frac{0.8x}{87}$$

Since Mn is neither lost nor created in the conversion to Mn_3O_4, its number of moles would remain constant.

$\therefore$ mass of Mn in the residue = $\left(\frac{0.8x}{87}\times 55\right)$g.

$$\% \text{ Mn in the residue} = \frac{\frac{0.8x}{87}\times 55}{\frac{0.8x}{87}\times\frac{1}{3}\times 229 + 0.15x}\times 100 = 59.36\%$$

[**Note** You may have noticed that the equation (1) is not balanced. To balance it , add O_2 to the right hand side of the equation.

$\therefore$ we have, $3MnO_2 \rightarrow Mn_3O_4 + O_2$

Some of you may feel that if MnO_2 is heated, the O_2 should occur on the left hand side of the equation. It is not necessary that if something is heated, it would react with oxygen. It would react with oxygen only if the product has more % of oxygen than the reactant. In this case, it is the other way round (36.78% O in MnO_2, 27.94% O in Mn_3O_4)].

Weight–volume relationship

Case 1: Mass of a substance with volume of the gas

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

In the above reaction, one can find out the volume of O_2 at STP required to react with 10 g of Mg. The moles of Mg is $\frac{10}{24}$. The moles of O_2 required would be ½ the moles of Mg. Therefore, moles of O_2 = $\frac{1}{2}\times\frac{10}{24}$. Since 1 mole of a gas (ideal) occupies 22.4L at STP, therefore $\frac{1}{2}\times\frac{10}{24}$ moles of O_2 would occupy, $\frac{1}{2}\times\frac{10}{24}\times 22.4\text{L} = 4.67\text{L}$.

Suppose we are provided with 'a' gms of $NaHCO_3$ in a vessel of capacity V L and the vessel is heated, so that $NaHCO_3$ decomposes as,

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

Now, we want to calculate the volume of CO_2 gas being produced.

Moles of $NaHCO_3$ taken = $\frac{a}{84}$

Now, since 2 moles of $NaHCO_3$ gives 1 mole of CO_2 at STP. Thus,

Moles of CO_2 produced = $\frac{1}{2}\times\frac{a}{84}$

As we know that 1 mole of any gas at STP occupies a volume of 22.4 L.

So, volume of CO_2 produced = $\left(\frac{1}{2}\times\frac{a}{84}\times 22.4\right)$L

Worked-out Examples

32. Calcium metal reacts with hydrochloric acid to yield hydrogen and calcium chloride. Write a balanced chemical equation for the reaction. Determine the volume of hydrogen gas at 1.00 atm pressure and 18 °C produced from the reaction of 12.2 g of calcium with excess HCl.

Solution

$$Ca + 2HCl \longrightarrow CaCl_2 + H_2 \quad (12.2\text{ g Ca})\left(\frac{1\text{ mol Ca}}{40.08\text{ g Ca}}\right)\left(\frac{1\text{ mol } H_2}{1\text{ mol Ca}}\right) = 0.304\text{ mol } H_2$$

$$V = \frac{nRT}{P} = \frac{(0.304\text{ mol})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(291\text{ K})}{1.00\text{ atm}} = 7.27\text{ L}$$

33. Calculate the volume of hydrogen liberated at 27°C and 760 mm pressure by treating 1.2 g of magnesium with excess of hydrochloric acid.

Solution The balanced equation is,

$Mg + 2HCl \rightarrow MgCl_2 + H_2$

1 mole 1 mole

24 g 22.4 litre at NTP

24 g of Mg liberate hydrogen = 22.4 litre

1.2 g of Mg will liberate hydrogen = $\frac{22.4}{24} \times 1.2 = 1.12$ litre

Volume of hydrogen under given condition can be calculated by applying,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$P_1 = 760$ mm $P_2 = 760$ mm

$T_1 = 273$ K

$T_2 = (27 + 273) = 300$ K

$V_1 = 1.12$ litres $V_2 = ?$

$$V_2 = \frac{760 \times 1.12}{273} \times \frac{300}{760} = 1.2308\text{ litres}$$

Case 2: Mass of a substance with volume of the solution

Worked-out Example

34. How many mL of 0.0250 M HBr are required to neutralize 25.0 mL of 0.0200 M $Ba(OH)_2$? (Assume complete neutralization.)

Solution $2HBr + Ba(OH)_2 \rightarrow BaBr_2 + 2H_2O$ $(25.0\text{ mL})(0.0200\text{ M}) = 0.500\text{ mmol } Ba(OH)_2$

This quantity of $Ba(OH)_2$ contains 1.00 mmol of OH^-, which will neutralize 1.00 mmol of HBr.

$$(1.00\text{ mmol})\left(\frac{1\text{ mL}}{0.0250\text{ mmol}}\right) = 40.0\text{ mL}$$

More about Principle of Atom Conservation (POAC)

In chemical reaction atoms are conserved, so moles of atoms shall also be conserved. This is known as principle of atomic conservation. This principle is helpful in solving problems of nearly all stoichiometric calculations e.g.,

$$KClO_{3(s)} \rightarrow KCl_{(s)} + O_{2(g)}$$

Applying POAC for K atoms

Moles of K atoms in $KClO_3$ = Moles of K atoms in KCl

Since one mole of $KClO_3$ contains 1 mol of K atom. Similarly, 1 mol of KCl contains one mole of K atoms.

$$\therefore \quad 1 \times n_{KClO_3} = 1 \times n_{KCl} \Rightarrow 1 \times \frac{W_{KClO_3}}{M_{KClO_3}} = \frac{W_{KCl}}{M_{KClO_3}} \text{ in gm (Mass-mass relationship)}$$

Applying POAC for 'O' atoms,

Moles of O atom in $KClO_3$ = Moles of O atom in O_2

$$\therefore \quad 3 \times n_{KClO_3} = 2 \times n_{O_2}$$

$$\Rightarrow 3 \times \frac{w_{KClO_3} \text{ in gm}}{M_{KClO_3}} = 2 \times \frac{PV}{RT} \text{ (Mass volume relationship of reactant and product)}$$

In this way, applying POAC, we can break the chemical equation into a number arithmetic equations without balancing the chemical equation. Moreover, number of reactions and their sequence from reactants to products are not required. It is important to note that POAC can be applied for the atoms which remain conserved in chemical reaction.



Worked-out Examples

Application of POAC

35. Gravimetric determination of P of an aqueous solution of dihydrogen phosphate in $H_2PO_4^-$ is treated with a mixture of ammonium and magnesium ions to precipitate magnesium ammonium phosphate $Mg(NH_4)PO_4.6H_2O$. This is heated and decomposed to magnesium pyrophosphate. $Mg_2P_2O_7$ which is weighed. A solution of $H_2PO_4^-$ yielded 1.054 g of ($Mg_2P_2O_7$) which is weighed. What weight of NaH_2PO_4 was present originally?

Solution $NaH_2PO_4 + Mg^{2+} + NH_4^+ \rightarrow Mg(NH_4)PO_4.6H_2O \xrightarrow{\Delta} Mg_2P_2O_7$

As P atoms are conserved, apply POAC for P atoms, moles of P in NaH_2PO_4 = moles of P in $Mg_2P_2IO_7$

$\Rightarrow$ 1 × moles of NaH_2PO_4 = 2 × 2 moles of $Mg_2P_2O_7$

$$\therefore \quad \frac{W_{NaH_2PO_4}}{M_{NaH_2PO_4}} = 2 \times \frac{W_{Mg_2P_2O_7}}{M_{Mg_2P_2O_7}} \Rightarrow \frac{W_{NaH_2PO_4}}{120} = 2 \times \frac{1.054}{222}$$

$$\therefore \quad W_{NaH_2PO_4} = 1.14 \text{ g}$$

36. 1 g sample of $KClO_3$ was heated under such conditions that a part of it decomposed according to the equation

(i) $2KClO_3 \rightarrow 2KCl + 3O_2$

(ii) and the remaining underwent change according to the equation

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

If the amount of O_2 evolved was 146.8 mL at STP, calculate percentage by weight of $KClO_4$ in the residue.

Solution $\underset{x}{KClO_3} \rightarrow KCl + O_2$ (Part – I)

$\underset{(1-x)}{KClO_3} \rightarrow \underset{y}{KClO_4} + KCl$ (Part – II)

To calculate (x) apply POAC for 'O' atom in Part (I)

For calculation of y, apply POAC for 'O' atom in Part (II) and calculate % of $KClO_4$ in the residue as follow.

$$\% \text{ of } KClO_4 = \frac{y}{W_{KCl_{(I)}} + W_{KCl_{(II)}} + y} \times 100$$

37. A mixture of KBr, NaBr weighing 0.56 g was treated with aqueous solution of Ag^+ and the bromide ion was recovered as 0.97 g of pure AgBr. What was the weight of KBr in the sample?

Solution

KBr	+	NaBr	+	Ag^+	→	AgBr
a g		(0.56 – a) g				0.97 g

Applying POAC for Br atoms

Moles of Br in KBr + moles of Br in NaBr = moles of Br in AgBr

or $1 \times$ moles of KBr + $1 \times$ moles of NaBr = $1 \times$ moles of AgBr

$$\Rightarrow \quad \frac{a}{119} + \frac{(0.56-a)}{103} = \frac{0.97}{188} \quad (M_{KBr} = 199, M_{NaBr} = 103, M_{AgBr} = 188)$$

$\therefore \quad a = 0.1332$ g

Percentage of KBr in the sample $= \frac{0.1332}{0.560} \times 100 = 23.78$ **In a**

Volume–volume relationship

(a) Eudiometry

Let us consider the reaction $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$. We are given 10L of H_2 at a given temperature and pressure. How many liters of O_2 would react with hydrogen at the same temperature and pressure?

From the ideal gas equation [PV = nRT] it is clear that the volume of an ideal gas is directly proportional to its number of moles. Therefore under the same conditions of P and T, $\frac{V_{H_2}}{V_{O_2}} = \frac{n_{H_2}}{n_{O_2}}$. Since the molar ratio is 2 : 1 (H_2 : O_2), therefore the volume ratio would also be 2 : 1. Therefore, the volume of O_2 required would be 5 L.

On the other hand, if we need to calculate the volume of O_2 at a different T and P, then,

$$P_{H_2} V_{H_2} = n_{H_2} R T_{H_2}, P_{O_2} V_{O_2} = n_{O_2} R T_{O_2}, \text{ and dividing we get } \frac{P_{H_2} V_{H_2}}{P_{O_2} V_{O_2}} = \frac{n_{H_2} T_{H_2}}{n_{O_2} T_{O_2}},$$

$$\therefore \quad V_{O_2} = \frac{P_{H_2} V_{H_2}}{P_{O_2}} \times \frac{n_{O_2} T_{O_2}}{n_{H_2} T_{H_2}}$$



Worked-out Example

38. 10 mL of gaseous hydrocarbon on combustion gives 40 mL of $CO_2(g)$ and 50 mL of H_2O (vapour). The hydrocarbon is

(a) C_4H_5 (b) C_8H_{10}

(c) C_4H_8 (d) C_4H_{10}

Solution $C_aH_b + \left(a + \frac{b}{4}\right)O_2 \rightarrow aCO_2 + b/2\ H_2O$

$10 \rightarrow$	excess	—	—
0	excess	10a	5b

Therefore,

$10a = 40$

So, $a = 4$

$5b = 50$

$b = 10$

$\therefore$ (d)

(b) Volumetric analysis

Titration: The process of determination of concentration of a solution of unknown concentration with the help of a solution of known concentration i.e., standard solution, is known as TITRATION.

Equivalent Weight: Number of parts by mass of an element which reacts or displaces from a compound 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of that element. E.g.,

$$2Mg + O_2 \longrightarrow 2MgO$$

48 g 32 g

12 g 8 g

$\therefore$ 32 g of O_2 reacts with 48 g of Mg

$\therefore$ 8 g of $O_2 = \frac{48 \times 8}{32} = 12$ g

$\therefore$ Equivalent weight of Mg = 12

Similarly, $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

65.5g 2×1.008

$\because$ 2×1.008 g of hydrogen is displaced by 65.5g

$\therefore$ 1.008 g of $H = \frac{65.5}{2 \times 1.008} = 32.75$g

$\therefore$ Equivalent weight of $Zn = \frac{65.5}{2} = 32.75$

$$Al + \frac{3}{2}Cl_2 \longrightarrow AlCl_3$$

$$32\text{ g} \quad \frac{3}{2}\times 71\text{ g} \quad \because \text{ 111.5 g chlorine reacts with 27 g of Al}$$

$$\therefore \text{ 35.5 g chlorine reacts with } \frac{27\times 35.5}{111.5} = 9.0\text{ g of Al}$$

$$\therefore \text{ Equivalent weight of aluminium} = \frac{27}{3} = 9.0$$

As we can see from the above examples that equivalent weight is the ratio of atomic weight and a factor (say n-factor) which is in above three cases is their respective valencies. So,

$$\text{Equivalent weight (E)} = \frac{\text{Atomic or molecualr weight}}{\text{n}-\text{factor}}$$

$$\text{Number of equivalents of solute} = \frac{\text{Wt}}{\text{Equilibrium weight}} = \frac{\text{W}}{\text{E}} = \frac{\text{W}}{\text{M/n}}$$

Number of equivalents of solute = Number of moles of solute × n-factor

Normality

Normality highlights the chemical nature of salts: in solution, salts dissociate into distinct reactive species (ions such as H^+, Fe^{3+}, or Cl^-). Normality accounts for any discrepancy between the concentrations of the various ionic species in a solution. For example, in a salt such as $MgCl_2$, there are two moles of Cl^- for every mole of Mg^{2+}, so the concentration of Cl^- is said to be 2 N (read: "two normal"). Further examples are given below. It may also refer to the concentration of a solute in any solution. The normality of a solution is the number of gram equivalent weight of a solute per litre of its solution. For example, hydrochloric acid(HCl). One litre of aqueous solution of HCl acid contains 36.5 grams HCl. It is called 1N (one normal)solution of HCl. It is given by the following formula:

$$\text{normality, N} = \left(\frac{\text{gram equivalents}}{\text{liters solution}}\right)$$

- Number of equivalents of solute = Normality x volume in litre
- Number of milli equivalents (meq) of solute = Normality x volume in mL
- Normality = n-factor × molarity of solution

Definition

A **normal** is one gram equivalent of a solute per liter of solution. The definition of a gram equivalent varies depending on the type of chemical reaction that is discussed—it can refer to acids, bases, redox species, and ions that will precipitate.

Usage

It is critical to note that normality measures a single ion which takes part in an overall solute. For example, one could determine the normality of hydroxide or sodium in an aqueous solution of sodium hydroxide, but the normality of sodium hydroxide itself has no meaning. Nevertheless, it is often used to describe solutions of acids or bases, in those cases it is implied that the normality refers to the H^+ or OH^- ion. For example, 2 Normal sulfuric acid (H_2SO_4), means that the normality of H^+ ions is 2, or that the molarity of the sulfuric acid is 1. Similarly, for 1 molar H_3PO_4, the normality is 3 as it contains three moles of H^+ ions for every mole of PO_4^{3-}.

Specific cases

As ions in solution can react through different pathways, there are three common definitions for normality as a measure of reactive species in solution:

- In acid-base chemistry, normality is used to express the concentration of protons **or** hydroxide ions in the solution. Here, the normality differs from the molarity by an integer value—each solute can produce n equivalents of reactive species when dissolved. For example: 1 M aqueous $Ca(OH)_2$ is 2 N (normal) in hydroxide.
- In redox reactions, normality measures the quantity of oxidizing or reducing agent that can accept or furnish one mole of electrons. Here, the normality scales from the molarity, most commonly, by a fractional value. Calculating the normality of redox species in solution can be challenging.
- In precipitation reactions, normality measures the concentration of ions which will precipitate in a given reaction. Here, the normality scales from the molarity again by an integer value.

Practical uses

The measure of normality is extremely useful for titrations—given two species that are known to react with a known ratio, one simply needs to scale the volumes of solutions with known normalities to get a complete reaction with the following equation:

$$N_a V_a = N_b V_b$$

However, normality cannot reliably represent an unambiguous measure of the concentration of a solution. Since the measure of normality depends on the reaction that the solute participates in, the same concentration of solute can possess two different normalities for two different reactions. For example, Mg^{2+} is 2 N with respect to a Cl^- ion, but it is only 1 N with respect to an O^{2-} ion.

Accordingly, normality is no longer used to represent the concentration of a solution as such. Instead, a solution should be labeled according to its molarity, and it is then possible to calculate the normality for a particular titration using the equation above. NIST has also stipulated that this unit is obsolete and recommends discontinuing its use.

Calculation of n-Factor for Acid-Base and Salt

For calculating the n-factor of any reactant in any reaction. One must know the kind of reaction it is, the reactions may be classified into the following three types

1. Acid-Base Reactions/Neutralization reactions
2. Redox Reactions
3. Precipitation Reactions/Double decomposition reactions

Acid-base reaction: According, to the Arrhenius, an acid is a substance that furnishes H^+ ion(s) in solution, a base is a substance that furnishes OH^- ion(s) in solution and neutralization is a reaction in which H^+ ion furnished by acid combines with OH^- ions furnished by base. The number of H^+ ion(s) furnished per molecule of the acid is its n-factor also called basicity. Similarly, the number of OH^- ion(s) furnished by the base per molecule is its n-factor, also called acidity.
Some examples

$$\underset{(n=1)}{HCl} \longrightarrow H^+ + Cl^-$$

$$\underset{(n=1)}{H_2SO_4} \longrightarrow H^+ + HSO_4^-$$

$$\underset{(n=2)}{H_2SO_4} \longrightarrow 2H^+ + SO_4^{2-}$$

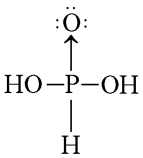
$$\underset{(n=1)}{H_3PO_4} \longrightarrow H^+ + H_2PO_4^-$$

$$\underset{(n=3)}{H_3PO_4} \longrightarrow 3H^+ + PO_4^{3-}$$

$$\underset{(n=1)}{H_3PO_3} \longrightarrow H^+ + H_2PO_3^-$$

$$\underset{(n=2)}{H_3PO_3} \longrightarrow 2H^+ + HPO_3^-$$

The n-factor of H_3PO_3 cannot be 3 as it has only two dissociable H^+ ions. So, its n-factor or dissociable protons is 1 or 2 as one of the H-atoms is linked with P atom directly.



Similarly, $\underset{(n=1)}{CH_3COOH} \longrightarrow CH_3COO^- + H^+$

n-factor of CH_3COOH is 1, because it contains only one dissociable H^+ ion.
Now, we will consider the n-factor of some bases.

$$\underset{(n=1)}{NaOH} \longrightarrow Na^+ + OH^-$$

$$\underset{(n=1)}{Ba(OH)_2} \longrightarrow [Ba(OH)]^- + OH^-$$

$$\underset{(n=2)}{Ba(OH)_2} \longrightarrow Ba^{2+} + 2OH^-$$

$$\underset{(n=3)}{Al(OH)_3} \longrightarrow Al^{3+} + 3OH^-$$

Similarly, n-factor of $Al(OH)_3$ can also be 1 or 2 or 3, depending upon the number of OH^- released.

Law of equivalence

For a general reaction,

$$aA + bB \rightarrow mC + nD$$

Eq. of A = Eq. of B = Eq. of C = Eq. of D

Or Meq. of A = Meq. of B = Meq. of C = Meq. of D

- In a compound A_xB_y, Eq. of A_xB_y = Eq. of A = Eq. of B
  For the chemical change,

$$aA + bB \rightarrow mC \xrightarrow{dD} nE \longrightarrow X$$

  Meq. of A used = Meq. of B used = Meq. of C formed = Meq. of D used = Meq. of E formed = Meq. of X formed.
- That is equivalent or meq. of reactants react in equal number to give the same number of equivalent or meq. of the products separately.



Worked-out Examples

39. 1.82 g of a metal required 32.5 mL of N – HCl to dissolve it what is the equivalent weight of metal?

(a) 54 (b) 56

(c) 28 (d) 86

Solution Meq. of metal = Meq. of HCl

$$\frac{1.82}{E_M} \times 1000 = 32.5 \times 1$$

$\therefore E_M = 56$

$\therefore$ (b)

40. What volume at NTP of ammonia gas will be required to be passed into 30 mL of NH_2SO_4 to bring down the acid normality to 0.2N?

(a) 556.5 mL (b) 480.5 mL

(c) 537.6 mL (d) 438.4 mL

Solution Meq. of H_2SO_4 (original) = $30 \times 1 = 30$

Meq. of H_2SO_4 after passing $NH_3 = 30 \times 0.2 = 6$

Meq. of H_2SO_4 reacted = Meq. of NH_3

$= 30 - 6 = 24$

$\therefore \quad \frac{w_{NH_3}}{17} \times 1000 = 24, \; w_{NH_3} = 0.408$ g

$\therefore \quad V_{NH_3}$ at STP $= \frac{0.408}{17} \times 22.4 = 0.5376$ lt

$= 537.6$ mL

$\therefore$ (c)

Titration is divided into the following four categories:

(i) Simple Titration
(ii) Double Titration
(iii) Back Titration
(iv) Iodimetric and Iodometric Titration

Simple Titration: A known volume of the solution of unknown concentration is taken in a flask and required reagents are added to it. The solution of known concentration is added from the burette in the solution of unknown concentration till the latter reacts completely. This process is called titration. At the end point (equivalence point) the equivalents or milliequivalents of the two reacting substances are equal.

Volume of solution (A) = V_A litres

Normality of solution (A) = N_A

Equivalents of substance (A) = $N_A V_A$

Similarly, equivalents of substance (B) = $N_B V_B$

At the equivalence point (end point) the equivalents (not the moles) of the two substance are equal.

$N_A V_A$ (litre) = $N_B \times V_B$ (litre)

Worked-out Example

41. 40 mL N/10 HCl and 60 mL N/20 KOH are mixed together. Calculate the normality of the acid or base left. What is the normality of the salt formed in the solution?

Solution Milli equivalents of HCl = N × V (mL) $= \frac{1\times 40}{10} = 4$

Milli equivalents of KOH = N × V (mL) $= \frac{1\times 60}{20} = 3$

One milli equivalent of an acid neutralizes one milli equivalent of a base,

Milli equivalent of HCl left = 4 – 3 = 1

Total volume of the solution = 40 + 60 = 100 mL

Milli equivalents of HCl = N × V (mL)

1 = N × 100

Normality (N) of HCl left in solution = 0.01

Salt formed = Milli equivalent of acid or base neutralized

Milli equivalents of the salt formed = N × V (mL)

3 = N × 100

Normality (N) of salt formed = 0.03

Double Titration: If an aqueous solution contains a mixture of any two of the three NaOH, $NaHCO_3$ and Na_2CO_3 and it has to be titrated against an acid HCl or H_2SO_4, the following reactions will take place.

$$NaOH + HCl \longrightarrow NaCl + H_2O \quad \text{..... (1)}$$

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \quad \text{..... (2)}$$

weak base | HCl

$$\longrightarrow NaCl + H_2O + CO_2 \quad \text{.....(3)}$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2 \quad \text{.....(4)}$$

The basic strengths are as follows:

NaOH> Na_2CO_3> $NaHCO_3$, hence the acid added will first react with NaOH, then Na_2CO_3 followed by $NaHCO_3$. Hence reaction (1) will take place first ,followed by reaction (2), there after, reaction (3) and (4) (virtually same reaction,only the sources of $NaHCO_3$ are different) will take place.

These reactions will require two indicators to determine the strength of the bases present. The two indicators used are phenolphthalein and methyl orange.

Method: A given volume of the aqueous solution of the bases is taken and phenophthalein indicator is added to it. This solution is titrated with an acid of known normality to the end point the volume of the acid used is noted. This end point is called first end point. Now in the same solution methyl orange is added and gain titrated with an acid of known strength to the end point. It is called second end point. The volume of acid, used in the second end point is also noted. The normality of the bases present is then calculated.

Principle:

Case 1:In the presence of phenolphthalein as indicator (pH range: 8-10)

Since phenolphthalein is a weak organic acid, and it changes its colour in weakly basic medium ($NaHCO_3$) (Below pH = 8), so as soon as the Na_2CO_3 is converted to $NaHCO_3$, phenolphthalein shows the colour change indicating the completion of the reaction.

Hence, **Reaction(1) and (2) will take place only.**
So we can write down,

$$n_{Na_2CO_3} + n_{NaoH} = n_{HCl}$$

Case 2: In the presence of Methyl orange (pH range:3-4.4) as indicator from the beginning
In the presence of methyl orange, all the basic substances left in the mixture will be neutralized by acid and methyl orange will show the colour change when the medium is weakly acidic ($H_2O + CO_2$ i.e., H_2CO_3).
Hence, all the reactions will take place, **So we can write down:**

$$2n_{Na_2CO_3} + n_{NaoH} + n_{NaHCO_3} = n_{HCl}$$



Worked-out Examples

42. NaOH and Na_2CO_3 are dissolved in 200 mL aqueous solution. In the presence of phenolphthalein indicator. 17.5 mL of 0.1 M HCl are used to titrate this solution. Now methyl orange is added in the same solution titrated and it requires 2.5 mL of the same HCl. Calculate the molarity of NaOH and Na_2CO_3 and their mass present in the solution.

Solution Milli mole(mm) of HCl used in the presence of phenolphthalein indicator.

$$= M \times V\,(mL)$$
$$= (0.1 \times 17.5)mm = 1.75mm$$

So we can write down,

$$n_{Na_2CO_3} + n_{NaoH} = n_{HCl}$$
$$\Rightarrow \quad x + y = 1.75 \text{ mm} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

[Where X = Number of mm of Na_2CO_3 taken and Y = Number of mm of NaOH taken]
Milli moles of HCl used in the presence of methyl orange indicator

$$= M \times V\,(mL)$$
$$= 0.1 \times 2.5mm = 0.25 \text{ mm}$$

This must be the number of mm of HCl required to react with $NaHCO_3$ formed from Na_2CO_3
So we can write down,

$$n_{Na_2CO_3} = n_{HCl} \Rightarrow x = 0.25 \text{ mm} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$0.25mm = 0.25\times10^{-3}\,\text{mole} = \frac{\text{mass}}{\text{molarmass}} = \frac{w(g)}{106} \Rightarrow W(g) = 106\times0.25\times10^{-3}\,g = 0.0265g$$

$$\text{Molarity of } Na_2CO_3 = \frac{0.25mm}{200ml} = \frac{1}{800}M$$

For NaOH solution: From equation (1) and (2)

$$\text{Milli moles acid used by NaOH} = a - b$$
$$= (1.75 - 0.25)mm$$
$$= 1.50mm$$

$$1.5mm = 1.5\times10^{-3}\ \text{mole} = \frac{\text{mass}}{\text{molar mass}} = \frac{w(g)}{40} \Rightarrow W(g) = 40\times1.5\times10^{-3}\,g = 0.06g$$

$$\text{Volume of NaOH solution} = 200 \text{ mL}$$

$$\text{Hence, molarity of NaOH solution} = \frac{1.5mm}{200ml} = \frac{3}{400}M$$

43. Both Na_2CO_3 and $NaHCO_3$ are present in an aqueous solution. In the presence of phenolphthalein indicator, 10 mL of this solution requires 2.5 mL of 0.1M H_2SO_4 for titration. After this methyl orange is added in the same solution and titration requires 5 mL M H_2SO_4. Calculate the concentration of Na_2CO_3 and $NaHCO_3$ in g/litre.

Solution Milli eq. (a) of H_2SO_4 used in the presence of phenolphthalein indicator

$$= N \times V\,(mL) = 0.1 \times 2 \times 2.5 = 0.5$$

$$a = 0.5 = \frac{1}{2} \text{ milli equivalents of } Na_2CO_3 \qquad \ldots(1)$$

Milli. eq. (b) of $NaHCO_3$ + ½ milli eq. of Na_2CO_3 ...(2)

For Na_2CO_3 solution: From equation (1)

Milli eq. of acid used by $Na_2CO_3 = 2 \times 0.5 = 1$

Suppose, Normality of Na_2CO_3 solution = N

Volume of Na_2CO_3 solution taken = 10 mL

Milli eq. of Na_2CO_3 taken = $N \times V\,(mL) = 10\,N$

Putting the milli eq. of H_2SO_4 and Na_2CO_3 equal,

$$1 = 10\,N$$

or (Normality of Na_2CO_3) $N = 0.1$

Strength (S) in g/litre $= N \times E$

$= 0.1 \times 53$ (E for $Na_2CO_3 = 53$)

$=$ **5.3 g/litre**

For $NaHCO_3$ solution: From equations (1) and (2) milli eq. of acid used by,

$NaHCO_3 = b - a = 1.0 - 0.5 = 0.5$

Suppose, Normality of $NaHCO_3$ solution = N

Volume of $NaHCO_3$ solution taken = 10 mL

Milli equivalents of $NaHCO_3$ taken = 10 N

Putting the milli eq. of H_2SO_4 and $NaHCO_3$ equal,

$$0.5 = 10\,N$$

or (Normality of $NaHCO_3$ solution) $N = 0.05$

Strength (S) in g/litre = $N \times E$

(E for $NaHCO_3 = 84$) $= 0.05 \times 84$

$=$ **4.2g/litre**

Back Titration: Let us consider that we have an impure solid substance 'Z' weighing 'w' g and we are required to calculate the percentage purity of 'Z' in the sample. We are also provided with two solutions 'X' and 'Y', where the concentration of 'Y' is known (N_1) and that of 'X' is unknown. For the back titration to work, the following conditions are to be satisfied:

(a) Compounds 'X', 'Y' and 'Z' should be such that 'X' and 'Y' reacts with each other.
(b) 'X' and pure 'Z' also reacts with each other but the impurity present in 'Z' does not react with 'X'.

$Z + X$ (excess) $\rightarrow$ Product 1

Remaining (X) + Y $\rightarrow$ Product 2

Note Product 1 should not react with Y

Milli equivalent of Y = N_2V_2

Where N_2 and V_2 (mL) is the normality and volume of Y

Initial mili equivalent of X = N_1V_1

Where N_1 and V_1 (mL) is the normality and volume of X

Remaining milli equivalents of X after reacting with Y = $N_1V_1 - N_2V_2$

Remaining milli equivalents of X = milli equivalents of Z

$$N_1V_1 - N_2V_2 = \frac{a \times 1000}{\text{Equivalent weight}}$$

Where 'a' is the weight of pure Z which is reacted.

$$a = \frac{\text{Molecular weight } (N_1V_1 - N_2V_2)}{n - \text{factor}}$$

$$\therefore \quad \text{Percentage purity of 'Z'} = \frac{(N_1V_1 - N_1V_2)}{n - \text{factor}} \times \frac{\text{Molar Mass of 'Z'}}{W} \times 100$$



Worked-out Example

44. 20 g of a sample of $Ba(OH)_2$ is dissolved in 10 mL. of 0.5N HCl solution. The excess of HCl was titrated with 0.2N NaOH. The volume of NaOH used was 10 cc. Calculate the percentage of $Ba(OH)_2$ in the sample.

Solution Milli eq. of HCl initially = $10 \times 0.5 = 5$

Milli eq. of NaOH consumed = Milli eq. of HCl in excess

$= 10 \times 0.2 = 2$

$\therefore$ Milli eq. of HCl consumed = Milli eq. of $Ba(OH)_2$

$= 5–2=3$

$\therefore$ eq. of $Ba(OH)_2 = 3/1000 = 3 \times 10^{-3}$

Mass of $Ba(OH)_2 = 3 \times 10^{-3} \times (171/2) = 0.2565$ g.

% $Ba(OH)_2 = (0.2565/20) \times 100 = 1.28\%$

Volume Strength of H_2O_2 Solution

The concentration of H_2O_2 is usually represented in terms of volume. If a sample of H_2O_2 is labeled as 'x volume', it means that 1 volume of H_2O_2 solution gives 'x volumes' of O_2 gas at STP on complete decomposition.

Consider the decomposition of H_2O_2 as,

$$\underset{2\times34g}{2H_2O_2} \xrightarrow{\Delta} 2H_2O + \underset{22.4\text{ L at STP}}{O_2}$$

$\because$ 22400 mL of O_2 gas is liberated by 68 g of H_2O_2 solution

$\therefore$ x mL of O_2 gas will be liberated by $= \frac{68x}{22400} = \frac{17x}{5600}$ g of H_2O_2

It means that $\frac{17x}{5600}$ g of H_2O_2 will be present in 1 mL of solution.

$\therefore$ 1000 mL of solution contains $H_2O_2 = \frac{17x}{5600} \times 1000 = \frac{17x}{5.6}$

Strength (g L^{-1}) = Normality × Equivalent weight

$$\frac{17x}{5.6} = N \times \frac{34}{2} \quad (\because \text{n-factor of } H_2O_2 = 2)$$

$$x = 5.6 \times N$$

i.e., Volume strength of $H_2O_2 = 5.6 \times$ Normality



Worked-out Example

45. 34 g of hydrogen peroxide is present in 1120 mL of solution. This solution is called

(a) 10 volume solution (b) 20 volume

(c) 30 volume (d) 32 volume

Solution Amount of H_2O_2 in one mL = $\frac{34}{1120}$ g

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

$\because$ 34 g of H_2O_2 gives 16 g or 11200 mL of O_2

$\therefore$ $\frac{34}{1120}$ g $H_2O_2 = \frac{11200}{34} \times \frac{34}{1120} = 10$ mL O_2

$\therefore$ Volume strength of $H_2O_2 = 10$ volume

$\therefore$ (a)

Percentage Labelling of Oleum

Oleum is nothing but a mixture of H_2SO_4 and SO_3 i.e., $H_2S_2O_7$. This is obtained by passing SO_3 in solution of H_2SO_4. To dissolve free SO_3, dilution of oleum is done with water. In that process, free SO_3 reacts with water to form H_2SO_4. Thus mass of the solution increases.

The dilution is continued till the entire SO_3 gets converted H_2SO_4. It is shown as under:

$$SO_3 + H_2O \longrightarrow H_2SO_4 \text{ (Pure) Or}$$

$$H_2SO_4 + SO_3 + H_2O \longrightarrow 2H_2SO_4 \text{ (Pure)}$$

In that way oleum is converted into pure H_2SO_4.

When 100 g sample of oleum is diluted with desired weight of H_2O (in g), then the total mass of H_2SO_4 obtained after dilution is known as % labeling in oleum. For example, if the oleum sample is labelled as "118% H_2SO_4", it means 100 g oleum is diluted with 18 g of H_2O which gives 118 g pure H_2SO_4.

$$\therefore \quad \underset{80\text{g}}{SO_3} + \underset{18\text{ g}}{H_2O} \longrightarrow \underset{98\text{ g}}{H_2SO_4}$$

Since 18 g will react with 80 g SO_3, it means that in 10 g oleum sample, wt. of SO_3 is 80 g. SO, wt. of H_2SO_4 will be 20 g

$\therefore$ % composition by wt. of H_2SO_4 = 20% in oleum

% composition by wt. of SO_3 = 80%

Oleum or fuming sulphuric acid contains SO_3 gas dissolved in sulphuric acid. When water is added to oleum, SO_3 reacts with H_2O to form H_2SO_4, thus mass of the solution increases.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The total mass of H_2SO_4 obtained by diluting 100 g of sample of oleum with desired amount of water, is equal to the percentage labeling of oleum.

$\therefore$ percentage labelling of oleum = Total mass of H_2SO_4 present in oleum after dilution.

= mass of H_2SO_4 initially present + mass of H_2SO_4 produced on dilution.



Worked-out Examples

46. Calculate the composition of 109% oleum.

Solution Let the mass of SO_3 in the sample be 'w' g, then the mass of H_2SO_4 would be (100 – w)g. On dilution,

$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$80\text{ g} \quad 18\text{ g}$$

Moles of SO_3 in oleum = $\frac{w}{80}$ = Moles of H_2SO_4 formed after dilution.

$\therefore$ Mass of H_2SO_4 formed on dilution = $\frac{98w}{80}$

Total mass of H_2SO_4 present in oleum after dilution = $\frac{98w}{80} + (100 - w) = 109$

$\therefore$ $w = 40$

Thus, oleum sample contains 40% SO_3 and 60% H_2SO_4.

47. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. This solution is completely neutralised by 26.7 mL of 0.4 N NaOH. The percentage of free SO_3 in the sample is

(a) 30.6% (b) 40.6%

(c) 20.6% (d) 50%

Solution Meq. of H_2SO_4 + Meq. of SO_3 = Meq. of NaOH

$\therefore$ $\frac{(0.5-x)}{98/2} \times 1000 + \frac{x}{80/2} \times 1000 = 26.7 \times 0.4$

$\therefore$ $x = 0.103$

$\therefore$ % of SO_3 = $\frac{0.103}{0.5} \times 100$

= 20.6%

$\therefore$ (c)

Hardness of Water

Soft water Water which produces lather with soap solution readily is called soft water.
Hard water Water which does not produce lather with soap solution readily is called hard water.

Cause of hardness of water

- The hardness of water is due to the presence of Mg and Ca salts like bicarbonates, chlorides and sulphates.
- Hard water does not produce lather with soap because the Mg^{+2} and Ca^{+2} cations react with soap to form Ca and Mg salts of fatty acids (which are not soaps).

$$Ca^{2+} + 2C_{17}H_{35}COONa \rightarrow (C_{17}H_{35}COO)_2Ca + 2Na^+$$
soap ppt. (not a soap)

$$Mg^{2+} + 2C_{17}H_{35}COONa \rightarrow (C_{17}H_{35}COO)_2Mg + 2Na^+$$
Soap ppt. (not a soap)

Types of hardness

(i) *Temporary hardness* (Carbonate hardness)
It is due to the presence of soluble bicarbonates of calcium and magnesium.

(ii) *Permanent hardness* (Non-carbonate hardness)
It is due to the presence of chlorides and sulphates of Ca and Mg.

Hardness of water is represented in ppm (mg/litre) of $CaCO_3$ i.e., milli grams of $CaCO_3$ present per litre of hard water. But hard water does not contain $CaCO_3$. Hard water contains $CaCl_2$, $MgCl_2$, $Ca(HCO_3)_2$ etc.

One mole $CaCl_2 \equiv$ one mole $CaCO_3$

or 111 g $CaCl_2 \equiv$ 100 g $CaCO_3$

Similarly, 120 g $MgSO_4 \equiv$ 100 g $CaCO_3$

- Thus mass of $CaCO_3$ corresponding to the mass of $CaCl_2$, $MgSO_4$ etc., present in hard water is calculated. Milligrams of $CaCO_3$ per litre of hard water is called hardness of water in ppm. (Parts per million ('ppm') denotes the amount of a given substance in a total amount of 1,000,000 regardless of the units of measure used as long as they are the same. e.g., 1 milligram per kilogram. 1 part in 10^6.)



Worked-out Examples

48. A sample of hard water contains 244 ppm of HCO_3^- ions. What is the minimum mass of CaO required to remove HCO_3^- ions completely from 1 kg of such water sample?

(a) 56 mg (b) 112 mg
(c) 168 mg (d) 244 mg

Solution Mass of HCO_3^- in 1 kg or 10^6 mg water = 244 mg

$$\text{Millimoles of } HCO_3^- = \frac{244}{61} = 4$$

$$2HCO_3^- + CaO \rightarrow CaCO_3 + H_2O + CO_2 + 2e^-$$

millimoles of CaO = 2

mass of CaO = 56 × 2 = 112 mg

∴ (b)

49. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^-, with Ca^{+2} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{+2} ions? (Assume $CaCO_3$ to be completely insoluble in water). If the Ca^{+2} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH? (one ppm means one part of the substance in one million part of water, mass/mass.)

Solution In 1000 kg of water the mass of HCO_3^- = 183 g

$$\text{moles of } HCO_3^- = \frac{183}{61} = 3$$

$$\text{moles of } SO_4^{2-} = \frac{96}{96} = 1$$

$\therefore$ total moles of Ca^{2+} in the solution = 1 + 1.5 = 2.5

$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$

moles of CaO required to be added to remove all HCO_3^- = 1.5.

Now, the Ca^{2+} in the solution will be only associated with SO_4^{2-}. Therefore moles of Ca^{+2} left in the solution = 1.

ppm of $Ca^{2+} = 1 \times 40 = 40$ ppm

moles of Ca^{2+} ions in 1 L of $H_2O = 10^{-3}$

moles of H^+ ions that Ca^{+2} will exchange with $= 2 \times 10^{-3}$

$\therefore$ $pH = -\log(2 \times 10^{-3}) = 2.7$

Solution Meq. of H_2SO_4 (original) $= 30 \times 1 = 30$

Meq. of H_2SO_4 after passing $NH_3 = 30 \times 0.2 = 6$

Meq. of H_2SO_4 reacted = Meq. of NH_3

$= 30 - 6 = 24$

$\therefore$ $\frac{w_{NH_3}}{17} \times 1000 = 24$, $w_{NH_3} = 0.408$ g

$\therefore$ V_{NH_3} at STP $= \frac{0.408}{17} \times 22.4 = 0.5376$ lt

$= 537.6$ mL

$\therefore$ (c)

50. 0.05 g of commercial sample of $KClO_3$ on decomposition liberated just sufficient oxygen for complete oxidation of 20 mL CO at 27°C and 750 mm pressure. Calculate % of $KClO_3$ in sample

Solution Applying PV = nRT for CO

$$\text{Moles of CO } (n_{CO}) = \frac{PV}{RT} = \frac{750 \times 20}{760 \times 0.821 \times 300 \times 1000} = 8.01 \times 10^{-4}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2, \quad \frac{n_{CO}}{n_{O_2}} = \frac{1}{2} = 2$$

$\therefore$ $\text{Moles of } O_2 \text{ required } (n_{O_2}) = \frac{n_{CO}}{2} = \frac{8.01 \times 10^{-4}}{2}$

$2KClO_3 \rightarrow 2KCl + 3O_2$

As 3 moles of O_2 are given by 2 mole of $KClO_3$,

$\therefore$ $\frac{8.01\times10^{-4}}{2}$ mol of O_2 are given by $= \frac{2}{3}\times\frac{8.01\times10^{-4}}{2}$ mol of $KClO_3$

$= 2.66 \times 10^{-4}$ mol of $KClO_3$

$\therefore$ Weight of $KClO_3 = 2.66 \times 10^{-4} \times 122.5$ g $= 3.27 \times 10^{-2}$ g

$\therefore$ % of $KClO_3$ in the mixture $= \frac{3.24\times10^{-2}}{0.5} \times 100 = 65.4\%$

51. Upon mixing 45.0 mL of 0.25 M lead nitrate solution with 25 mL of 0.10 M chromic sulphate solution precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the concentrations of the species left behind in final solution. Assume that lead sulphate is completely insoluble.

Solution

	$Pb(NO_3)_2$ +	$Cr_2(SO_4)_3$ →	$PbSO_4\downarrow$ +	$Cr(NO_3)_2$
Meq. (initial)	$45 \times 0.25 \times 2$	$25 \times 0.1 \times 6$	0	0
	$= 22.5$	$= 15$ (limiting reagent)		
Meq. (final	7.5	0	15	15

Meq. of $PbSO_4$ precipitated = 15

Moles of $PbSO_4 = \frac{15}{2\times1000}$ (n-factor = 2) ($Cr_2(SO_4)_3$ is the limiting reagent)

$= 7.5 \times 10^{-3}$

$[Pb^{2+}] = \frac{7.5}{70\times2} = 5.36 \times 10^{-2}$ M

$[NO_3^-] = \frac{(7.5+15)}{1\times70} = 0.32$ M

$[Cr^{3+}] = \frac{15}{3\times70} = 7.14 \times 10^{-2}$ M

52. A solution contains mixture of H_2SO_4 and $H_2C_2O_4$. 25 mL of this solution requires 35.5 mL of N/10 for neutralization and 23.45 mL of N/10 $KMnO_4$ for oxidation, calculate

(i) Normality of $H_2C_2O_4$ and H_2SO_4

(ii) Strength of $H_2C_2O_4$ and H_2SO_4 molecular weight of $H_2C_2O_4 = 126$

Solution Meq. of H_2SO_4 + Meq. of $H_2C_2O_4$ = Meq. of NaOH

$= 3.55 \times \frac{1}{10} = 3.55$ ...(1)

Meq. of $H_2C_2O_4$ = Meq. of $KMnO_4$

$= 23.45 \times \frac{1}{10} = 2.345$

$\therefore$ Meq. of $H_2SO_4 = 3.55 - 2.345 = 1.205$

$\therefore$ $N_{H_2SO_4} = \frac{1.205}{0.25} = 0.0482 \left[N = \frac{\text{Meq.}}{\text{Volume in ml}}\right]$

Strength = N × Eq. wt. = $0.0482 \times \frac{98}{2} = 2.362$ g /litre

Meq. of $H_2C_2O_4 = 2.345$ (in 25 mL) (n-factor = 2)

$\therefore \quad N_{H_2SO_4} = \frac{2.345}{25} = 0.0938$ $H_2C_2O_4 \rightarrow 2CO_2$

$\therefore$ Strength = N × Equivalent weight

$= 0.0938 \times \frac{126}{2}$ (n-factor = 2) = 5.909 g

53. A definite amount of $BaCl_2$ was dissolved in HCl solution of unknown normality 20 mL of this solution was treated with 21.4 mL of N/10 NaOH for complete neutralization. Further 20 mL of solution was added to 50 mL of N/10 Na_2CO_3 and precipitate was filtered off. The filtrate reacted with 10.5 mL of 0.8 N/10 H_2SO_4 in the presence of phenolphthalein as indicator. Calculate strength of $BaCl_2$ and HCl in the mixture.

Solution Meq. of HCl in 20 mL solution = Meq. of NaOH

$\Rightarrow \quad 20 \times N = 21.4 \times \frac{1}{10} = 2.14$

$\therefore \quad N_{HCl} = \frac{21.4 \times 1}{10 \times 20} = 0.107$

Strength of HCl = $0.107 \times 36.5 = 3.9055$ g /litre

Meq. of Na_2CO_3 added to 20 mL solution = $50 \times \frac{1}{10} = 5$

Meq. of Na_2CO_3 left after reaction in between $BaCl_2 + NaCO_3$ and $(HCl + Na_2CO_3)$

= 2 × Meq. of H_2SO_4 using phenolphthalein as indicator

($\frac{1}{2}$ Meq. of Na_2CO_3 left = Meq. of H_2SO_4)

$\therefore$ Meq. of Na_2CO_3 left = 2 × Meq. of H_2SO_4)

$= 2 \times \frac{0.5 \times 0.8}{10} = 1.6$

$\therefore$ Meq. of Na_2CO_3 usedf for $(HCl + BaCl_2)$

= Meq. of Na_2CO_3 added – Meq. of Na_2CO_3 left

= (5 – 1.68) = 3.32

$\therefore$ Meq. of HCl + Meq. of $BaCl_2 = 3.32$

$\therefore$ Meq. of $BaCl_2$ = (3.32 – Meq. of HCl)

= 3.32 – 2.14 (meq. of of HCl in 20 mL) = 3.32 – 2.14 = 1.18

$\frac{W_{BaCl_2}}{208} \times 2 \times 1000 = 1.18$ (n-factor for $BaCl_2 = 2$)

$\therefore$ W_{BaCl_2} in 20 mL = 0.122 of g

$\therefore$ W_{BaCl_2} in 1 litre = $\frac{0.122}{20} \times 1000$ = 6.135 g /lit

54. Potassium selenate is isomorphous with potassium sulphate and contains 45.52% selenium by weight. Calculate the atomic weight of selenium. Also report the equivalent weight of potassium selenate.

Solution Potassium selenate is isomorphous to K_2SO_4 and thus its molecular formula is K_2SeO_4.

Now molecular weight of K_2SeO_4 = $(39 \times 2 + a + 4 \times 16)$

= $(142 + a)$

Where, a is atomic weight of Se

$(142 + a)$g K_2SeO_4 has Se = ag

$\therefore$ 100 g K_2SeO_4 has Se = $\frac{a \times 100}{142 + a}$

$\because$ % of Se = 45.52

$\therefore$ $\frac{a \times 100}{142 + a} = 45.52$

$\therefore$ a = 118.2

Also, equivalent of K_2SeO_4 = $\frac{\text{Mol. wt.}}{2} = \frac{2 \times 39 + 118.2 + 64}{2} = 130.1$

55. A sample of H_2SO_4 (density 1.787 g mL^{-1}) is labelled as 86% by weight. What is molarity of acid? What volume of acid has to be used to make 1 litre of 0.2m H_2SO_4?

Solution H_2SO_4 is 86% by weight

$\therefore$ Weight of H_2SO_4 = 86 g

Weight of solution = 100 g

$\therefore$ Volume of solution = $\frac{100}{1.787}$mL = $\frac{100}{1.787 \times 1000}$litre

$\therefore$ $M_{H_2SO_4} = \frac{86}{98 \times \frac{100}{1.787 \times 1000}} = 15.68$

Let V mL of this H_2SO_4 are used to prepare 1 litre of 0.2 M H_2SO_4

$\therefore$ mM of concentrated H_2SO_4 = mM of dilute H_2SO_4

$V \times 15.68 = 1000 \times 0.2$ $\therefore$ V = 12.75 mL

56. The molecular mass of an organic acid was determined by the study of its barium salt 4.290 g of salt was quantitatively converted to free acid by the reaction with 21.64 mL of 0.477 M H_2SO_4. The barium salt was found to have two mole of water of hydration per Ba^{2+} ion and the acid is mono basic. What is molecular weight of anhydrous acid?

Solution Meq. of barium salt = Meq. of acid

$\frac{4.290}{M/2} \times 1000 = 21.64 \times 0.4777 \times 2$

Molecular weight of salt = 415.61

Molecular weight of anion = $\frac{415.61-137-36}{2}=121.31$

$\therefore$ Molecular weight of acid = 121.31 + 1 = 122.31

57. 25 mL of a solution of Na_2CO_3 having a specific gravity of 1.25 g mL^{-1} required 32.9 mL of a solution of HCl containing 109.5 g of the acid per litre for complete neutralization. Calculate the volume of 0.84 N H_2SO_4 that will be completely neutralized by 125 g of Na_2CO_3 solution.

Solution $N_{HCl}=\frac{109.5}{36.5\times1}=3$

Since Na_2CO_3 is completely neutralized by HCl

$\therefore$ Meq. of Na_2CO_3 = Meq. of HCl

$N \times 25 = 32.9 \times 3$

$\therefore$ $N_{Na_2CO_3} = 3.948$

Now Na_2CO_3 fresh solution reacts with H_2SO_4

$\therefore$ Volume of Na_2CO_3 solution = $\frac{125}{1.25}=100\,mL$

$\therefore$ Meq. of H_2SO_4 = Meq. of Na_2CO_3

$0.84 \times V = 100 \times 3.948$

$\therefore$ Volume of H_2SO_4 = **470 mL**

58. Borax in water gives:

$$B_4O_7^{2-}+7H_2O\longrightarrow 4H_3BO_3+2OH^-$$

How many gram of borax ($Na_2B_4O_7.10H_2O$) are required to?

(a) Prepare 50 mL of 0.2 M solution

(b) neutralize 25 mL of 0.1934 M of HCl and H_2SO_4 separately

Solution $\left(\because \text{Molarity}=\frac{\text{Normality}}{\text{No. of replaceable } OH^-}\right)$

$\therefore$ $N = M \times 2$

Thus, Meq. of borax in solution = $50 \times 0.2 \times 2 = 20$

$\therefore$ $\frac{w}{M/2}\times1000=20$

$\therefore$ $\frac{w}{382/2}\times1000=20$

$\therefore$ w = 3.82g

For neutralization of HCl,
Meq. of HCl = Meq. of borax

$$25\times0.1934=\frac{w}{382/2}\times1000$$

$\therefore$ Weight of borax = 0.09235g

For neutralization of H_2SO_4

Meq. of borax = Meq. of H_2SO_4

$$\frac{w}{382/2}\times 1000 = 25\times 0.1934\times 2$$

$\therefore$ Weight of borax = **1.847 g**

59. 1.249 g of a sample of pure $BaCO_3$ and impure $CaCO_3$ containing some CaO was treated with dil. HCl and it evolved 168 mL of CO_2 at NTP. From this solution, $BaCrO_4$ was precipitated, filtered and washed. The precipitate was dissolved in dilute sulphuric acid and diluted to 100 mL. 10 mL of this solution, when treated with KI solution, liberated iodine which required exactly 20 mL of 0.05N $Na_2S_2O_3$. Calculate the percentage of CaO in the sample.

Solution $n_{CaCO_3} + n_{BaCO_3} = n_{CO_2} = \frac{168}{22400} = 7.5 \times 10^{-3}$ ----- (1)

$$2BaCO_3 \rightarrow 2BaCrO_4 \xrightarrow{H^+} BaCr_2O_7 \xrightarrow{KI} I_2 + Na_2S_2O_3$$

eq. of $Na_2S_2O_3$ = eq. of I_2 = eq of $BaCr_2O_7$ = $\frac{20\times 10^{-3}\times 0.05\times 100}{10}$

$= 1 \times 10^{-12}$

Moles of $BaCr_2O_7 = \frac{1}{6} \times 10^{-2}$

Moles of $BaCrO_4 = \frac{2}{6}(1 \times 10^{-2})$

Moles of $BaCO_3 = \frac{1}{3} \times 10^{-2} = 3.33 \times 10^{-3}$ ---- (2)

Weight of $BaCO_3$ = 0.650 g

From equation (1) and (2) we get,

$n_{CaCO_3} = 4.17 \times 10^{-3}$

Weight of $CaCO_3 = 100\times 4.17\times 10^{-3} = 0.417$ g

Weight of CaO = 1.249 – 0.656 – 0.417 = 0.176

Percentage of CaO = $\frac{0.176}{1.249}\times 100 = 14.09\%$

60. In a quality control analysis for sulphur impurity 5.6 g steel sample was burnt in a stream of oxygen and sulphur was converted into SO_2 gas. The SO_2 was then oxidized to sulphate by using H_2O_2 solution to which had been added 30 mL of 0.04M NaOH. The equation for reaction is:

$$SO_{2(g)} + H_2O_{2(aq)} + 2OH^-_{(aq)} \rightarrow SO_4^{-2}{}_{(aq)} + 2H_2O_{(l)}$$

22.48 mL of 0.024M HCl was required to neutralize the base remaining after oxidation reaction. Calculate % of sulphur in given sample.

Solution Meq. of alkali added = 30 × 0.04 = 1.2

Meq. of alkali left = 22.48 × 0.024 = 0.54

$\therefore$ Meq. of alkali for SO_2 and $H_2O_2 = 1.2 - 0.54 = 0.66$

$\therefore$ Weight of alkali used $= \dfrac{0.66 \times 40}{1000} = 0.0264$

$\because$ 80 g NaOH reacts with 64 g SO_2

$\therefore$ 0.026 4 g NaOH reacts $= \dfrac{64 \times 0.0264}{80} = 0.021$ g SO_2

Now, $\because$ 64 g SO_2 required = 32 g S

$\therefore$ 0.021 g SO_2 required $= \dfrac{32 \times 0.021}{64} = 0.0105$ g

$\therefore$ % of S $= \dfrac{0.0105}{5.6} \times 100 = 0.1875\%$

61. A granulated sample of aircraft alloy (Al, Mg, Cu) weighing 8.72 g was first treated with alkali and then with very dilute HCl, leaving a residue. The residue after alkali boiling weighed 2.10 g and the acid insoluble residue weighed 0.69 g. What is the composition of the alloy?

Solution Let Al, Mg and Cu be a, b and c g respectively.

$$2Al + 2NaOH \xrightarrow{2H_2O} 2NaAlO_2 + 3H_2$$

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

$Cu + HCl \rightarrow$ No reaction

i.e., only Al reacts with NaOH and then only Mg reacts with HCl

$\therefore$ $a + b + c = 8.72$

$b + c = 2.10$ (Residue left after alkali treatment)

$c = 0.69$ (Residue left after acid treatment)

$\therefore$ $b = 6.62$g

$\therefore$ % of Al $= \dfrac{6.62}{8.72} \times 100 = 75.9$

% of Mg $= \dfrac{1.41}{8.72} \times 100 = 16.2$

% of Cu $= \dfrac{0.69}{8.72} \times 100 = 7.9$

62. 25 mL from a stock solution containing $NaHCO_3$ and Na_2CO_3 was diluted to 250 mL with CO_2 free distilled water. 25 mL of the diluted solution when titrated with 0.12 M HCl required 8 mL when phenolphthalein was used as an indicator. When 20 mL of diluted solution was titrated with same acid required 18 mL when methyl orange was used as an indicator. Calculate concentration of $NaHCO_3$ in the stock solution in g /litre and in mole/litre. To 100 mL of the stock solution how much NaOH should be added so that all bicarbonate will be converted into carbonate?

Solution When phenolphthalein used, $NaHCO_3$ remains unaffected and Na_2CO_3 will be converted into $NaHCO_3$,

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$\dfrac{1}{2}$ eq of Na_2CO_3 = eq. of HCl $\qquad \dfrac{1}{2}\dfrac{w}{53} = 0.12 \times 8 \times 10^{-3} \times 10$

w = 1.017 g in 25 mL = 40.7 g /litre = 0.38 mole/litre

When methyl orange is used $NaHCO_3$ and Na_2CO_3 both will be converted into CO_2

Eq. (Na_2CO_3) + eq$(NaHCO_3)$ = eq (HCl)

$$\left(1.92\times10^{-3}+\frac{W}{84}\right) = 18\times0.12\times10^{-3}\times\frac{250}{20}$$

$$1.92\times10^{-2}+\frac{W}{84} = 2.7\times10^{-2}$$

For $NaHCO_3$ W = 0.6552 g in 250 mL = 26.2 g /litre = 0.312 M

equilibrium of bicarbonate = eq of NaOH

$$0.78\times10^{-2}\times\frac{100}{25} = \frac{W}{40}$$

$$W = 1.248 \text{ g}$$

63. A polyvalent metal weighing 0.1 g and having atomic weight of 51 reacted with dilute H_2SO_4 to give 43.90 mL of hydrogen at N.T.P. This solution containing the metal in the lower oxidation state was found to require 58.8 mL of 0.02 M $KMnO_4$ for complete oxidation. What are the oxidation states of the metal in the two reactions?

Solution Let lower oxidation state of metal be n,

$$\text{equivalents of metal} = \frac{0.1\times n}{51} = \text{equivalents of } H_2 \text{ evolved} = \frac{43.90}{22400}\times2$$

$\therefore$ n = 2

Let final oxidation state = $'$

Then equivalents of metal = equivalents of oxidant

$$\frac{0.1(n'-2)}{51} = \frac{58.8\times0.02\times5}{1000} \quad \therefore n' = 5$$

64. 1.20 g of sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 mL of a solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralisation. Calculate the weight of Na_2CO_3 in mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$ what will be the weight of the precipitate?

Solution Let weight of Na_2CO_3 = x g

Weight of K_2CO_3 = y g

$\therefore$ x + y = 1.20 g ...(1)

For neutralisation reaction of 100 mL of,

Meq. of Na_2CO_3 + Meq. of K_2CO_3 = Meq. of HCl

$$\Rightarrow \frac{x}{M_{Na_2CO_3}}\times2\times1000+\frac{y}{138}\times2\times1000 = \frac{40\times0.1\times100}{20}$$

$\therefore$ 69x + 53y = 73.14

65. How many grams of sodium bicarbonate are required to neutralize 10.0 mL of 0.902 M vinegar?

(a) 8.4g (b) 1.5g

(c) 0.75g (d) 1.07g

Solution $NaHCO_3 + \underset{\text{Vinegar}}{CH_3COOH} \rightleftharpoons CH_3COONa + CO_2 + H_2O$

$$\text{Equivalent of acid} = \frac{10 \times 0.902}{1000}$$

$$\text{Equivalent of } NaHCO_3 = 9.02 \times 10^{-5}$$

$$\text{Amount of } NaHCO_3 = 9.02 \times 10^{-5} \times \frac{1000}{10} \times 84$$

$$= 0.758$$

$\therefore$ (c)

66. A sample of hard water contains 244 ppm of HCO_3^- ions. What is the minimum mass of CaO required to remove HCO_3^- ions completely from 1 kg of such water sample?

(a) 56 mg (b) 112 mg
(c) 168 mg (d) 244 mg

Solution Mass of HCO_3^- in 1 kg or 10^6 mg water = 244 mg

$$\text{Millimoles of } HCO_3^- = \frac{244}{61} = 4$$

$$2HCO_3^- + CaO \rightarrow CaCO_3 + H_2O + CO_2 + 2e^-$$

Millimoles of CaO = 2

Mass of CaO = 56 × 2 = 112 m

$\therefore$ (b)

67. 100 mL of each of 0.5 N NaOH, N/5 HCl and N/10 H_2SO_4 are mixed together. The resulting solution will be

(a) Acidic (b) Neutral
(c) Alkaline (d) None

Solution Meq. of NaOH = 100 × 0.5 = 50

$$\text{Meq. of HCl} = \frac{1}{5} \times 100 = 20$$

$$\text{Meq. of } H_2SO_4 = \frac{1}{10} \times 100 = 10$$

Total meq. of acid = 20 + 10 = 30

Total meq. of NaOH = 50

$\therefore$ meq. of NaOH left = 50 – 30 = 20

$\therefore$ (c)

68. The chloride of a metal (M) contains 65.5% of chlorine. 100 mL of the vapour of the chloride of the metal at STP weight 0.72g. the molecular formula of the metal chloride is

(a) MCl_3 (b) MCl
(c) MCl_2 (d) MCl_4

Solution Molecular mass of chloride of metal = weight of 22,400 mL vapour of metal at STP

$$= \frac{0.72 \times 22,400}{100} = 161.28\text{g}$$

100 g of metal chloride contains = 65.5 g chloride

$\therefore$ 161.28 g metal chloride contains = $\frac{65.5 \times 161.28}{100}$ = 105.6g

Therefore, the number of mole of chlorine atoms per mole of metal chloride

= 105.6/35.5 = 3

Hence the molecular formula of metal chloride is MCl_3

$\therefore$ (a)

69. If 0.5 mole of $BaCl_2$ is mixed with 0.2 mole of Na_3PO_4 the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is

(a) 0.7 (b) 0.5

(c) 0.3 (d) 0.1

Solution $3BaCl_2 + 2Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + 6NaO$

From the molar ratio we see,

$BaCl_2 : Na_3PO_4 : Ba_3(PO_4)_2 : NaCl$

3 : 2 : 1 : 6

$\therefore$ (d)

70. The per cent loss in weight after heating a pure sample of potassium chlorate (Molecular weight = 122.5) will be

(a) 12.25 (b) 24.50

(c) 39.18 (d) 49

Solution $2KClO_3 \rightarrow 2KCl + 3O_2\uparrow$

245 g $KClO_3$ on heating shows a weight loss of 96 g

$\therefore$ 100 g $KClO_3$ on heating shows a weight loss of = $\frac{96 \times 100}{245} = 39.18\%$

$\therefore$ (c)

71. The chloride of a metal contains 71% chlorine by weight and the vapour density of it is 50. The atomic weight of the metal will be

(a) 29 (b) 58

(c) 35.5 (d) 71

Solution Molecular weight of metal chloride = 50 × 2 = 100

Let metal chloride be MCl_n then

Eq. of metal = eq. of chloride, or $\frac{29}{E} = \frac{71}{35.5}$

$\therefore$ $E = \frac{29}{2}$

Now, a + 35.5n = 100

or n.E + 35.5n = 100

n = 2

Therefore, a = 2 × E = 2 × 29/2 = 29

$\therefore$ (a)

72. 3.0 molal NaOH solution has a density of 1.110 g/mL. The molarity of the solution is

(a) 2.97 (b) 3.05

(c) 3.64 (d) 3.050

Solution Mole = 3

Weight of solvent = 1000g

$\therefore$ wt. of solution = $100 + 3 \times 40 = 1120$g

$\therefore$ volume of solution = $\frac{1120}{1.110}$ml

$\therefore$ $M = \frac{3}{\frac{1120}{1.110 \times 1000}} = 2.97$

$\therefore$ (a)

73. A mixture of magnesium chloride and magnesium sulphate is known to contain 0.6 moles of chloride ions and 0.2 moles of sulphate ions. The number of moles of magnesium ions present is

(a) 0.4 (b) 0.5

(c) 0.8 (d) 1.0

Solution In $MgCl_2$, the ratio of moles of Mg^{+2} to Cl^- is 1:2. Therefore, 0.6 moles of chloride combine with 0.3 moles of magnesium. In $MgSO_4$, 0.2 moles of sulphate combine with 0.2 moles of magnesium. Therefore, the number of moles of magnesium ion present is 0.3 + 0.2 = 0.5.

$\therefore$ (b)

74. The reaction between aluminium metal and dilute hydrochloric acid produces $H_{2(g)}$ and Al^{3+} ions. The molar ratio of aluminium used to hydrogen produced is

(a) 1:2 (b) 2:1

(c) 2:3 (d) 3:2

Solution $Al_{(s)} + \underset{\text{(from HCl)}}{3H^+_{(aq)}} \rightarrow \frac{3}{2}H_{2(g)} + Al^{3+}$ (aq.)

The molar ratio of $Al_{(s)}$ used to H_2 produced is 1: $\frac{3}{2}$ or 2:3. $\therefore$ (c)

75. Element X reacts with oxygen to produce a pure sample of X_2O_3. In an experiment it is found that 1.00 g of X produces 1.16 g of X_2O_3. Calculate the atomic weight of X.

Given: atomic weight of oxygen, 16.0 g mol^{-1}.

(a) 67 (b) 100.2

(c) 125 (d) 150

Solution The mass of O atoms = 1.16 – 1.00 = 0.160g

Number of moles of O atom = $\frac{0.160}{16} = 0.01$

In X_2O_3

$\frac{\text{No. of moles of X}}{\text{No. of moles of O}} = \frac{2}{3}$

Number of moles of X = $\frac{2}{3} \times 0.01 = \frac{0.02}{3} = 0.00666$

Atomic weight of X = $\frac{\text{mass in g}}{\text{no. of moles}} = \frac{1.0}{0.00666} = 150$

$\therefore$ (d)

76. In an aqueous solution of barium nitrate, the $[NO_3^-]$ is 0.80M. This solution is labelled as

(a) 0.080 N $Ba(NO_2)_2$ (b) 0.160 M $Ba(NO_3)_2$

(b) 0.040 M $Ba(NO_3)_2$ (d) 0.080 MNO_3^-

Solution In $Ba(NO_3)_2$, the molar ratio of $Ba(NO_3)_2$ to NO_3^- is 1 : 2. Therefore, the molarity of the $Ba(NO_3)_2$ solution is $\frac{1}{2} \times 0.080 = 0.040$ M.

$\therefore$ (c)

77. 10 mL of gaseous hydrocarbon on combustion gives 40 mL of CO_2(g) and 50 mL of H_2O (vapour). The hydrocarbon is

(a) C_4H_5 (b) C_8H_{10}
(c) C_4H_8 (d) C_4H_{10}

Solution $C_aH_b + \left(a + \frac{b}{4}\right) O_2 \rightarrow aCO_2 + b/2\ H_2O$

10	excess	—	—
0	excess	10a	5b

Therefore,

$10a = 40$

So, $a = 4$

$5b = 50$

$b = 10$

$\therefore$ (d)

78. How many grams of KCl would have to be dissolved in 60 g H_2O to give 20% by weight of solution

(a) 15 g (b) 1.5 g
(c) 11.5 g (d) 31.5 g

Solution $\%\ \text{by weight} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 100$

or $20 = \frac{w}{(w+60)} \times 100$

$w = 15$ g

$\therefore$ (a)

79. The amount of oxalic acid (hydrated) required to prepare 500 mL of its 0.01 N solution is

(a) 0.315g (b) 6.3g
(c) 3.15g (d) 63g

Solution Meq. of oxalic acid = 500 × 0.1 = 50

$\frac{w}{E} \times 1000 = 50$

$W = \frac{126}{2} \times \frac{50}{1000} = 3.15\text{g}$

$\therefore$ (c)

80. A compound was found to contain nitrogen and oxygen in the ratio nitrogen 28 g and 80 g of oxygen. The formula of the compound is

(a) NO (b) N_2O_3
(c) N_2O_5 (d) N_2O_4

Solution g atom of N = $\frac{28}{14} = 2$

g atom of O = $\frac{80}{16} = 5$

Thus, the formula is N_2O_5

$\therefore$ (c)

81. Density of water at room temperature is 1g/mL. How many molecules are there in a drop of water, if its volume is 0.05 mL

(a) 1.67×10^{21} (B) 16.7×10^{21}

(c) 6.023×10^{23} (D) 1.67×10^{23}

Solution Density of water at room temperature = 1 g /mL

$\therefore$ 1 mL contain $\frac{1}{18}$ moles of H_2O

0.05 mL will contain $0.05 \times \frac{1}{18}$ moles

$\therefore$ 1 mole = 6.022×10^{23} moles

Total number of molecules in a drop of water = $6.023 \times 10^{23} \times 0.05 \times \frac{1}{18} = 1.67 \times 10^{21}$

$\therefore$ (a)

82. How many molecules are present in 12 L of liquid CCl_4? The density of the liquid is 1.59 g cm^{-3}

(a) 7.44×10^{26} (b) 0.744×10^{26}

(c) 1.59×10^{26} (d) 15.9×10^{26}

Solution 1 cc of CCl_4 contains 1.59 g s

or $= \frac{1.59}{154}$

$\therefore$ 12 L of liquid CCl_4 will contain = $12 \times 1000 \times 0.0103$

$\Rightarrow$ 0.744×10^{26} molecules of it

$\therefore$ (b)

83. 13.4 g of a sample of unstable hydrated salt: $Na_2SO_4 \times nH_2O$ was found to contain 6.3 g of water. Determine the number of water of crystallisation.

(a) 6 (b) 5

(c) 7 (d) 8

Solution $\frac{\text{wt. of water}}{\text{wt. of sample}} = \frac{\text{wt. of water in the compound}}{\text{mol. wt. of the compound}}$

$$\frac{6.3}{13.4} = \frac{x \times 18}{142 + 18x} = 7$$

$\therefore$ (c)

84. 25.4 g of iodine and 14.2 g of chlorine are made to react completely to yield a mixture of ICl and ICl_3. Calculate the ratio of moles of ICl and ICl_3.

(a) 1:1 (b) 1:2

(c) 1:3 (d) 2:3

Solution $I_2 + 2Cl_2 \rightarrow ICl + ICl_3$

25.4 g of Iodine contains 0.1 moles of it

14.2 g of chlorine contains 0.2 moles of it

$\therefore$ Moles of ICl and ICl_3 produced will be 0.1 and 0.1. Hence, Molar ratio 1: 1

$\therefore$ (a)

85. Calculate the weight of iron which will be converted into its oxide by the action of 18 g of steam on it.

(a) 37.3 g (b) 3.73 g

(c) 56 g (d) 5.6 g

Solution $2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2$

3×18 g of steam will react with 2×56 g of iron

$\therefore$ 18 g of steam will convert = $\frac{18 \times 2 \times 56}{3 \times 18}$ = 37.3 g of Fe

$\therefore$ (a)

86. The hourly energy requirement of an astronaut can be satisfied by the energy released when 34 g of sucrose are burnt in his body. How many g of oxygen would be needed to be carried in space capsule to meet his requirement for one day?

(a) 916.2 g (b) 91.62 g

(c) 8.162 g (d) 9.162 g

Solution $C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$

1 mole of starch requires 12 mole of oxygen

$\therefore$ $\frac{34}{342}$ mole of starch requires $\frac{34}{342} \times 12 \times 32 \times 24$ = 916.2 g

$\therefore$ (a)

87. If 0.5 mole of $BaCl_2$ is mixed with 0.2 mol of Na_3PO_4, the maximum amount of $Ba_3(PO_4)_2$ that can be formed is:

(a) 0.7 mol (b) 0.5 mol

(c) 0.2 mol (d) 0.1 mol

Solution Let us first solve this problem by writing the complete balanced reaction.

$3BaCl_2 + 2\,Na_3PO_4 \rightarrow Ba_3(PO_4)_2 \downarrow + 6NaCl$

We can see that the moles of $BaCl_2$ used is $\frac{3}{2}$ times the moles of Na_3PO_4. Therefore, to react with 0.2 mol of Na_3PO_4, the moles of $BaCl_2$ required would be $0.2 \times \frac{3}{2} = 0.3$. Since $BaCl_2$ is 0.5 mol, we can conclude that Na_3PO_4 is the limiting reagent. Therefore, moles of $Ba_3(PO_4)_2$ formed is $0.2 \times \frac{1}{2}$ = 0.1 mol.

$\therefore$ (d)

Alternatively,

We can use the concept of equivalents to arrive at the answer. $BaCl_2$ and Na_3PO_4 must be reacting without undergoing any change in oxidation state since in $Ba_3(PO_4)_2$ the oxidation states of Ba, P and O remain fixed at +2, +5 and –2 respectively and the other product is expected to be NaCl

Equivalents of $BaCl_2 = 0.5 \times 2$ (Calculate 'n' factor as number of moles of cation in 1 mole of substance × oxidation state of each cation).

Equivalents of $Na_3PO_4 = 0.2 \times 3$

$= 0.6$

Therefore, Na_3PO_4 is the limiting reagent.

$\Rightarrow$ Equivalents of $Ba_3(PO_4)_2$ formed = 0.6

'n' factor of $Ba_3(PO_4)_2 = 6$ ($\because$ 'n' factor of Na_3PO_4 is 3, $\therefore$ Na_3PO_4 and $Ba_3(PO)_4$ will be in the molar ratio of 2:1)

$\therefore$ Moles of $Ba_3(PO_4)_2 = \frac{0.6}{6} = 0.1$

$\therefore$ (d)

... (2)

From equation (1) and (2)

x = 0.5962 g

y = 0.604 g

Solution of Na_2CO_3 and K_2CO_3 gives ppt. of $BaCO_3$ with $BaCl_2$

(meq. of Na_2CO_3 + Meq. of K_2CO_3) in 20 mL = meq. of $BaCO_3$

$\Rightarrow$ Meq. of HCl for 20 mL mixture = Meq. of $BaCO_3$

$\Rightarrow$ Meq. of $BaCO_3 = 40 \times 0.1 = 4$

$$\frac{W_{BaCO_3}}{M_{BaCO_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{BaCO_3}}{197} \times 2 \times 1000 = 4$$

$\therefore$ $W_{BaCO_3} = 0.394$ g

Redox Reactions

Those reactions which involve the transfer of electrons are called redox reactions.

Oxidation and reduction

Oxidation is the loss of electron from the atoms, ions, or molecules

$$\underset{\text{O.N.} = 0}{Fe} \rightarrow \underset{+2}{Fe^{2+}} + 2e^-$$

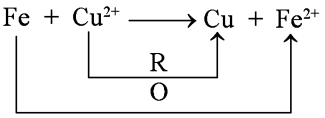
- Fe loses electrons
- There is increase in oxidation number
- Hence Fe is said to be oxidized
- It is a source of electrons hence it can act as a reducing agent (R.A.)
- Any species that can be oxidized is a reducing agent (R.A.)

Reduction is the gain of electrons by atoms, ions or molecules.

$$Cu^{2+} + 2e \rightarrow Cu$$

O.N. = +2 0

- Cu^{2+} gains electron
- There is decrease in Oxidation Number
- Hence Cu^{2+} is said be reduced.
  Since it can gain electrons, hence it can act as an oxidizing agent (O.A.)
- Any species that can be reduced is an oxidising agent (O.A.), or oxidant.
  Above examples represent half reactions.
  A complete reaction showing oxidation and reduction together is called a redox reaction.



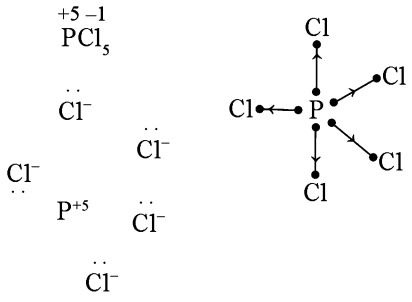
- Oxidation and reduction can not happened independently they always take place simultaneously.
- Oxidising agent are reduced and the reducing agents are oxidized.

If you observe the above reaction, you cannot really see the free electrons.Therefore, you will find it difficult to figure out which atom or ion is oxidized and which one is reduced. This is why we define oxidation number. This oxidation number help you understand the transfer of electrons in a chemical reaction.

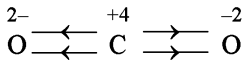
Oxidation number

Oxidation no of an atom is the hypothetical formal charge on the atom when all the polar bonds attached to it are considered to be completely ionic in nature

For example, in NaCl, Na exists as Na^+ and Cl exists as Cl^-. Therefore the oxidation state of Na in NaCl is +1 and that of Cl^- is –1. But in covalent molecules, the charge on an atom would be so small that sometimes it becomes impossible to calculate the exact charge on each atom of a molecule. Therefore, the Oxidation State (O.S.) or Oxidation Number (O.N.) is defined as ***the charge, an atom would have in a molecule if all the polar bonds associated with this atom in the molecule are considered to be completely ionic***. For example, in H_2O, there are two O–H bonds. If we assume both the O – H bonds to be completely ionic, then each H would possess a charge of +1, while O possess a charge of –2. This is because oxygen is more electronegative than hydrogen. On the other hand, in H_2O_2 there are two O–H bonds and one O – O bond (H – O – O – H). Considering each O–H bond to be ionic both the oxygen atoms acquire a charge of –1 and both the H, +1. This is because O–O bond can not be assumed to be ionic as both the atoms have the same electronegativity. Similarly, phosphorous in PCl_5 is in the +5 oxidation state and each chlorine is in –1 oxidation state.



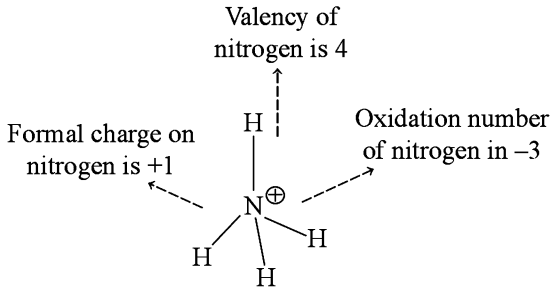
In CO_2, carbon is in the +4 oxidation state and each oxygen is in the -2 state.



To calculate the oxidation state of an element in a molecule you need not always know the structure of the molecule. There are certain set of rules used to assign oxidation states in polyatomic molecules:

All the oxidation number is hypothetical. The change in oxidation number actually gives us the number of e^- lost or gained.

Oxidation number is neither valency or the formal charge of the bonded atom—see the following example to understand the difference.



Rules for the determination of oxidation number of an atom: The following rules are followed in ascertaining the oxidation number of an atom,

(i) If there is a covalent bond between two same atoms then oxidation numbers of these two atoms will be zero. Bonded electrons are symmetrically distributed between two atoms. Bonded atoms do not acquire any charge. So oxidation numbers of these two atoms are zero.

$$A : A \text{ or } A - A \rightarrow A^* + A^*$$

For example, Oxidation number of Cl in Cl_2, O in O_2 and N in N_2 is zero.

(ii) If covalent bond is between two different atoms, then electrons are counted towards more electronegative atom. Thus, oxidation number of more electronegative atom is negative and oxidation number of less electronegative atom is positive. Total number of charges on any element depends on number of bonds.

$$A - B \longrightarrow A^+ + B^- :$$

$$A - B \longrightarrow A^{+2} + : B^{-2} :$$

The oxidation number of less electronegative element (A) is +1 and +2 respectively.

(iii) If there is a coordinate bond between two atoms then oxidation number of donor atom will be +2 and of acceptor atom will be –2.

$$A \rightarrow B \longrightarrow A^{2+} + :B^{-2} :$$

(iv) The oxidation number of all the atoms of different elements in their respective elementary states is taken to be zero. For example, in N_2, Cl_2, H_2, P_4, S_8, O_2, Br_2, Na, Fe, Ag etc., the oxidation number of each atom is zero.

(v) The oxidation number of a monoatomic ion is the same as the charge on it. For example, oxidation numbers of Na^+, Mg^{2+} and Al^{3+} ions are +1, +2 and +3 respectively while those of Cl^-, S^{2-} and N^{3-} ions are –1, –2 and –3 respectively.

(vi) The oxidation number of hydrogen is +1 when combined with non-metals and is –1 when combined with active metals called metal hydrides such as LiH, KH, MgH_2, CaH_2 etc.

(vii) The oxidation number of oxygen is –2 in most of its compounds, except in peroxides like H_2O_2, BaO_2 etc., where it is –1. Another interesting exception is found in the compound OF_2 (*oxygen difluoride*) where the oxidation number of oxygen is +2. This is due to the fact that fluorine being the most electronegative element known has always an oxidation number of –1.

(viii) In compounds formed by union of metals with non-metals, the metal atoms will have positive oxidation numbers and the non-metals will have negative oxidation numbers.
For example,
(a) The oxidation number of alkali metals (*Li*, *Na*, *K* etc.) is always +1 and those of alkaline earth metals (*Be*, *Mg*, *Ca* etc.,) is +2.
(b) The oxidation number of halogens (*F*, *Cl*, *Br*, *I*) is always –1 in metal halides such as *KF*, $AlCl_3$, $MgBr_2$, CdI_2 etc.,

(ix) In compounds formed by the union of different elements, the more electronegative atom will have negative oxidation number whereas the less electronegative atom will have positive oxidation number.
For example,
(a) *N* is given an oxidation number of –3 when it is bonded to less electronegative atom as in NH_3 and NI_3, but is given an oxidation number of +3 when it is bonded to more electronegative atoms as in NCl_3.
(b) Since fluorine is the most electronegative element known so its oxidation number is always –1 in its compounds i.e., oxides, interhalogen compounds etc.,
(c) In interhalogen compounds of *Cl*, *Br*, and *I;* the more electronegative of the two halogens gets the oxidation number of –1. For example, in $BrCl_3$, the oxidation number of *Cl* is –1 while that of *Br* is +3.

(x) For neutral molecule, the sum of the oxidation numbers of all the atoms is equal to zero. For example, in NH_3 the sum of the oxidation numbers of nitrogen atom and 3 hydrogen atoms is equal to zero. For a complex ion, the sum of the oxidation numbers of all the atoms is equal to charge on the ion. For example, in SO_4^{2-} ion, the sum of the oxidation numbers of sulphur atom and 4 oxygen atoms must be equal to –2.

(xi) It may be noted that oxidation number is also frequently called as oxidation state. For example, in H_2O, the oxidation state of hydrogen is +1 and the oxidation state of oxygen is –2. This means that oxidation number gives the oxidation state of an element in a compound.

(xii) In the case of representative elements, the highest oxidation number of an element is the same as its group number while highest negative oxidation number is equal to (8 – Group number) with negative sign with a few exceptions. The most common oxidation states of the representative elements are shown in the following table:

Group	***Outer shell configuration***	***Common oxidation numbers (states) except zero in free state***
I A	ns^1	+1
II A	ns^2	+2
III A	ns^2np^1	+3, +1
IV A	ns^2np^2	+4, +3, +2, +1, –1, –2, –3, –4
V A	ns^2np^3	+5, +3, +1, –1, –3
VI A	ns^2np^4	+6, +4, +2 ,–2
VII A	ns^2np^5	+7, +5, +3, +1, –1

(xiii) Transition metals exhibit a large number of oxidation states due to involvement of $(n-1)$ *d* electron besides *ns* electron.

(xiv) Oxidation number of a metal in carbonyl complex is always zero.

Example: Ni has zero oxidation state in $\left[Ni(CO)_4\right]$.

(xv) Those compounds which have only ***C***, ***H*** and ***O*** the oxidation number of carbon can be calculated by following formula,

$$\text{Oxidation number of 'C'} = \frac{(n_O \times 2 - n_H)}{n_C}$$

Where, n_O is the number of oxygen atom, n_H is the number of hydrogen atom, n_C is the number of carbon atom.

For example,

(a) $\overset{*}{C}H_3OH$; $n_H = 4, n_C = 1, n_O = 1$

$$\text{Oxidation number of '}C\text{'} = \frac{(1\times 2 - 4)}{1} = -2$$

(b) $H\overset{*}{C}OOH$; $n_H = 2,\ n_O = 2, n_c = 1$

$$\text{Oxidation number of carbon} = \frac{(2\times 2 - 2)}{1} = +2$$

Procedure for calculation of oxidation number: By applying the above rules, we can calculate the oxidation numbers of elements in the molecules/ions by the following steps:

(i) Write down the formula of the given molecule/ion leaving some space between the atoms.
(ii) Write oxidation number on the top of each atom. In case of the atom whose oxidation number has to be calculated write *x*.
(iii) Beneath the formula, write down the total oxidation numbers of each element. For this purpose, multiply the oxidation numbers of each atom with the number of atoms of that kind in the molecule/ion.
(iv) Equate the sum of the oxidation numbers to zero for neutral molecule and electron.

Table 3.1 Oxidation number of some elements in compounds, ions or chemical species

Element	Oxidation Number	Compounds, Ions or Chemical Species
Sulphur (S)	− 2	H_2S, ZnS, $NaHS$v $(SnS_3)^{2-}$, BaS, CS_2
	0	S, S_4, S_8, SCN^-
	+ 1	S_2F_2, S_2Cl_2
	+ 4	SO_2, H_2SO_3, $(SO_3)^{2-}$, $SOCl_2$, $NaHSO_3$, $Ca[HSO_3]_2$, $[HSO_3]^-$, SF_4
	+ 6	H_2SO_4, $(SO_4)^{2-}$, $[HSO_4]^-$, $BaSO_4$, $KHSO_4$, SO_3, SF_6, $H_2S_2O_7$, $(S_2O_7)^{2-}$
Nitrogen (*N*)	− 3	NH_3, $(NH_4)^+$, AlN, Mg_3N_2, $(N)^{3-}$, Ca_3N_2, CN^-
	− 2	N_2H_4, $(N_2H_5)^+$
	− 1	NH_2OH
	−1/3	NaN_3, N_3H
	0	N_2
	+ 1	N_2O
	+ 2	NO
	+ 3	HNO_2, $(NO_2)^-$, $NaNO_2$, N_2O_3, NF_3
	+ 4	NO_2
	+ 5	HNO_3, $(NO_3)^-$, KNO_3, N_2O_5

(Contd)

Element	Oxidation Number	Compounds, Ions or Chemical Species
Chlorine (***Cl***)	– 1	***HCl***, ***NaCl***, ***CaCl***$_2$, ***AlCl***$_3$, ***ICl***, ***ICl***$_5$, ***SOCl***$_2$, ***CrO***$_2$***Cl***$_2$, ***KCl***, ***K***$_2$***PtCl***$_6$, ***HAuCl***$_4$, ***CCl***$_4$***H***
	0	***Cl***, ***Cl***$_2$
	+ 1	***HOCl***, ***NaOCl***, $(OCl)^-$, ***Cl***$_2$***O***
	+ 3	***KClO***$_2$, $(ClO_2)^-$, ***HClO***$_2$
	+ 4	***ClO***$_2$
	+ 5	$(ClO_3)^-$, ***KClO***$_3$, ***NaClO***$_3$, ***HClO***$_3$
	+ 7	***HClO***$_4$, ***Cl***$_2$***O***$_7$, ***KClO***$_4$, $(ClO_4)^-$
Hydrogen (***H***)	– 1	***NaH***, ***CaH***$_2$, ***LiAlH***$_4$, ***LiH***
	+ 1	***NH***$_3$, ***PH***$_3$, ***HF***
Phosphorus (***P***)	– 3	***PH***$_3$, $(PH_4)^+$, ***Ca***$_3$***P***$_2$
	0	***P***$_4$
	+ 1	***H***$_3$***PO***$_2$, ***KH***$_2$***PO***$_2$, ***BaH***$_4$***P***$_2$***O***$_4$
	+ 3	***PI***$_3$, ***PBr***$_3$, ***PCl***$_3$, ***P***$_2$***O***$_3$, ***H***$_3$***PO***$_3$
	+ 5	$(PO_4)^{3-}$, ***H***$_3$***PO***$_4$, ***Ca***$_3$$(PO_4)_2$, ***H***$_4$***P***$_2$***O***$_7$, ***P***$_4$***O***$_{10}$, ***PCl***$_5$, $(P_2O_7)^{4-}$, ***Mg***$_2$***P***$_2$***O***$_7$, ***ATP***
Oxygen (***O***)	– 2	***H***$_2$***O***, ***PbO***$_2$, $(CO_3)^{2-}$, $(PO_4)^{2-}$, ***SO***$_2$, $(C_2O_4)^{2-}$, ***HOCl***, $(OH)^-$, $(O)^{2-}$
	– 1	***Na***$_2$O$_2$, ***BaO***$_2$, ***H***$_2$***O***$_2$, $(O_2)^{2-}$, Peroxides
	– 1/2	***KO***$_2$
	0	***O***, ***O***$_2$, ***O***$_3$
	+ 1	***O***$_2$***F***$_2$
	+ 2	***OF***$_2$
Carbon (***C***)	– 4	***CH***$_4$
	– 3	***C***$_2$***H***$_6$
	– 2	***CH***$_3$***Cl***, ***C***$_2$***H***$_4$
	– 1	***Ca***C_2, ***C***$_2$***H***$_2$
	0	Diamond, Graphite, ***C***$_6$***H***$_{12}$***O***$_6$, ***C***$_2$***H***$_4$***O***$_2$, ***HCHO***, ***CH***$_2$***Cl***$_2$
	+ 2	***CO***, ***CHCl***$_3$, ***HCN***
	+ 3	***H***$_2$***C***$_2$***O***$_4$, $(C_2O_4)^{2-}$
	+ 4	***CO***$_2$, ***H***$_2$***CO***$_3$, $(HCO_3)^-$, ***CCl***$_4$, ***Na***$_2$***CO***$_3$, ***Ca***$_2$***CO***$_3$, ***CS***$_2$, ***CF***$_4$, $(CO_3)^{-2}$
Chromium (***Cr***)	+ 3	***Cr***$_2$$(SO_4)_3$, ***CrCl***$_3$, ***Cr***$_2$***O***$_3$, $[Cr(H_2O)_4Cl_3]$
	+ 6	***K***$_2$***CrO***$_4$, $(CrO_4)^{2-}$, ***K***$_2$***Cr***$_2$***O***$_7$, $(Cr_2O_7)^{2-}$, ***KCrO***$_3$***Cl***, ***CrO***$_2$***Cl***$_2$, ***Na***$_2$Cr$_3$O$_{10}$, ***CrO***$_3$
Manganese (***Mn***)	+ 2	***MnO***, ***MnSO***$_4$, ***MnCl***$_2$, ***Mn***$(OH)_2$
	+ 8/3	***Mn***$_3$***O***$_4$
	+ 3	***Mn***$(OH)_3$

(Contd)

Element	Oxidation Number	Compounds, Ions or Chemical Species
	+ 4	MnO_2, K_2MnO_3
	+ 6	K_2MnO_4, $(MnO_4)^{2-}$
	+ 7	$KMnO_4$, $(MnO_4)^-$, $HMnO_4$
Silicon (*Si*)	– 4	SiH_4, Mg_2Si
	+ 4	SiO_2, K_2SiO_3, $SiCl_4$
Iron (*Fe*)	$+\frac{8}{3}$	Fe_3O_4
	+ 2	$FeSO_4$. $(NH_4)_2SO_4$ (Ferrous ammonium sulphate), $K_4Fe(CN)_6$, $FeCl_2$
	+ 3	$K_3[Fe(CN)_6]$, $FeCl_3$
Iodine (*I*)	+ 7	$H_4IO_6^-$, KIO_4
Osmium (*Os*)	+ 8	OsO_4
Xenon (*Xe*)	+ 6	XeO_3, XeF_6

The oxidation number of the element cannot go beyond the inert gas configuration

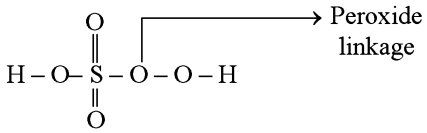
Exceptional cases of evaluation of oxidation numbers: The rules described earlier are usually helpful in determination of the oxidation number of a specific atom in simple molecules but these rules fail in following cases. In these cases, the oxidation numbers are evaluated using the concepts of chemical bonding involved.

Type I. In molecules containing peroxide linkage in addition to element-oxygen bonds. For example,

(i) **Oxidation number of S in H_2SO_5**
(Permonosulphuric acid or Caro's acid)
By usual method; H_2SO_5

$$2\times1+x+5\times(-2)=0 \text{ or } x=+8$$

But this cannot be true as maximum oxidation number for S cannot exceed +6. Since S has only 6 electrons in its valence shell. This exceptional value is due to the fact that two oxygen atoms in H_2SO_5 shows peroxide linkage as shown below,



Therefore, the evaluation of o.n. of sulphur here should be made as follows,

$$2\times(+1) + x + 3\times(-2) + 2\times(-1)$$

(for H) (for S) (for O) (for O–O)

or $2 + x - 6 - 2 = 0$

or $x = +6$.

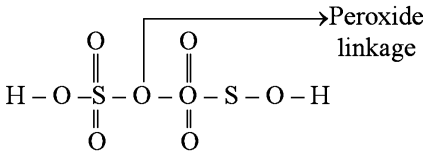
(ii) **Oxidation number of *S* in $H_2S_2O_8$**
(Peroxidisulphuric acid or Marshall's acid)

By usual method ; $H_2S_2O_8$

$$1 \times 2 + 2x + 8\,(-2) = 0$$

$$2x = +16 - 2 = 14 \quad \text{or} \quad x = +7$$

Similarly, Caro's acid, Marshall's acid also has a peroxide linkage so that in which S shows +6 oxidation state.



Therefore, the evaluation of oxidation state of sulphur should be made as follows:

$$2 \times (+1) \;+\; 2 \times (x) \;+\; 6 \times (-2) \;+\; 2 \times (-1) = 0$$

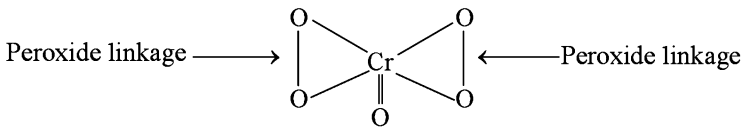
(for H) (for S) (for O) (for O–O)

or $2 + 2x - 12 - 2 = 0$ or $x = +6$.

(iii) **Oxidation number of *Cr* in CrO_5**
(Blue perchromate)

By usual method, CrO_5 ; $x - 10 = 0$ or $x = +10$

This cannot be true as maximum O. N. of Cr cannot be more than + 6. Since Cr has only five electrons in 3d orbitals and one electron in 4s orbital. This exceptional value is due to the fact that four oxygen atoms in CrO_5 are in peroxide linkage.
The chemical structure of CrO_5 is



Therefore, the evaluation of o.n. of *Cr* should be made as follows:

$$x \;+\; 1 \times (-2) \;+\; 4\,(-1) = 0$$

(for *Cr*) (for *O*) (for *O–O*)

or $x - 2 - 4 = 0$ or $x = +6$.

Type II. In molecules containing covalent and coordinate bonds, following rules are used for evaluating the oxidation numbers of atoms.

(i) For each covalent bond between dissimilar atoms the less electronegative element is assigned the oxidation number of +1, while the atom of the more electronegative element is assigned the oxidation number of –1.

(ii) In case of a coordinate-covalent bond between similar or dissimilar atoms is the donor atom is less electronegative than the acceptor atom, an oxidation number of +2 is assigned to the donor atom and an oxidation number of –2 is assigned to the acceptor atom.

Conversely, if the donor atom is more electronegative than the acceptor atom, the contribution of the coordinate bond is neglected.

Examples,

(a) *Oxidation number of C in* $HC \equiv N$ *and* $HN \cong C$

The evaluation of oxidation number of ***C*** cannot be made directly by usual rules since no standard rule exists for oxidation numbers of ***N*** and ***C.***

In such cases, evaluation of oxidation number should be made using indirect concept or by the original concepts of chemical bonding.

(b) *Oxidation number of carbon in* $H - N \cong C$

The contribution of coordinate bond is neglected since the bond is directed from a more electronegative *N* atom (donor) to a less electronegative carbon atom (acceptor).

Therefore the oxidation number of *N* in $HN \cong C$ remains – 3 as it has three covalent bonds.

$$1 \times (+1) \; + \; 1 \times (-3) \quad +x \; = \; 0$$

(for *H*) (for *N*) (for *C*)

or $1 + x - 3 = 0$ or $x = +2.$

(c) *Oxidation number of carbon in* $HC \equiv N$

In $HC \equiv N$, *N* is more electronegative than carbon, each bond gives an oxidation number of –1 to *N*. There are three covalent bonds, the oxidation number of N in $HC \equiv N$ is taken as – 3

Now $HC \equiv N$

$\therefore \; +1 + x - 3 = 0 \Rightarrow x = +2$

Type III. In a molecule containing two or more atoms of same or different elements in different oxidation states.

(i) ***Oxidation number of S in*** $Na_2S_2O_3$

By usual method $Na_2S_2O_3$,

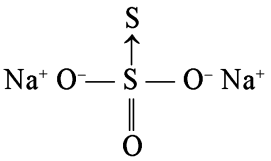
$\therefore \quad 2 \times (+1) + 2 \times x + 3 \, (-2) = 0$ or $2 + 2x - 6 = 0$

or $x = 2.$

But this is unacceptable as the two sulphur atoms in $Na_2S_2O_3$ cannot have the same oxidation number because on treatment with dil. H_2SO_4, one sulphur atom is precipitated while the other is oxidised to SO_2,

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S + H_2O$$

In this case, the oxidation number of sulphur is evaluated from concepts of chemical bonding. The chemical structure of $Na_2S_2O_3$ is,



Due to the presence of a co-ordinate bond between two sulphur atoms, the acceptor sulphur atom has oxidation number of – 2 whereas the other *S* atom gets oxidation number of +2.

$$2 \times (+1) \quad + 3 \times (-2) \; + \; x \; \times \; 1 \quad + \; 1 \times (-2) \; = 0$$

(for *Na*) (for *O*) (for *S*) (for coordinated *S*)

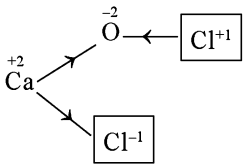
or $+2 - 6 \; + \; x - 2 = 0$ or $x = +6$

Thus, two sulphur atoms in $Na_2S_2O_3$ have oxidation number of – 2 and +6.

(ii) ***Oxidation number of chlorine in $CaOCl_2$***
(bleaching powder)

$(+2) + (-2) + 2x = 0$

$x = 0$



In bleaching powder, one chromine remains in (+1) oxidation state and another chlorine remains in (–1) oxidation state.

In bleaching powder, *Ca(OCl)Cl*, the two *Cl* atoms are in different oxidation states *i.e.*, one Cl^- having oxidation number of –1 and the other as OCl^- having oxidation number of +1.

(iii) ***Oxidation number of N in NH_4NO_3***
By usual method $N_2H_4O_3$; $2x + 4 \times (+1) + 3 \times (-1) = 0$

$2x + 4 - 3 = 0$ or $2x = +1$ (*wrong*)

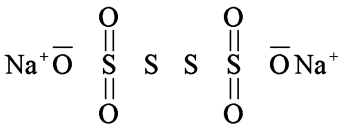
No doubt NH_4NO_3 has two nitrogen atoms but one N has negative oxidation number (attached to H) and the other has positive oxidation number (attached to O). Hence the evaluation should be made separately for NH_4^+ and NO_3^-

NH_4^+ $x + 4 \times (+1) = +1$ or $x = -3$

NO_3^- $x + 3\ (-2) = -1$ or $x = +5$.

(iv) ***Oxidation number of Fe in Fe_3O_4***
In Fe_3O_4, Fe atoms are in two different oxidation states. Fe_3O_4 can be considered as an equimolar mixture of FeO [iron (II) oxide] and Fe_2O_3 [iron (III) oxide]. Thus in one molecule of Fe_3O_4, two Fe atoms are in +3 oxidation state and one Fe atom is in +2 oxidation state.

(v) ***Oxidation number of S in sodium tetrathionate*** ($Na_2S_4O_6$)
Its structure can be represented as follows:



The two *S*-atoms which are linked to each other have oxidation number zero.



Worked-out Examples

88. Calculate the O.S of all the atoms in the following species:

(i) ClO^- (ii) NO_2^- (iii) NO_3^-

(iv) CCl_4 (v) K_2CrO_4 (vi) $KMnO_4$

Solution (i) In ClO^-, the net charge on the species is –1 and therefore the sum of the oxidation states of Cl and O must be equal to –1. Oxygen will have an O.S. of –2 and if the O.S. of Cl is assumed to be '*x*' then $x - 2$ should be equal to –1.

$\therefore$ x is +1

(ii) NO_2^-: $(2 \times -2) + x = -1$ (where 'x' is O.S. of N)

$\therefore \quad x = +3$

(iii) NO_3^-: $x + (3 \times -2) = -1$ (where 'x' is O.S. of N)

$\therefore \quad x = +5$

(iv) In CCl_4, Cl has an O.S. of -1

$\therefore \quad x + 4 \times -1 = 0$

$\therefore \quad x = +4$ (where 'x' is O.S. of C)

(v) K_2CrO_4: K has O.S. of +1 and O has O.S. of -2 and let Cr has O.S. 'x' then, $2 \times +1 + x + 4 \times -2 = 0$

$\therefore \quad x = +6$

(vi) $KMnO_4$: $+1 + x + (4 \times -2) = 0$

$\therefore \quad x = +7$ (where x is O.S. of Mn).

89. The compound $YBa_2Cu_3O_7$, which shows superconductivity, has copper in oxidation state..... Assume that the rare earth element yttrium is in its usual +3 oxidation state. **(1994-1 Mark)**

Solution +7/3; As $YBa_2Cu_3O_7$ is neutral.

$(+3) + 2(+2) + 3(x) + 1(-2) = 0$

$3x + 7 - 14 = 0$ or $x = +7/3$

90. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is: **(1990-1 IITJEE)**

(a) +3 (b) +2

(c) +1 (d) -1

Solution (c) $2 + 2(2 + x - 4) = 0$ or $x = 2 - 1 \Rightarrow x = +1$

91. The oxidation states of the most electronegative element in the products of the reaction, BaO_2 will dil.H_2SO_4 is **(1991-1 IITJEE)**

(a) 0 and -1 (b) -1 and -2

(c) -2 and 0 (d) -2 and -1

Solution (b) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O$

Oxygen being the most electronegative element in the reaction has the oxidation states of -1 (in H_2O_2) and -2 (in $BaSO_4$)

92. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are **(1999-1 IITJEE)**

(a) 0, +1 and -2 (b) +2, +1 and -2

(c) 0, +1 and +2 (d) -2, +1 and -2

Solution (a) ON of S in $S_8 = 0$; ON of S in $S_2F_2 = +1$; ON of S in $H_2S = -2$;

93. Amongst the following, identify the species with an atom in +6 oxidation state **(2001-IITJEE)**

(a) MnO_4^- (b) $Cr(CN)_6^{3-}$

(c) NiF_6^{2-} (d) CrO_2Cl_2

Solution $\overset{}{Cr}\ \overset{(-2\times2)}{O_2}\ \overset{(-2\times1)}{Cl_2}$ Cr is in +6 oxidation state

94. The reaction, $3ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$, is an example of **(1-IITJEE)**

(a) oxidation reaction (b) reduction reaction

(c) disproportionation reaction (d) decomposition reaction

Solution (c) In the given reaction, the oxidation state of the chlorine atom changes from +1(in ClO^-) to +5 (in ClO_3^-) and −1(in Cl^-). This means that chlorine is getting oxidized as well as reduced. Such reactions are called disproportionate reactions.

95. The pair of the compounds in which both the metals are in the highest possible oxidation state is **(IITJEE)**

(a) $[Fe(CN)_6]^{3-}, [Co(CN)_6]^{3-}$ (b) CrO_2Cl_2, MnO_4^-

(c) TiO_3, MnO_2 (d) $[Co(CN)_6]^{3-}$, MnO_3

Solution (b) The highest oxidation states for Fe, Co, Cr, Mn and Ti, in the given compounds, are +3, +6, +6. +7 and +4 respectively.

$\overset{+6}{Cr}O_2Cl_2$, $\overset{+7}{Mn}O_4^-$

Some examples of redox reactions are,

(a) $Sn^{2+} + 2Hg^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$

R

O

(b) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

R

O

(c) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

O

R

(d) $3Cu + 2NO_3^- + 8H^+ \longrightarrow 2NO + 3Cu^{2+} + 4H_2O$

O

R

- If one of the half reactions does not take place, other half will also not take place. We can say oxidation and reduction go side by side.

$$3Cl_2 + 6OH^- \longrightarrow 5Cl^- + ClO_3^- + 3H_2O$$

O.N. = 0 −1 +5

R

O

In this we find that Cl_2 has been oxidized as well as reduced. Such type of redox reaction is called Disproportionation reaction. Examples are,

$2Cu^+ \xrightarrow{\text{Disproportionates}} Cu + Cu^{2+}$

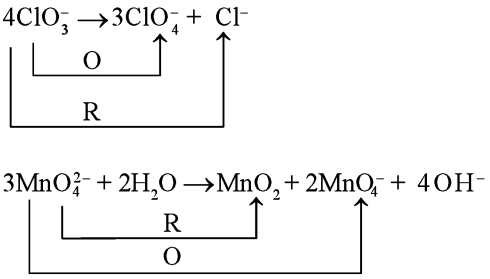
R

O

$2HCHO + OH^- \longrightarrow CH_3OH + HCOO^-$

R

O



How to balance a redox reaction

Molecular and Ionic equations

1. An equation must be balanced from two different aspects:
   (a) Mass Balance – The number of atoms of a given element should be equal on reactant and product side
   (b) Charge Balance – The net charge of the reactant should be equal to the net charge of the product.

1. **Molecular equations:** When the reactants and products involved in a chemical change are written in molecular forms in the chemical equation, it is termed as molecular equation.

   Example: $MnO_2 + 4\,HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

   In above example, the reactants and products have been written in molecular forms, thus the equation is termed as *molecular equation*.
2. **Ionic equations:** When the reactants and products involved in a chemical change are ionic compounds, these will be present in the form of ions in the solution. The chemical change is written in ionic forms in chemical equation, it is termed as ionic equation. Example,

   $MnO_2 + 4H^+ + 4Cl^- \rightarrow Mn^{2+} + 2Cl^- + 2H_2O + Cl_2$

   In above example, the reactants and products have been written in ionic forms, thus the equation is termed as *ionic equation*.
3. **Spectator ions:** In ionic equations, the ions which do not undergo any change and equal in number in both reactants and products are termed as spectator ions and are not included in the final balanced equations. Example,

   $Zn + 2H^+ + 2Cl^- \rightarrow Zn^{2+} + H_2 + 2Cl^-$ (*Ionic equation*)

   $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ (*Final ionic equation*)

   In above example, the Cl^- ions are the *spectator ions* and hence are not included in the final ionic balanced equation.

To get the ionic equation, the spectator ions should be removed first

An ionic equation can be balanced either in the acidic or alkaline medium when an equation is balanced the acidic medium H^+ ions will be present in the expression (either in the reactant or the product side) and hydroxyl ion will not be in the expression.

When the same equation is balanced in the alkaline medium OH^- is found in the expression but H^+ ions will be absent. H_2O molecule can always be there.

Same equation can be balanced in the acidic or basic medium.

Ion electron method

This method involves the following steps:

(i) Divide the complete equation into two half reactions, one representing oxidation and the other reduction.

(ii) Balance the atoms in each half reaction separately according to the following steps:
(a) First of all balance the atoms other than H and O.
(b) In a reaction taking place in acidic or neutral medium, oxygen atoms are balanced by adding molecules of water to the side deficient in oxygen atoms while hydrogen atoms are balanced by adding H^+ ions to the other side deficient in hydrogen atoms. On the other hand, in alkaline medium (OH^-), for every excess of oxygen atom on one side is balanced by adding one H_2O to the same side and $2OH^-$ to the other side. In case hydrogen is still unbalanced, then balance by adding one OH^-, for every excess of H atom on the same side and one H_2O on the other side.
(c) Equalize the charge on both sides by adding suitable number of electrons to the side deficient in negative charge.

(iii) Multiply the two half reactions by suitable integers so that the total number of electrons gained in one half reaction is equal to the number of electrons lost in the other half reaction.

(iv) Add the two balanced half equations and cancel any term common to both sides.

There have been the common practices to balance the redox reaction by different methods like O.N. method and electron balance method. In the entrance examination, it is never mentioned what method is to be used. We adopt here "quick" method that will certainly be a time-saving method.



Worked-out Examples

96. (a) $NO_3^- + H_2S \xrightarrow[\text{acidic medium}]{H^+} HSO_4^- + NH_4^+$

(b) $Fe + N_2H_4 \xrightarrow[\text{alkaline medium}]{OH^-} Fe(OH)_2 + NH_3$

Solution (a) Step 1 $N^{5+} + 8e \rightarrow N^{3-}$

$S^{2-} \rightarrow S^{6+} + 8e$

Step 2 $N^{5+} + S^{2-} \rightarrow N^{3-} + S^{6+}$

Step 3 $NO_3^- + H_2S \rightarrow NH_4^+ + HSO_4^-$

Step 4 NO other atom (except H and O) is unbalanced therefore no need for this step.

Step 5: Balancing O atom. This is made by using H_2O and H^+ ions. Add desired molecules of H_2O on the side deficient in O atom and double H^+ on opposite side. Therefore,

$NO_3^- + H_2S + H_2O \rightarrow NH_4^+ + HSO_4^- + 2H^+$

Step 6 Balance charge by H^+

$NO_3^- + H_2S + H_2O + 3H^+ \rightarrow NH_4^+ + HSO_4^- + 2H^+$

$\therefore$ Balanced equation is,

$NO_3^- + H_2S + H_2O + H^+ \rightarrow NH_4^+ + HSO_4^-$

(b) Step 1 $Fe \rightarrow Fe^{2+} + 2e$

$N_2^{2-} + 2e \rightarrow 2N^{3-}$

Step 2 $Fe + N_2^{2-} \rightarrow Fe^{2+} + 2N^{3-}$

Step 3 $Fe + N_2H_4 \rightarrow Fe(OH)_2 + 2NH_3$

Step 4 No other atom (except H and O) is unbalanced and therefore no need for this step.

Step 5 $Fe + N_2H_4 + 4OH^- \rightarrow Fe(OH)_2 + 2NH_3 + 2H_2O$

Step 6 Balance charge by H^+,

$\therefore Fe + N_2H_4 + 4OH^- + 4H^+ \rightarrow Fe(OH)_2 + 2NH_3 + 2H_2O$

Finally, $Fe + N_2H_4 + 2H_2O \rightarrow Fe(OH)_2 + 2NH_3$

Illustration

$$MnO_4^- + Fe^{+2} \longrightarrow Fe^{+3} + Mn^{+2} \ldots \text{Acidic medium}$$

The oxidation and reduction are known as the half reaction. Before Balancing the equation H^+ ion, on$^-$ ion and the water molecule should be removed from the reaction.

$$5e^- + \underbrace{\overbrace{8H^+ + MnO_4^-}^{+7}}_{8\times(+1)+(-1)} \longrightarrow \underbrace{Mn^{+2} + 4H_2O}_{\boxed{+2}}$$

- Any atom other than oxygen and hydrogen should be balanced in the HALF REACTION.
- To balance oxygen atom us have to add required number of water molecular when we do so, hydrogen atom will be excess on the side. To balance hydrogen atom we have to add required. Number of H^+ ion to the other side. Now mass balance is completed.
- To balance the charge we have to add required no, of electrons to the desired side.

$$5Fe^{+2} \xrightarrow{\text{oxidation}} 5Fe^{+3} + 5e^- \ldots \times 5$$

$$5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$$

$$\underbrace{MnO_4^- + 5Fe^{+2} + 8H^+} \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

$$\underbrace{-1+5\times2+8}_{+17} \qquad \underbrace{5\times3+2}_{+17}$$

- This ionic equation is now balanced in the acidic medium.
- We can again convert ionic equation to the molecular equation by adding those spectator ions.

$$KMnO_4 + 5\,FeSO_4 + 4H_2SO_4 \rightarrow \frac{5}{2}Fe(SO_4)_3 + MnSO_4 + 4H_2O + \frac{1}{2}K_2SO_4$$

$$2MnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2\,MnSO_4 + K_2SO_4 + 8H_2O$$

The same equation could be balanced in basic medium

$$MnO_4^- + 5Fe^{+2} + 8H_2O \rightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

$$MnO_4^- + 5Fe^{+2} + 4H_2O \rightarrow 5Fe^{+3} + Mn^{+2} + 8H^-$$

To balance the equation in the basic medium, we have to add equal number of hydroxyl ions to both the ions. The number of hydroxyl ion added should be equal to the number of H^+ ion in the equation.

More examples

Balance the following equations:

1. $MnO_2 + Cl^- \longrightarrow Mn^{2+} + Cl_2$ in acidic medium

$$2e^- + \underbrace{4H^+ + MnO_2}_{+4} \longrightarrow \underbrace{Mn^{+2} + 2H_2O}_{+2}$$

$$\underbrace{2Cl^-}_{-2} \longrightarrow \underbrace{Cl_2}_{0} + 2e^-$$

$$MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + 2H_2O$$

2. $MnO_2 + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$.... acidic solution

$2e^- + 4H^+ + MnO_2 \rightarrow Mn^{+2} + 2H_2O$

$$\frac{C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-}{MnO_2 + 4H^+ + C_2O_4^{2-} \longrightarrow 2CO_2 + Mn^{+2} + 2H_2O}$$

3. $Mn^{2+} + Br_2 \rightarrow MnO_2 + Br^-$.... acidic solution

$2H_2O + Mn^{+2} \rightarrow MnO_2 + 4H^+ + 2e^-$

$$\frac{2e^- + Br_2 + 2Br^-}{Mn^{+2} + Br_2 + 2H_2O \longrightarrow MnO_2 + 2Br^- + 4H^-}$$

$$\frac{2e^- + Br_2 \longrightarrow 2Br^-}{Mn^{+2} + Br_2 + 2H_2O \longrightarrow MnO_2 + 2Br^- + 4OH^-}$$

4. $Br_2 \longrightarrow BrO_3^- + Br^-$ .... basic medium

$$\underbrace{6H_2O + Br_2}_{} \rightarrow \underbrace{2BrO_3^- + 12H^+}_{\underbrace{-2+12}_{10}} + 10e^-$$

$2e^- + Br_2 \rightarrow 2Br^- \ldots \times 5$

$$\frac{10e^- + 5Br^2 \longrightarrow 10Br^-}{6Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 10Br^- + 12H^+}$$

$3Br_2 + 6OH^- \rightarrow BrO_3^- + 5Br^- + 3H_2O$

5. $K_2Cr_2O_7 + \overset{-}{K}\overset{-}{I} + \overset{-}{H}\overset{-}{Cl} \rightarrow \overset{0}{I_2} + Cr\overset{-}{Cl}_3 + H_2O + \overset{-}{K}\overset{-}{Cl}$ ....in acidic medium

$Cr_2O_7^{2-} + I^- + H^+ \rightarrow I_2 + Cr^{+3} + H_2O$

$Cr_2O_7^{2-} + I^- \rightarrow I_2 + Cr^{+3}$

$$6e^- + \underbrace{14H^+ + Cr_2O_7^{2-}}_{+12} \longrightarrow \underbrace{2Cr^{+3}}_{+6} + 7H_2O$$

$6I^- \rightarrow 3I_2 + 6e^- \ldots \times 3$

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{+3} + 3I_2 + 7H_2O$

$K_2Cr_2O_7 + 14HCl + 6KI \rightarrow 2CrCl_3 + 3I_2 + 7H_2O + 8KCl$

$N_2H_4 + Fe^{+3} \rightarrow Fe^{+2} + \underset{\substack{\text{balance it in acidic} \\ \text{\& basic medium}}}{N_2}$

$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^-$

$$\frac{4e \mp 4Fe^{+3} \longrightarrow 4Fe^{+2} \ldots . \times 4}{N_2H_4 + 4Fe^{+3} \longrightarrow 4Fe^{+2} + N_2 + 4H^+}$$

Oxidation number method

This method is based on the principle that the number of electrons lost in oxidation must be equal to the number of electrons gained in reduction. The steps to be followed are:

(i) Write the equation (if it is not complete, then complete it) representing the chemical changes.
(ii) By knowing oxidation number of elements, identify which atom(s) is (are) undergoing oxidation and reduction. Write down separate equations for oxidation and reduction.

(iii) Add required electrons on the right hand side of oxidation reaction and on the left hand side of reduction reaction. Care must be taken to ensure that the net charge on both the sides of the equation is same.

(iv) Multiply the oxidation and reduction reactions by suitable numbers to make the number of electrons lost in oxidation reactions equal to the number of electrons gained in reduction reactions.

(v) Transfer the coefficients of the oxidizing and reducing agents and their products to the main equation.

By inspection, arrive at the co-efficients of the species not undergoing oxidation o reduction.



Worked-out Examples

97. Balance the equation $K_2Cr_2O_7 + HCl \rightarrow KCl + CrCl_3 + H_2O + Cl_2$

Solution Remember that alkali and alkaline earth metals have only one oxidation number and as long as they remain in the compound they do not undergo oxidation or reduction.

$$\overset{+6}{K_2Cr_2O_7} + \overset{-1}{H}Cl \rightarrow KCl + \overset{+3}{C}rCl_3 + H_2O + \overset{0}{Cl_2}$$

Thus, here Cr of $K_2Cr_2O_7$ is reduced to $CrCl_3$(+6→ +3) and Cl of HCl is oxidised to Cl_2(−1 → 0). In short,

Oxidation: $2Cl^{-1} \rightarrow Cl_2^0 \uparrow 2$ ... (a)

Reduction: $Cr_2^{+6} \rightarrow 2Cr^{+3} \downarrow 6$ ... (b)

Step (iii) $2Cl^{-1} \rightarrow Cl_2^0 + 2e^-$; $Cr_2^{+6} + 6e^- \rightarrow 2Cr^{3+}$

Step (iv) Multiply equation (a) by 6 and (b) by 2

$$12Cl^{-1} \longrightarrow 6Cl_2^0 + 12e^-$$

$$2Cr_2^{+6} + 12e^- \longrightarrow 4Cr^{+3}$$

$$2Cr_2^{+6} + 12Cl^{-1} \longrightarrow 4Cr^3 + 6Cl_2^0$$

or $Cr_2^{+6} + 6Cl^- \rightarrow 2Cr^{+3} + 3Cl_2^0$

Step (v) $K_2Cr_2O_7 + 6HCl \rightarrow 2CrCl_3 + 3Cl_2$

Step (vi) Making provision of KCl and H_2O in the product: Since the reactant has 7 oxygen atoms in the product $7H_2O$ must be present. For accounting 14 hydrogen atoms of water in the product, the reactants must have 12 HCl molecules (the only H containing species). For accounting the 2K atoms and 14 – 12 = 2 additional Cl atoms in the reactant, the product must have 2KCl. Hence the balanced equation is.

$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

98. For the redox reaction: **(1992-1 Mark)**

$MnO_4^- + C_2O_4^- + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$

The correct coefficients of the reactants for the balanced reaction are, **(1992-1 Mark)**

	MnO_4^-	$C_2O_4^-$	H^+		MnO_4^-	$C_2O_4^-$	H^+
(a)	2	5	16	(b)	16	5	2
(c)	5	16	2	(d)	2	16	5

Solution (a) Oxidation reaction : $C_2O_4^{-2} \rightarrow 2CO_2 + 2e^-] \times 5$

Reduction reaction : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 8H_2O] \times 2$

Net reaction: $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Oxidizing and Reducing agents

1. **Definition:** The substance (atom, ion or molecule) that gains electrons and is thereby reduced to a low valency state is called an ***oxidizing agent***, while the substance that loses electrons and is thereby oxidized to a higher valency state is called a ***reducing agent.***
   Or
   An ***oxidizing agent*** is a substance, the oxidation number of whose atom or atoms decreases while a *reducing agent* is a substance the oxidation number of whose atom increases.
2. **Important oxidizing agents**
   (i) Molecules made up of electronegative elements.
   Example: O_2, O_3 and X_2 (halogens).
   (ii) Compounds containing an element which is in the highest oxidation state.
   Example: $KMnO_4, K_2Cr_2O_7$, $Na_2Cr_2O_7$, CrO_3, H_2SO_4,
   $HNO_3, NaNO_3, FeCl_3, HgCl_2, KClO_4, SO_3, CO_2, H_2O_2$ etc.
   (iii) Oxides of elements, $MgO, CuO, CrO_3, CO_2, P_4O_{10}$, etc.
   (iv) Fluorine is the strongest oxidizing agent.
3. **Important reducing agents**
   (i) All metals e.g., Na, Zn, Fe, Al, etc.
   (ii) A few non-metals e.g., C, H_2, S etc.
   (iii) Hydracids: HCl, HBr, HI, H_2S etc.
   (iv) A few compounds containing anelement in the lower oxidation state (ous).
   Example: $FeCl_2$, $FeSO_4$, $SnCl_2$, Hg_2Cl_2, Cu_2O etc.
   (v) Metallic hydrides e.g., NaH, LiH etc.
   (vi) Organic compounds like HCOOH and $(COOH)_2$ and their salts, aldehydes, alkanes etc.
   (vii) Lithium is the strongest reducing agent in solution.
   (viii) Cesium is the strongest reducing agent in absence of water. Other reducing agents are $Na_2S_2O_3$ and KI.
   (ix) Hypo prefix indicates that central atom of compound has the minimum oxidation state so it will act as a reducing agent.
   Example: H_3PO_2 (hypophosphorous acid).
4. **Substances which act as oxidizing as well as reducing agents**
   Examples: H_2O_2, SO_2, H_2SO_3, HNO_2, $NaNO_2$, Na_2SO_3, O_3 etc.
5. **Tips for the identification of oxidizing and educing agents**
   (i) If an element is in its highest possible oxidation state in a compound, the compound can function as an oxidising agent.
   Example: $KMnO_4$, $K_2Cr_2O_7$, HNO_3, H_2SO_4, $HClO_4$ etc.
   (ii) If an element is in its lowest possible oxidation state in a compound, the compound can function only as a reducing agent.
   Example: H_2S, $H_2C_2O_4$, $FeSO_4$, $Na_2S_2O_3$, $SnCl_2$ etc.

(iii) If an element is in its intermediate oxidation state in a compound, the compound can function both as an oxidizing agent as well as reducing agent.

Example: H_2O_2, H_2SO_3, HNO_2, SO_2 etc.

(iv) If a highly electronegative element is in its highest oxidation state in a compound, that compound can function as a powerful oxidizing agent.

Example: $KClO_4$, $KClO_3$, $KBrO_3$, KIO_3 etc.

(v) If an electronegative element is in its lowest possible oxidation state in a compound or in free state, it can function as a powerful reducing agent.

Example: I^-, Br^-, N^{3-} etc.

6. Equivalent weight of oxidising and reducing agents

Equivalent weight of a substance (oxidant or reductant) is equal to molecular weight divided by number of electrons lost or gained by one molecule of the substance in a redox reaction.

$$\text{Eq. wt. of } \textbf{O. A.} = \frac{\text{Molecular weight}}{\text{No. of electrons gained by one molecule}} = \frac{\text{Molecular weight}}{\text{Change in O. N. per mole}}$$

$$\text{Eq. wt. of } \textbf{R. A.} = \frac{\text{Molecular weight}}{\text{No. of electrons lost by one molecule}} = \frac{\text{Molecular weight}}{\text{Change in O. N. per mole}}$$

Agents	*O. N.*	*Product*	*O. N.*	*Change in O. N. per atom*	*Total Change in O. N. per mole*	*Eq. wt.*
$Cr_2O_7^{2-}$	+6	Cr^{3+}	+3	3	$3 \times 2 = 6$	Mol. wt./6
$Cr_2O_4^{2-}$	+3	CO_2	+4	1	$1 \times 2 = 2$	Mol. wt./2
$S_2O_3^{2-}$	+2	$S_4O_6^{2-}$	+2.5	0.5	$0.5 \times 2 = 1$	Mol. wt./1
H_2O_2	−1	H_2O	−2	1	$1 \times 2 = 2$	Mol. wt./2
H_2O_2	−1	O_2	0	1	$1 \times 2 = 2$	Mol. wt./2
MnO_4^- (Acidic medium)	+7	Mn^{2+}	+2	5	$5 \times 1 = 5$	Mol. wt./5
MnO_4^- (Neutral medium)	+7	MnO_2	+4	3	$3 \times 1 = 3$	Mol. wt./3
MnO_4^- (Alkaline medium)	+7	MnO_4^{2-}	+6	1	$1 \times 1 = 1$	Mol. wt./1

n factor

- The 'n factor' of any oxidizing or reducing agent is the net charge in the oxidation number of all the atoms per molecule of oxidizing or reducing agent.Remember a reaction does not have 'n-factor', it is defined separately for each reactant and each product

$$\overset{+7}{MnO_4^-} \longrightarrow \overset{+4}{MnO_2}$$

Change in the oxidation number of Mn = 7 – 4 = 3 = 'n-factor' of MnO_4^-

Or,

- The n-factor is actually the number of e^- taken up by one molecule of oxidizing agent or the number of electrons given up by one molecule of reducing agent.

$$3e^- + 4H^+ + MnO_4^- \xrightarrow{(n-3)} MnO_2 + 2H_2O$$

3electrons are consumed by one MnO_4^- ion. Hence, the 'n factor' of MnO_4^- is 3.

- The greater the value of n factor. The more is the oxidising power (quantitatively) of the oxidizing agent or more is the reducing power (quantitatively) of the reducing agent.
- Number of moles is inversely proportional to the n factor
- Dichromate ion can function as oxidising agent in the acidic medium.

$$6e + 14H^+ + \boxed{Cr_2O_7^{2-}} \xrightarrow{\text{acidic med.}} 2Cr^{+3} + 7H_2O$$

$$\text{n-factor of } Cr_2O_7^{2-} = \frac{\text{mole of electron}}{\text{mole of } Cr_2O_7^{2-}} = \frac{6}{1} = 6$$

$K_2Cr_2O_7$ (n-factor = 6)

- **Aluminium dichromate**

$Al_2(Cr_2O_7)_3 \Rightarrow$ n-factor of $Al_2(Cr_2O_7)_3 = 6 \times 3 = 18$

(as one $Al_2(Cr_2O_7)_3$ Contains three $Cr_2O_7^{2-}$ ions

- **Oxalate ion**

$$\overset{+3}{C_2O_4^{2-}} \longrightarrow \overset{+4}{2CO_2}$$

- (n = 2) $\boxed{\text{2 unit oxidation}}$ of 2 carbon atom (n = 1)

Or,

$$\underset{(n=2)}{C_2O_4^{2-}} \longrightarrow \underset{(n=1)}{2CO_2} + 2e^-$$

- 1 unit oxidation of Iron

$$\overset{+2}{Fe}\overset{+3}{C_2O_4} \longrightarrow Fe^{+3} + \overset{+4}{2CO_2}$$

Two unit Ox of 2 'C'

n factor of Ferrous oxalate = $\boxed{2+1=3}$

or, balancing

- $\underbrace{FeC_2O_4}_{\text{charge}=3} \rightarrow \underbrace{Fe^{+3}}_{\text{charge}=3} + 2CO_2 + 3e^-$

(n-factor of Ferrous oxalate = 3)

- Fe^{+3} $C_2O_4^{2-}$

$Fe_2(C_2O_4)_3$
(Ferric oxalate)

6 unit oxidation of C

$$\overset{+3}{Fe_2}(\overset{+3}{C_2}O_4)_3 \longrightarrow Fe^{+2} + CO_2$$

$\boxed{2 \times 1 = \text{unit redn}}$ of 2 'Fe' atom

If one element is oxidized and another element of the same molecule is reduced, the difference in their change in the oxidation number is there n factor.

Or, balancing

$$\underbrace{\overset{+3}{F}_2(C_2O_4)}_{(n\text{ Factor} = 4)^3} \longrightarrow 2Fe^{+2} + 6CO_2 + 4e^-$$



Worked-out Example

99. 1 mol of ferric oxalate is oxidized by x mol of MnO^{4-} and also 1 mol of ferrous oxalate is oxidised by y mol of MnO^{4-} in acidic medium. The ratio x/y is

(a) 2 : 1 (b) 1 : 2

(c) 3 : 1 (d) 1 : 3

Solution $Fe_2(C_2O_4)_3 + MnO_4^- \longrightarrow Fe^{+3} + CO_2 + Mn^{+2}$

$$\underset{\text{(ferrous oxlate)}}{FeC_2O_4} + \underset{(n=5)}{MnO_4^-} \longrightarrow Fe^{+3} + CO_2 + Mn^{+2}$$

$$\frac{n_{Fe_2(C_2O_4)_3}}{n_{MnO_4^-}} = \frac{5}{6} = \frac{1}{x}$$

$$x = \frac{6}{5}$$

Number of moles is inversely proportional to the n factor,

$$\frac{n_{FeC_2O_4}}{n_{M_nO_4^-}} = \frac{5}{3} = \frac{1}{y}$$

$$\boxed{y = \frac{3}{5}}$$

$$\frac{x}{y} = 2$$

- **'n factor' of chlorate ion, periodate ion, ammonia can be calculated from the following reaction as follows:**

$$\overset{+5}{Cl}O_3^- \longrightarrow \overset{-1}{Cl}^-$$

(n-factor of $ClO_3^{\ominus} = 6$

$$6e^- + 6H^+ + ClO_3^{\ominus} \longrightarrow Cl^- + 3H_2O$$

$$\underset{\substack{\text{(periodate ion)}\\(n=7)}}{IO_4^-} \longrightarrow \underset{(n=7\times2)=14}{I_2}$$

$$\underset{\text{(n factor=8)}}{\overset{-3}{N}H_3} \longrightarrow \underset{\text{(n factor=8)}}{\overset{+5}{N}O_3^-}$$

Or, balancing

$$3H_2O + NH_3 \longrightarrow NO_3^- + 9H^+ + 8e^-$$

$$\boxed{\text{n factor} = 8}$$

Worked-out Examples

100. 20 mL 0.1 M $Al_2(Cr_2O_7)_3$ consumed x g of FeC_2O_4 . Calculate x.

Solution As number of moles is inversely proportional to the n factor:

$$\frac{n_{FeC_2O_4}}{n_{Al_2(Cr_2O_7)}} = \frac{18}{3} = 6$$

$$\frac{\frac{x}{144}}{\left(\frac{20}{10^3}\right) \times (0.1)} = 6$$

$$x = 1.728$$

101. 0.1 M $FeSO_4$ solution is consumed 20 mL 0.2 N $K_2Cr_2O_7$ in acidic medium calculate the vol. of $FeSO_4$ consumed.

Solution In this reaction, $FeSO_4$ is acting as reducing agent and it is itself oxidised to the Fe^{+3} state. Hence, the n factor of $FeSO_4$ is one.

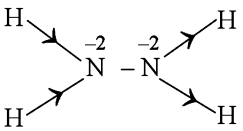
$$n_{meq\,(FeSO_4)} = n_{meq} n_{meq(K_2Cr_2O_7)}$$

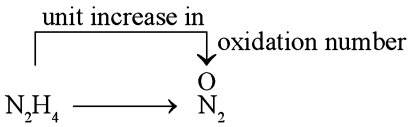
$$V(mL) = 20\ mL\ (2)$$

$$V = 40\ mL$$

Hydrazine (N_2H_4)

It is a reducing agent. Hydrazine itself is oxidized to N_2.





(n-factor = 2 × 2 = 4)

$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^-$$

$$\text{n-factor} = \frac{\text{moles of electrons}}{\text{moles of } N_2H_4} = \frac{4}{1}$$

Hydrazine can reduce the Fe^{+3} ion to the Fe^{2+} state.

$$\underset{(n=1)}{Fe^{+3}} + \underset{(n=4)}{\overset{-2}{N_2H_4}} \longrightarrow \underset{(n=1)}{Fe^{+2}} + \underset{(n=4)}{\overset{0}{N_2}}$$

$$\underset{(n\,factor=2)}{\overset{+3}{Fe_2(SO_4)_3}} \longrightarrow \underset{(n\,factor=1)}{\overset{+2}{2FeSO_4}}$$

Worked-out Examples

102. 3.2 g of hydrazine consumed 20 mL $Fe_2(SO_4)_3$. Calculate the molarity of $Fe_2(SO_4)_2$.

Solution As number of moles is inversely proportional to the n factor:

$$\frac{n_{N_2H_4}}{n_{Fe_2(SO_4)_3}} = \frac{2}{4} = \frac{1}{2} \quad (n = 2 \text{ for } Fe_2(SO_4)_2.)$$

$$\frac{\left(\frac{3.2}{32}\right)}{\left(\frac{20}{10^3}\right) \times M} = \frac{n_{N_2H_4}}{n_{Fe_2(SO_4)_3}}.$$

$M=10$

103. 1 mol of N_2H_4 loses 10 mol e^- to forma a new compound y. Assuming that all the nitrogen appear in the new compound what is the oxidation state of nitrogen in y?

Solution Since 1 mol g hydrazine losses 10 mol of e^-. The n factor of hydrazine should be 10 since the H is not changing the oxidation state. The change in oxidation number. of two N atoms per molecule is 10 unit. Hence, the change for one nitrogen should be 5 units. Since e^- are lost, the oxidation number of one nitrogen atom should increase by 5 units.

$$\overset{-2}{N_2}H_4 \longrightarrow \overset{+x}{N}$$

$$2[x-(-2)] = 10$$

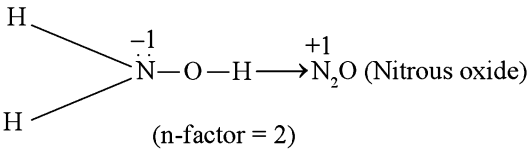
$$2[x+2] = 10$$

$$x+2 = 5$$

$$\boxed{x = +3}$$

Hydroxyl amine

It is a reducing agent. It can reduce Fe^{3+} to Fe^{+2} and itself it is oxidized to nitrous oxide.



(n-factor = 2)

$$NH_2OH + Fe^{3+} \rightarrow Fe^{+2} + N_2O$$

$$2H^+ + NH_2OH \rightarrow N_2O + 6H^+ + H_2O$$

$$\boxed{2NH_2OH} \rightarrow N_2O + 4H^+ + 2H_2O \quad \boxed{+4e^-}$$

$$\text{n factor of hydroxyl amine} = \frac{ne}{n_{NH_2OH}} \frac{4}{2} = 2$$



Worked-out Example

104. 6.6 g of NH_2OH can reduce 100 mL $Fe_2(SO_4)_3$, calculate the molarity of $Fe_2(SO_4)_3$.

Solution No of moles $n_{NH_2OH} = n_{Fe_2(SO_4)_3} = \frac{6.6}{33} = (0.1\ L)\ (\text{molarity})$

Molarity = 2

IO_3^- (Iodate ion)

Oxidizing agent

$$\overset{+5}{IO_3}^- \xrightarrow[\text{dil. HCl}]{} \overset{0}{I_2}$$

Iodate ion cannot oxidise the Ferrous ion to the Ferric State but it can oxidize hydrazine to the nitrogen.

$$N_2H_4 \xrightarrow{IO_3^-} N_2$$



Worked-out Example

105. X g of N_2H_4 was oxidized by 100 mL 0.1 M $\underset{(n=4)}{KIO_3}$ in concentrated HCl. Calculate 'x'.

Solution $\underset{(n=4)}{N_2H_4} + \underset{(n=4)}{IO_3^-} \longrightarrow ICl + N_2$

$$n_{N_2H_4} = n_{KIO_3}$$

$$\left(\frac{x}{32}\right) = (0.1\ L)\ (0.1M)$$

$$\boxed{x = 0.32}$$

H_2O_2 (can be oxidizing as well as reducing agent)

H_2O_2 as oxidizing agent

$$H_2\overset{-1}{O_2} \xrightarrow{\text{red}} H_2O^{-2}$$

factor = 2

$2e^- + 2H^+ + H_2O_2 \rightarrow H_2O + H_2O$

(hydrogen = 2)

H_2O_2 or Reducing agent

$$\underset{(n=2)}{H_2\overset{-1}{O_2}} \rightarrow \overset{0}{O_2}$$

$$\underset{(n=2)}{H_2O_2} \longrightarrow O_2 + 2H^+ + 2e^-$$

HNO_3 (Oxidizing agent)

$$H\overset{+5\ (max)}{\boxed{N}}O_3 \longrightarrow \overset{+4}{NO_2}$$

(conc. acid)

(n-factor of concentrated HNO_3=1)

$$\underset{\boxed{n=3}}{\overset{+5}{HNO_3}} \longrightarrow \overset{+2}{NO_2}$$

(dil. acid)



Worked-out Examples

106. 'x' g of Cu_2S is oxidized by 100 mL 0.1 M HNO_3 as follows calculate x.

$$XO_4^- + \underset{(n=3)}{HNO_3} \longrightarrow Cu^{2+} + SO_2 + NO$$

Solution $\dfrac{(\text{Atomic mass})}{\begin{pmatrix} Cu = 35.5 \\ S = 32 \end{pmatrix}}$

$$\underbrace{2H_2O + Cu_2S}_{(n=8)} \longrightarrow 2Cu^{+2} + SO_2 + 4H^+ + 8e^-$$

$$\frac{n_{Cu_2S}}{n_{HNO_3}} = \frac{3}{8} = \frac{\left(\dfrac{x}{159}\right)}{(0.01L)\,(0.1M)}$$

'n' Factor

107. Calculate the n-factor in the following chemical changes.

(i) $KMnO_4 \xrightarrow{H^+} Mn^{2+}$

(ii) $KMnO_4 \xrightarrow{H_2O} Mn^{4+}$

(iii) $KMnO_4 \xrightarrow{HO^-} Mn^{6+}$

(iv) $K_2Cr_2O_7 \xrightarrow{H^+} Cr^{3+}$

(v) $C_2O_4^{2-} \longrightarrow CO_2$

(vi) $FeSO_4 \longrightarrow Fe_2O_3$

(vii) $Fe_2O_3 \longrightarrow FeSO_4$

Solution (i) In this reaction, $KMnO_4$ which is an oxidizing agent, itself gets reduced to Mn^{2+} under acidic conditions.

$$n = |1\times(+7) - 1\times(+2)| = 5$$

(ii) In this reaction, $KMnO_4$ gets reduced to Mn^{4+} under neutral or slightly (weakly) basic conditions.

$$n = |1\times(+7) - 1\times(+4)| = 3$$

(iii) Here, $KMnO_4$ gets reduced to Mn^{6+} under basic conditions.

$$n = |1\times(+7) - 1\times(+6)| = 1$$

(iv) Here, $K_2Cr_2O_7$ which acts as an oxidizing agent gets reduced to Cr^{+3} under acidic conditions. (It does not react under basic conditions).

$$n = |2\times(+6) - 2\times(+3)| = 6$$

(v) $C_2O_4^{2-}$ (oxalate ion) gets oxidized to CO_2 when it is reacted with an oxidizing agent.

$$n = |2\times(+3) - 2\times(+4)| = 2$$

(vi) Ferrous ions get oxidized to ferric ions.

$$n = |1\times(+2) - 1\times(+3)| = 1$$

(vii) Here, ferric ions are getting reduced to ferrous ions.

$$n = |2\times(+3) - 2\times(+2)| = 2$$

108. Predict the molar ratio in which the following two substances would react if they are assumed to be salts of category (a)

$Ba_3(PO_4)_2$ and $AlCl_3$

Solution n factor of $Ba_3(PO_4) = 3 \times (+2) = 6 = n_1$

While n factor of $AlCl_3 = 1 \times (+3) = 3 = n_2$

$$\frac{n_1}{n_2} = \frac{6}{3}$$

If $\frac{n_1}{n_2} = \frac{x}{y}$

Molar ratio = $\frac{y}{x}$ (inverse of equivalent ratio)

$\therefore$ Molar ratio in which $Ba_3(PO_4)$ and $AlCl_3$ will react = 3:6 = 1:2

109. Find the n-factor for the reactants in each of the following cases:

(i) $I^- \rightarrow I_2$

(ii) $I_2 \rightarrow I^-$

(iii) $S_2O_3^{2-} \rightarrow S_4O_6^{2-}$

(iv) $IO_3^- \rightarrow I^+$

(v) $CuS \rightarrow Cu^{2+} + SO_2$

Solution (i) n factor = $1 \times |0-(-1)| = 1$

(ii) n factor = $2 \times |-1 - 0| = 2$

(iii) n factor = $2 \times |2.5 - 2| = 1$

(iv) n factor = $1 \times |1 - 5| = 4$

(v) n factor = $1 \times |4 - (-2)| = 6$

110. Calculate the n-factor in the following redox change.

$$FeC_2O_4 \longrightarrow Fe^{3+} + CO_2$$

Solution Here, Fe^{2+} is getting oxidized to Fe^{3+} and C^{3+} is getting oxidised to C^{4+}. The n factor w.r.t. Fe is +1 and w.r.t. $C_2O_4^{2-}$ is 2 (as calculated earlier). Therefore, total n factor is 3.

Exercise

Calculate the n factor when $FeCr_2O_4$ gets oxidized to Fe^{3+} and Cr^{3+} and Cu_2S gets oxidised to Cu^{2+} and SO_2.

(i) *When only one atom undergoing either reduction or oxidation e.g.,*

$$\underset{n=5}{\overset{+7}{MnO_4^-}} \xrightarrow{H^+} \overset{+2}{Mn^{2+}}$$

In such a case, we consider the change in oxidation state of atom undergoing oxidation or reduction change per molecule as the n-factor of the species.

n-factor = $|(+2) \times 1 - (+7) \times 1| = 5$

$$\underset{n=1}{\overset{+2}{Fe^{2+}}} \longrightarrow \overset{+3}{Fe^{3+}}$$

n-factor = $|(+3) \times 1 - (+2) \times 1| = 1$

$$\underset{n=2}{\overset{+3\times2}{C_2O_4^{-2}}} \longrightarrow \overset{+4\times2}{2CO_2} \qquad \text{n-factor} = |(+4)\times 2 - (+3)\times 2| = 2$$

$$\underset{n=6}{\overset{+6\times2}{Cr_2O_7^{2-}}} \longrightarrow \overset{+3\times2}{2Cr^{3+}} \qquad \text{n-factor} = |(+3)\times 2 - (+6)\times 2| = 6$$

Calculate the n-factor of the reactant (oxidant or reductant) in the following cases:

(i) $IO_3^- \rightarrow I_2$
(ii) $Zn \rightarrow ZnO_2^{2-}$
(iii) $NO_3^- \rightarrow NH_3$
(iv) $NH_4^+ \rightarrow NH_2OH$

(ii) *Salts which reacts in such a way that only one atom undergoes change in oxidation state but appears in two products with the same oxidation state:*

In such a case, the method of calculation of n-factor remains the same i.e., we will calculate the change in oxidation state of the atom per mole of that substance (reactant).

$$\overset{+6\times2}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{3+}{Cr^{3+}}$$

In this example, oxidation state of Cr changes from +6 to +3 in both the products. So

$$\text{n-factor} = |(+6)\times 2 - (+3)\times 2| = 6$$

(iii) *Salts which react in such a way that only one atom undergoes change in oxidation state but goes in two products with different oxidation state as a result of either only oxidation or only reduction.*

$$3\overset{+7}{MnO_4^-} \longrightarrow 2\overset{+2}{Mn^{2+}} + \overset{+6}{Mn^{+6}}$$

In such a case, it is impossible to calculate the n-factor until and unless one knows that how much of MnO_4^- is changing to Mn^{2+} and how much to Mn^{6+} and if one knows the balanced equation then there is no need of calculation of n-factor. Nevertheless, in such case, the n-factor can be calculated by deducing the total change in oxidation state divided by total number of atom undergoing reduction/ oxidation change. So, for the calculation of n-factor in the above example, out of three moles of MnO_4^-, two moles are being converted to Mn^{2+} and one mole changes to Mn^{6+}. So total decrease in oxidation state of Mn.

$$= |\,[2\times(+2) - 2\times(+7)]\,| + |\,[1\times(+6) - 1\times(+7)]\,|$$

$$= |\,4 - 14\,| + |\,6 - 7\,| = 11$$

$$\text{So, n-factor} = \frac{11}{3}$$

Calculate the n-factor of the reactant (oxidant or reductant) in following cases.
(i) $3MnO_4^- \rightarrow 2Mn^{2+} + Mn^{4+}$
(ii) $2MnO_4^- \rightarrow Mn^{2+} + Mn^{6+}$

(iv) *Salts which react in such a way that only one atom undergoes change in oxidation state in two product, in one product with changed oxidation state and in other product with same oxidation state as that of reactant.*

In such case, also one cannot calculate the n-factor without knowing the balanced chemical equation because one must know how much of atom has changed its oxidation state. For example.

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Let us calculate the n-factor of HCl. Out of 14 moles of Cl^- (in HCl), only 6 moles of Cl^- are changing its oxidation state from –1 to 0 in the product Cl_2 and the oxidation state of remaining 8 Cl^- ions remains same in KCl and $CrCl_3$. So, total number of moles of electrons lost by 14 moles of HCl is 6. So each mole of HCl takes up 6/14 i.e., 3/7 moles of electrons and hence n-factor of HCl is 3/7.

Calculate the n-factor of the reactant (oxidant or reductant) in following cases:

(i) $2MnO_4^- \rightarrow MnO_4^- + MnO_2$

(ii) $3MnO_4^- \rightarrow 2MnO_4^- + Mn^{2+}$

(v) *Salts which react in such a way that two or more atoms in the salt undergoes change in oxidation states as a result of either oxidation or reduction. Let us consider the following example*:

$$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2$$

In this case, the oxidation of both Fe^{2+} and C^{3+} are changing from +2 and +3 to +3 and +4 respectively. In such a case we will calculate the n-factor of the salt as the total increase or decrease in oxidation state per mole of the salt. As one can see that one mole of FeC_2O_4 contains one mole of Fe^{2+} and one mole of $C_2O_4^{2-}$ (i.e. 2 carbon atoms per mole of $C_2O_4^{2-}$.)

Total change in oxidation state,

$= |1 \times (+2) - 1 \times (+3)| + |2 \times (+3) - 2 \times (+4)|$

$= 1 + 2 = 3$

So, n-factor of FeC_2O_4 is 3

Calculate the n-factor of the reactant (oxidant or reductant) in following cases

(i) $FeS_2 \rightarrow Fe_2O_3 + SO_2$

(ii) $[Fe(CN)_6]^{4-} \rightarrow Fe^{3+} + CO_2 + NO_3^-$

(iii) $Cu_2S \rightarrow Cu^{2+} + SO_2$

(iv) $Fe_2(SO_4)_3 \rightarrow Fe^{2+} + SO_2$

(vi) *Salts which react in such a way that two atoms undergoing change in oxidation state but one undergoing oxidation and other reduction reaction. In such a case one has to calculate the change in oxidation state of either the atom being oxidized or the atom being reduced. For example,*

$$\overset{-3\times2}{(NH_4)_2}\overset{+6\times2}{Cr_2O_7} \longrightarrow \overset{0\times2}{N_2} + \overset{+3\times2}{Cr_2}O_3 + 4H_2O$$

In this reaction, the oxidation state of N is increasing by 6 units and that of Cr is decreasing by 6 unit. So, we can consider either oxidation or reduction product for the calculation of n-factor and it will be the same.

n-factor of $(NH_4)_2Cr_2O_7$ considering oxidation

$= |(-3) \times 2 - (0) \times 2| = 6$

n-factor of $(NH_4)_2Cr_2O_7$ considering reduction

$= |(+6) \times 2 - (+3) \times 2| = 6$

Calculate the n-factor of the reactant (oxidant or reductant) in following case:

$$KClO_3 \rightarrow KCl + O_2$$

(vii) *Species which undergoes disproportionation reaction: Those reaction in which oxidant and reductant are the same species or the same element from the species is getting oxidized as well as reduced.*

When the number of moles of atoms being oxidized is equal to the number of moles of atoms being reduced.

The n-factor can be calculated by knowing the balanced chemical equation and considering any of the change taking place. Say for example,

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Out of 2 moles of H_2O_2 consumed in the reaction, one mole of H_2O_2 is being oxidized ($H_2O_2 \rightarrow O_2$) and one mole of H_2O_2 is being reduced ($H_2O_2 \rightarrow 2H_2O$). First consider the oxidation reaction

$$\overset{(-1)\times 2}{H_2O_2} \longrightarrow \overset{2\times 0}{O_2}$$

n-factor = $|2 \times 0 - (-1) \times 2| = 2$

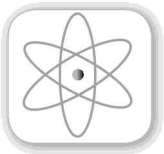
Again, considering reduction reaction

$$\overset{(-1)\times 2}{H_2O_2} \longrightarrow \overset{(-2)\times 2}{2H_2O}$$

n-factor = $|(-2) \times 2 - (-1) \times 2| = 2$

So, n-factor of H_2O_2 either considering oxidation or reduction reaction is same i.e., 2.

IODIMETRIC AND IODOMETRIC TITRATIONS



The redox-titration using iodine directly or indirectly as an oxidizing agent are called Iodine Titrations. These are of two types:

(1) Iodimetric Titrations

Iodimetric titrations are defined as those iodine titrations in which a standard iodine solution is used as an oxidant and iodine is directly titrated against a reducing agent. Iodimetric procedures are used for the determination of strength of reducing agent like thiosulphates, sulphites, arsenites and stannous chloride etc., by titrating them against standard solution of iodine taken in a burette. Some cases of oxidation-reduction reactions are given as under:

(i) $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

(ii) $Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$

(iii) $Na_3AsO_3 + H_2O \longrightarrow Na_3AsO_4 + 2HI$

(2) Iodometric Titrations

Iodometric titrations are defined as those iodine titrations in which some oxidizing agent liberates iodine from an iodine solution and then lilberated iodine is titrated with a standard solution of a reducing agent added from a Burette. In such titrations, a neutral or an acidic solution of oxidizing agent is employed. The amount of iodine liberated from an iodide, (i.e., KI) is equivalent to the quantity of the oxidizing agent present. Iodometric titrations are used for the determination of $CuSO_4$, $K_2Cr_2O_7$, $KMnO_4$, ferric ions, antimonite ions, H_2O_2, MnO_2, bromine and chlorine etc. The equations for some of the reactions are as follows:

(i) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

(ii) $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

$10KI + 5H_2SO_4 + 5O \longrightarrow 5K_2SO_4 + 5H_2O + 5I_2$

(iii) $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

$6KI + 3H_2SO_4 + 3O \longrightarrow 3K_2SO_4 + 3H_2O + 3I_2$

In the above reactions, the liberated iodine is titrated with a standard sodium thiosulphate.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$



Worked-out Examples

Application of Equivalent Concept in Redox Reactions

111. What is the weight of sodium bromate and molarity of solution to prepare 85.5 mL of 0.672 N solution when half cell reaction is,

$$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O$$

Solution Meq. of sodium bromate = $85.5 \times 0.672 = 57.456$

Let weight of sodium bromate be w

Eq. wt. of sodium bromate = $\frac{M}{6}$ (as n-factor = 6)

$\therefore \frac{W}{151/6} \times 1000 = 57/456$, $W_{NaBrO_3} = 1.446$ g

As molarity × n-factor = Normality

$\therefore$ Molarity = $\frac{0.672}{n-factor} = \frac{0.672}{6} = 0.112M$

112. A solution 0.1 M $KMnO_4$ is used for the reaction,

$$S_2O_3^{2-} + 2MnO_4^- + H_2O \rightarrow MnO_2 + SO_4^{2-} + OH^-$$

What volume of solution in mL will be required to react with 0.158 g of $Na_2S_2O_3$?

Solution Redox changes are: $Mn^{7+} + 3e \rightarrow Mn^{+4}$

$S_2^{2+} \rightarrow 2S^{6+} + 8e$

Meq. of $KMnO_4$ = Meq. of $S_2O_3^{2-}$

Let volume of $KMnO_4$ required = V

$\Rightarrow V \times 0.1\ 3 = \frac{0.158}{158} \times 8 \times 1000$ ($M_{Na_2S_2O_3} = 158$, n-factor = 8)

$\therefore$ V = 26.67 mL (n-factor for $MnO_4^- = 3$)

113. A sample of $MnO_4.4H_2O$ is strongly heated in air. The residue Mn_3O_4 left was dissolved in 100 mL of 0.1 N $FeSO_4$ containing dil. H_2SO_4. This solution was completely reacted with 50 mL of $KMnO_4$ solution. 20 mL of this $KMnO_4$ solution was completely reduced by 30 mL of 0.1 N $FeSO_4$ solution. Calculate the amount of $MnSO_4.4H_2O$ in sample.

Solution $MnSO_4 + H_2O \xrightarrow{\Delta} Mn_3O_4$

Redox change $3Mn^{2+} \rightarrow Mn_3^{8/3+} + 2e$

The residue Mn_3O_4 is titrated by another $FeSO_4$. The normality of $KMnO_4$ is determined by $FeSO_4$.

Meq. of $KMnO_4$ = Meq. of $FeSO_4$

$25 \times N = 30 \times 0.1 \therefore N = \frac{3}{25}$

Meq. of $FeSO_4$ added to $Mn_3O_4 = 100 \times 0.1 = 10$

Meq. of $FeSO_4$ left after reaction with Mn_3O_4

= Meq. of $KMnO_4$ used = $50 \times \frac{3}{25} = 6$

$\therefore$ Meq. of $FeSO_4$ used for $Mn_3O_4 = 10 - 6 = 4$

$\therefore$ Meq. of $Mn_3O_4 = 4$

$\therefore$ Meq. of $MnSO_4.4H_2O = 4$

$3MnSO_4.4H_2O \rightarrow Mn_3^{+8/3}O_4$ (n-factor = 8/3 – 2 = $\frac{2}{3}$)

$\therefore$ Let weight of hydrated salt be w and molecular weight = M

$\therefore \frac{w}{M} \times \frac{2}{3} \times 1000 = 4$ (as $\frac{W}{M} \times n \times 1000 = \text{Meq.}) \Rightarrow \frac{w}{223} \times \frac{2}{3} \times 1000 = 4$

$\therefore$ w = 1.338 g

114. 25 mL of H_2O_2 solution were added toe excess of acidified solution of KI. The iodine so liberated required 20 mL of 0.1 N $Na_2S_2O_3$ for titration. Calculate the strength of H_2O_2 in terms of normality and volume strength.

Solution Redox change is,

$O_2^{-1} + 2e \rightarrow 2O^{2-}$

$2I^- \rightarrow I_2 + 2e$

$2S_2^{2+} \rightarrow S_4^{+5/2} + 2e$

$I_2 + 2e \rightarrow 2I^-$

Meq. of H_2O_2 = Meq. of I_2 = Meq. of $Na_2S_2O_3 = 20 \times 0.1 = 2$

$\therefore N_{H_2O_2} = \frac{\text{Meq.}}{\text{Volume in ml}} = \frac{2}{25}$

Volume strength (x) = N × 5.6

$\therefore$ Volume strength = $\frac{2}{25} \times 5.6 = 0.448$ volume

115. 0.2 M $KMnO_4$ solution completely reacts with 0.05 M $FeSO_4$ solution under acidic conditions. The volume of $FeSO_4$ used is 50 mL. What volume of $KMnO_4$ was used?

Solution $0.2 \times 5 \times V = 0.05 \times 50$

$V = 2.5$ mL.

116. A solution of H_2O_2, labelled as '20 volumes', was left open. Due to this some H_2O_2 decomposed and the volume strength of the solution decreased. To determine the new volume strength of the H_2O_2 solution, 10 mL of the solution was taken and it was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.0245 M $KMnO_4$ solution under acidic condition. Calculate the volume strength of the H_2O_2 solution.

Solution Volume strength of a H_2O_2 solution : If a solution of H_2O_2 is labelled as 'x volumes' it means that 1 mL of the H_2O_2 solution on complete decomposition would release O_2 measuring × mL at STP.

Normality of $KMnO_4$ solution = $0.0245 \times 5 = 0.1225$ N

Equivalents of $KMnO_4$ used = $\frac{0.1225 \times 25}{1000} = 3.0625 \times 10^{-3}$

$\therefore$ Equivalents of H_2O_2 in the 10 mL that is titrated = 3.0625×10^{-3}

Equivalents of H_2O_2 in 100 mL = $3.0625 \times 10^{-3} \times 10$

$= 3.0625 \times 10^{-2}$

Equivalents of H_2O_2 in the original 10 mL = 3.0625×10^{-2}

[$\because$ on adding water equivalents of a substance does not change]

$$\text{Moles of } H_2O_2 \text{ in the original 10 mL} = \frac{3.0625 \times 10^{-2}}{2} = 1.53 \times 10^{-2}$$

['n' factor of H_2O_2 is 2 because as reacting with $KMnO_4$ O^{-1} becomes O^{-2}]

$$\text{Moles of } H_2O_2 \text{ in 1 mL of the original 10 mL} = \frac{1.53 \times 10^{-2}}{10} = 1.53 \times 10^{-3}$$

$$\text{Moles of } O_2 \text{ that it would give on decomposing } \frac{1.53 \times 10^{-3}}{2} \left[\because H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2\right] = 7.65 \times 10^{-4}$$

$$\text{Volume of } O_2 \text{ at STP in mL} = 7.65 \times 10^{-4} \times 22400 = 17.136$$

$\therefore$ Volume strength = 17.136

117. A solution contains mixture of H_2SO_4 and $H_2C_2O_4$. 25 mL of this solution requires 35.5 mL of N/10 for neutralization and 23.45 mL of N/10 $KMnO_4$ for oxidation, calculate.

(i) Normality of $H_2C_2O_4$ and H_2SO_4

(ii) Strength of $H_2C_2O_4$ and H_2SO_4 molecular weight of $H_2C_2O_4$ = 126

Solution Meq. of H_2SO_4 + Meq. of $H_2C_2O_4$ = Meq. of NaOH

$$= 3.55 \times \frac{1}{10} = 3.55 \qquad \ldots(1)$$

Meq. of $H_2C_2O_4$ = Meq. of $KMnO_4$

$$= 23.45 \times \frac{1}{10} = 2.345$$

$\therefore$ Meq. of H_2SO_4 = 3.55 – 2.345 = 1.205

$$\therefore \quad N_{H_2SO_4} = \frac{1.205}{0.25} = 0.0482 \left[N = \frac{\text{Meq.}}{\text{Volume in ml}}\right]$$

$$\text{Strength} = N \times \text{Eq. wt.} = 0.0482 \times \frac{98}{2} = 2.362 \text{ g /litre}$$

Meq. of $H_2C_2O_4$ = 2.345 (in 25 mL) (n-factor = 2)

$$\therefore \quad N_{H_2SO_4} = \frac{2.345}{25} = 0.0938$$

$H_2C_2O_4 \rightarrow 2CO_2$

$\therefore$ Strength = N $\times$ Equivalent weight

$$= 0.0938 \times \frac{126}{2} \text{ (n-factor = 2)} = 5.909 \text{ g}$$

118. 1.6 g of pyrolusite was treated with 50 mL of 0.5 M oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL this solution when treated with 0.02 M $KMnO_4$ required 32 mL of the solution. Find the % of MnO_2 in the sample and also the percentage of available oxygen.

Solution Meq. of MnO_2 = Meq. of oxalic acid taken – Meq. of oxalic acid left

$$= 50 \times 0.5 \times 2 - 32 \times 0.02 \times 5 \times 10 \text{ (in 250 mL)} = 18$$

Redox changes are $C_2O_4^{2-} \rightarrow 2CO_2$ (n-factor = 2)

$MnO_4^- \rightarrow Mn^{2+}$ (n-factor = 5)

$MnO_2 \rightarrow Mn^{2+}$ (n-factor = 2)

$$\frac{W_{MnO_2}}{M_{MnO_2}} \times 2 \times 1000 = 18 \Rightarrow \frac{W_{MnO_2}}{87} \times 2 \times 1000 = 18, \therefore w_{MnO_2} = 0.7821 \text{ g}$$

$$\therefore \quad \% \text{ of } MnO_2 = \frac{0.7821}{1.6} \times 100 = 48.88\%$$

Meq. of MnO_2 = Meq. of O_2

$$\frac{w_{O_2}}{16} \times 2 \times 1000 = 18, \therefore w_{O_2} = 0.144 \text{ g}$$

$$\% \text{ of available } O_2 = \frac{0.144}{1.6} \times 100 = 9$$

119. A mixture of $Na_2C_2O_4$ and $KHC_2O_4.H_2C_2O_4$ required equal volumes of 0.1 M $KMnO_4$ and 0.1 M NaOH separately. What is the molar ratio of $Na_2C_2O_4$ and $KHC_2O_4.H_2C_2O_4$ in the mixture?

Solution Let moles of $Na_2C_2O_4$ and $KHC_2O_4.H_2C_2O_4$ be x and y respectively

NaOH reacts with H^+ and $KMnO_4$ reacts with $C_2O_4^{2-}$

$(2x + 2y + 2y) \times 1000 = V \times 0.1 \times 5$ ...(1)

$(y + 2y) \times 1000 = V \times 0.1$ ...(2)

$C_2O_4^{2-} \rightarrow 2CO_2$ (n-factor = 2)

For KHC_2O_4, n-factor = 1 in neutralization reaction

For $H_2C_2O_4$, n-factor = 2 in redox reaction

From equation (1) and (2),

$$\frac{(2x+4y)}{3y} = \frac{V \times 0.5}{V \times 0.1} = 5$$

$\therefore \quad 2x + 4y = 15y$

$\therefore \quad 2x = 11y$

$$\therefore \quad \frac{x}{y} = \frac{11}{2} = 5.5$$

$\therefore \quad x : y :: 1 : 5.5$

120. Calculate the amount of SeO_3^{-2} in a solution on the basis of following data.20 mL of M/60 solution of $KBrO_3$ was added to a definite volume of SeO_3^{-2} solution. The bromine evolved was removed by boiling and excess of $KBrO_3$ was back titrated with 5.1 mL of M/25 solution of $NaAsO_2$. The reactions are given below: (Atomic mass of Se = 79).

(a) $SeO_3^{-2} + BrO_3^- + H^+ \rightarrow SeO_4^{-2} + Br_2 + H_2O$

(b) $BrO_3^- + AsO_2^- + H_2O \rightarrow Br^- + AsO_4^{-3} + H^+$

Solution If you observe both the reactions carefully, you will come to know that in the first reaction when $KBrO_3$ is reacting with SeO_3^{-2}, its n-factor is 5 but when excess of $KBrO_3$ is titrated with $NaAsO_2$, its n factor is 6. Equivalents of excess of $KBrO_3$ can be subtracted from the initial equivalents of $KBrO_3$ only when both the reactions have same n factor for $KBrO_3$, which in this case cannot be done. We present the solution by two methods.

Equivalent Method:

Initial moles of $KBrO_3 = 20 \times \frac{1}{60} \times 10^{-3}$

Initial equivalents of $KBrO_3$ (n = 5) = $20 \times \frac{1}{60} \times 10^{-3} \times 5 = 1.66 \times 10^{-3}$

Equivalents of AsO_2^- reacted with excess of $KBrO_3$ =

$5.1 \times \frac{1}{25} \times 10^{-3} \times 2 = 4.08 \times 10^{-4}$ [$\because$ n factor of AsO_2^- is 2]

$\therefore$ equivalents of excess of $KBrO_3$ (n = 6) = 4.08×10^{-4}

[**Note:** Here, the equivalents of excess of $KBrO_3$ of n = 6 has to be converted to equivalents of excess of $KBrO_3$ of n factor 5 because equivalents of a substance with same n factor in two different reactions can only be added or subtracted.]

Moles of excess $KBrO_3 = \frac{4.08 \times 10^{-4}}{6} = 6.8 \times 10^{-5}$

Eq. of excess of $KBrO_3$ (based on n factor 5) = $5 \times 6.8 \times 10^{-5} = 3.4 \times 10^{-4}$

$\therefore$ Equivalents of $KBrO_3$ reacted with $SeO_3^{2-} = 1.66 \times 10^{-3} - 3.4 \times 10^{-4} = 1.32 \times 10^{-3}$

$\therefore$ Equivalents of $SeO_3^{2-} = 1.32 \times 10^{-3}$

$\therefore$ Moles of $SeO_3^{2-} = \frac{1.32 \times 10^{-3}}{2} = 6.6 \times 10^{-4}$ (as n factor of $SeO_3^{2-} = 2$)

$\therefore$ Amount of $SeO_3^{2-} = 6.6 \times 10^{-4} \times 127 = 0.084$ g

Mole method:

Initial moles of $KBrO_3 = 20 \times \frac{1}{60} \times 10^{-3} = 3.33 \times 10^{-4}$

Moles of AsO_2^- reacted with excess of $KBrO_3 = 5.1 \times \frac{1}{25} \times 10^{-3}$

$\therefore$ Moles of excess of $KBrO_3 = \frac{1}{3} \times 5.1 \times \frac{1}{25} \times 10^{-3} = 6.8 \times 10^{-5}$

[**Note:** As the n–factor of BrO_3^- and AsO_2 in second reaction is 6 and 2 respectively i.e., in the ratio of 3:1 $\therefore$ their molar ratio will be 1:3]

$\therefore$ Moles of $KBrO_3$ reacted with $SeO_3^{2-} = 3.33 \times 10^{-4} - 6.8 \times 10^{-5} = 2.65 \times 10^{-4}$

$\therefore$ Moles of $SeO_3^{2-} = \frac{5}{2} \times 2.65 \times 10^{-4} = 6.625 \times 10^{-4}$

$\therefore$ Amount of $SeO_3^{2-} = 0.084$ g

121. A solution of 0.2 g of a compound containing Cu^{+2} and $C_2O_4^{-2}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL of the oxidant. The resultant solution is neutralized with Na_2CO_3, acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 N $Na_2S_2O_3$ solution for complete reduction. Find out the molar ratio of Cu^{+2} to $C_2O_4^{-2}$ in the compound. Write down the balanced redox reactions involved in the above titration.

Solution The mixture of Cu^{2+} and $C_2O_4^{2-}$ are reacting separately first with $KMnO_4$ solution and then solid KI to liberate iodine. It can be seen that Cu^{+2} cannot be oxidised and $C_2O_4^{-2}$ cannot be reduced. This is because Cu is already in its highest oxidation state +2.

$\therefore$ Equivalents of $KMnO_4$ solution $= \dfrac{0.02 \times 5 \times 22.6}{1000} = 2.26 \times 10^{-3}$

$\therefore$ Moles of $C_2O_4^{2-} = \dfrac{2.26 \times 10^{-3}}{2} = 1.13 \times 10^{-3}$

This is because only $C_2O_4^{-2}$ is oxidised by $KMnO_4$ to CO_2 ('n' factor 2)

Equivalents of $Na_2S_2O_3$ solution $= \dfrac{0.05 \times 11.3}{1000} = 5.65 \times 10^{-4}$

$\therefore$ Moles of $Cu^{+2} = \dfrac{5.65 \times 10^{-4}}{1} = 5.65 \times 10^{-4}$

This is because only Cu^{+2} is reduced by KI to Cu^{+}.

(**Note:** Whenever a metal ion is reduced it always goes to lower oxidation state but generally never goes to oxidation state zero).

$\therefore$ Molar ratio of Cu^{+2} to $C_2O_4^{2-} = \dfrac{5.65 \times 10^{-4}}{1.13 \times 10^{-3}} = 0.5$

Reactions: $2MnO_4^- + 5C_2O_4^{-2} + 16H^+ \rightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$

$2Cu^{+2} + 4I^- \rightarrow Cu_2I_2 + I_2$

$I_2 + 2S_2O_3^{-2} \rightarrow 2I^- + S_4O_6^{2-}$.

122. An aqueous solution containing 0.10 g KIO_3 (formula wt = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45 mL of thiosulphate solution to decolourise the blue-starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

Solution Moles of $KIO_3 = \dfrac{0.1}{214} = 0.00047$

$\therefore$ Moles of I_2 liberated from $KIO_3 = \dfrac{0.00047}{2} = 0.000235$

Moles of KI reacting = $0.00047 \times 5 = 0.00235$ ($\because$ 'n' factor for KIO_3 and KI are 5 ad 1 respectively)

Moles of I_2 produced from KI $= \dfrac{0.00235}{2} = 0.001175$

Total moles of I_2 produced and reacted = 0.000235 + 0.001175 = 0.00141 equivalents of I_2 reacted = $0.00141 \times 2 = 0.00282$ = equivalents of thiosulphate solution.

Molarity $= \dfrac{0.00282 \times 1000}{45} = 0.063$ M

(For thiosulphate 'n' factor = 1)

123. A 10 g sample of only CuS and Cu_2S was treated with 100 mL of 1.25 M $K_2Cr_2O_7$. The products obtained were Cr^{3+}, Cu^{2+} and SO_2. The excess oxidant was reacted with 50 mL of Fe^{2+} solution. 25 mL of the same Fe^{2+} solution required 0.875 M $KMnO_4$ under acidic condition, the volume of which used was 20 mL. Find the % of CuS and Cu_2S in the sample.

Solution Equivalents of dichromate initially $= \dfrac{1.25 \times 6 \times 100}{1000} = 0.75$

Equivalents of Fe^{2+} in 25 mL = $\frac{0.875 \times 5 \times 5 \times 20}{1000} = 0.0875$

Equivalents of Fe^{2+} in 50 mL = $0.0875 \times 2 = 0.175$

Equivalents of excess dichromate = 0.175

$\therefore$ Equivalents of dichromate consumed by (CuS and Cu_2S)

$= 0.75 - 0.175 = 0.575$

If x g is the mass of CuS, the mass of Cu_2S is (10 – x)g

$$\frac{x}{95.5} \times 6 + \frac{(10-x)}{159} \times 8 = 0.575$$

$\therefore$ x = 5.74 g

$$\% \text{ CuS} = \frac{5.74}{10} \times 100 = 57.4\%$$

$\% Cu_2S = 42.6\%$

124. For estimating ozone in the air, a certain volume of air is passed through an alkaline KI solution when O_2 is evolved and Iodide is oxidised to Iodine. When such a solution is acidified, free iodine is evolved which can be titrated with standard $Na_2S_2O_3$ solution. In an experiment 10 L of air at 1 atm and 27°C were passed through an alkaline KI solution, and at the end, the iodine was entrapped in a solution which on titration as above required 1.5 mL of 0.01N $Na_2S_2O_3$ solution. Calculate volume percentage of ozone in the sample.

Solution The equations required are $H_2O + KI + O_3 \rightarrow I_2 + O_2 + KOH$

Milliequivalents of Iodine = Milliequivalents of KI = Milli equivalents of O_3 reacted

Milliequivalents of $Na_2S_2O_3 = 1.5 \times 0.01 = 1.5 \times 10^{-2}$

$$\text{Millimoles of Iodine} = \frac{1.5 \times 10^{-2}}{2} = 7.5 \times 10^{-3}$$

[$\because$ 'n' factor for Iodine = 2]

Millimoles of ozone $= 7.5 \times 10^{-3}$

$$\text{Volume of ozone} = \frac{nRT}{P} = \frac{7.5 \times 10^{-6} \times 0.0821 \times 300}{1} = 184.725 \times 10^{-6} \text{ litre}$$

$$\text{Volume percentage of ozone} = \frac{184.725 \times 10^{-6}}{10} \times 100 = 1.847 \times 10^{-3}$$

125. 12 g of an impure sample of arsenious oxide (As_2O_3, which is acidic in nature) was dissolved in water containing sodium bicarbonate (which is basic in nature) and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidised by 22.4 mL of a solution of iodine, 25 mL of this iodine solution reacted with same volume of a solution containing 24.8 g of hydrated sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in one litre. Calculate the percentage of arsenious oxide in the sample.

Solution In this reaction, As_2O_3 acts as acidic oxide and $NaHCO_3$ as a base, giving acid base neutralization reaction which is non – redox process. Here, As_2O_3 does not act as basic oxide because in that case, it will form $As_2(CO_3)_3$ which does not exist as non-metals do not form carbonates.

n-factor of As_2O_3 is 6 and that of $NaHCO_3$ is 1. After the reaction As^{3+} is oxidized by I_2 to As^{+5} while I_2 is reduced to I^-.

$$\text{Normality of } Na_2S_2O_3.5H_2O = \frac{24.8}{248} = 0.1$$

Normality of I_2 = Normality of $Na_2S_2O_3.5H_2O = \frac{24.8}{248}$

$\therefore$ Equivalents of $I_2 = 0.1 \times 22.4 \times 10^{-3}$ = Equivalent of As^{3+} reacted in 25 mL = 2.24×10^{-3}

$\therefore$ Equivalents of As^{3+} reacted in 250 mL = 2.24×10^{-2}

Moles of As^{3+} in 250 mL = $\frac{2.24 \times 10^{-2}}{2} = 1.12 \times 10^{-2}$

Moles of As_2O_3 reacted = $\frac{1.12 \times 10^{-2}}{2} = 5.6 \times 10^{-3}$

% Percentage of $As_2O_3 = \frac{5.6 \times 10^{-3} \times 198 \times 100}{12} = 9.24\%$

126. The minimum quantity of H_2S needed to precipitate 64.5 g of Cu^{2+} will be nearly.

(a) 63.5 g (b) 31.75 g
(c) 34 g (d) 2.0 g

Solution Meq. of H_2S = Meq. of Cu^{2+}

$\therefore \quad \frac{w_{H_2S}}{34/2} \times 1000 = \frac{63.5}{63.5/2} \times 1000 \quad \therefore \; w_{H_2S} = 34$ g

127. How many grams of $NaHSO_3$ will be required to react with one litre of $NaIO_3$ solution containing 5.8 g of $NaIO_3$ according to the reaction.

$IO_3^- + 3HSO_3^- \rightarrow I^- + 3H^+ + 3SO_4^{2-}$

(a) 10.2 g (b) 9.8 g
(c) 9.14 g (d) 8.2 g

Solution Meq. of $NaHSO_3$ = Meq. of $NaIO_3$

$= N \times V = \frac{5.8}{198} \times 6 \times 1000$ (n-factor for $NaIO_3 = 6$) = 175.76

$\frac{W_{NaHSO_3}}{M_{NaHSO_3}} \times 2 \times 1000 = 175.76$

$\therefore \quad W_{NaHSO_3} = \frac{175.76 \times 104}{2000} = 9.14$ g

$\therefore$ (c)

128. A 5 mL solution of H_2O_2 liberates 0.508 g of Iodine from an acidified KI solution. What is the volume strength of the H_2O_2 solution?

(a) 2.2% (b) 3.8%
(c) 4.48% (d) None of these

Solution Meq. of H_2O_2 = Meq. of I_2

$\Rightarrow \quad \frac{W_{H_2O_2}}{34} \times 2 \times 1000 = \frac{0.508}{254} \times 2 \times 1000 \quad \therefore \; W_{H_2O_2} = 0.06$ g

$H_2O_2 \rightarrow H_2O_2 + \frac{1}{2}O_2$

$\because$ 34 g H_2O_2 gives 11.2 litre of O_2 at STP

$\therefore$ 0.068 g gives $= \frac{11.2}{34} \times 0.068 = 22.4$ mL O_2

$\therefore$ Volume Strength of $H_2O_2 = \frac{22.4}{5} = 4.48$ volume

$\therefore$ (c)

129. A 0.1097 g sample of As_2O_3 required 26.10 mL of $KMnO_4$ solution for its titration. The molarity of $KMnO_4$ solution is

(a) 0.02 (b) 0.04

(c) 0.018 (d) 0.3

Solution $\underset{\text{n-factor} = 4}{As_2O_3} + \overset{\text{n-factor} = 5}{MnO_4^-} \longrightarrow 2AsO_4^{3-} + Mn^{2+}$

Let molarity of $KMnO_4$ solution be M

$\therefore$ Eq. of As_2O_3 = Eq. of $KMnO_4$ solution

$$\frac{0.1097}{198} \times 4 = \frac{26.10 \times M \times 5}{1000} \quad \left(\text{Equivalent weight } As_2O_3 = \frac{198}{4}\right)$$

Molarity = 0.017M $\approx$ 0.018

$\therefore$ (c)

- There are some problems where both the concepts –mole concept as well as equivalent concept should be used. The following example is one of those:



Worked-out Example

130. A 2.18 g sample containing a mixture of XO and X_2O_3. It takes 0.015 mole of $K_2Cr_2O_7$ to oxidize the sample completely to form XO_4^- and Cr^{3+}. If 0.0187 mole of XO_4^- is formed, what is the atomic mass of X?

Solution $XO + K_2Cr_2O_7 \rightarrow Cr^{+3} + XO_4^-$

$X_2O_3 + K_2Cr_2O_7 \rightarrow Cr^{+3} + XO_4^-$

Let weight of XO in the mixture be x g

Equivalent of $K_2Cr_2O_7$ consumed by the mixture = 0.015 × 6

Equivalents of XO $= \frac{x}{x+16} \times 5$

Equivalents of $X_2O_3 = \frac{2.18-x}{2x+48} \times 8$ $\quad \therefore \frac{x}{x+16} \times 5 + \frac{2.18-x}{2x-148} \times 8 = 0.015 \times 6$

Since 1 mole of XO gives 1 mole XO_4^- and 1 moles of X_2O_3 gives 2 moles of XO_4^-

$\therefore \frac{x}{x+16} + \frac{2x(2.18-x)}{2x+48} = 0.0187$

Solving this, x = 99

ONE CORRECT OPTION TYPE QUESTIONS

1. It takes 2.56×10^{-3} equivalent of KOH to neutralize 0.1254 g H_2XO_4. The number of neutrons in 'X' is
(a) 16 (b) 8
(c) 7 (d) 32

2. A sample of hard water contains 244 ppm of HCO_3^- ions. What is the minimum mass of CaO required to remove HCO_3^- ions completely from 1 kg of such water sample?
(a) 56 mg (b) 112 mg
(c) 168 mg (d) 244 mg

3. 100 mL of each of 0.5 N NaOH, N/5 HCl and N/10 H_2SO_4 are mixed together. The resulting solution will be
(a) Acidic (b) Neutral
(c) Alkaline (d) None

4. The chloride of a metal (M) contains 65.5% of chlorine. 100 mL of the vapour of the chloride of the metal at STP weight 0.72 g, the molecular formula of the metal chloride is
(a) MCl_3 (b) MCl
(c) MCl_2 (d) MCl_4

5. In an experiment, 50 mL of 0.1 M solution of a salt reacted with 25 mL of 0.1 m solution of sodium sulphite. The half equation for the oxidation of sulphite ion:

$$SO^{2-}_{2(aq)} + H_2O \longrightarrow SO^{2-}_{4(aq)} + 2H^+_{(aq)}$$

If the oxidation number of the metal in the salt was 3, what would be the new oxidation number of the metal?
(a) 0 (b) 1
(c) 2 (d) 4

6. The chloride of a metal contains 71% chlorine by weight and the vapour density of it is 50. The atomic weight of the metal will be
(a) 29 (b) 58
(c) 35.5 (d) 71

7. 3.0 molal NaOH solution has a density of 1.110 g/mL. The molarity of the solution is
(a) 2.97 (b) 3.05
(c) 3.64 (d) 3.050

8. Element X reacts with oxygen to produce a pure sample of X_2O_3. In an experiment it is found that 1.00 g of X produces 1.16 g of X_2O_3. Calculate the atomic weight of X.
Given: atomic weight of oxygen, 16.0 g mol^{-1}.
(a) 67 (b) 100.2
(c) 125 (d) 150

9. In an aqueous solution of barium nitrate, the $[NO_3^-]$ is 0.80M. This solution is labelled as
(a) 0.080 N $Ba(NO_2)_2$ (b) 0.160 M $Ba(NO_3)_2$
(b) 0.040 M $Ba(NO_3)_2$ (d) 0.080 MNO_3^-

10. The number of atoms is greatest in
(a) 71 g of chlorine (b) 48 g of magnesium
(c) 127 g of iodine (d) 4 g of hydrogen

11. Which has maximum molecules?
(a) 7 g N_2 (b) 2 g H_2
(c) 16 g NO_2 (d) 16 g O_2

12. Urea solution is one molal. Urea present in one kg solution is:
(a) 60 g (b) 56.6 g
(c) 10.60 g (d) 10.0 g

13. H_2SO_4 is 98% by eight of solution. Hence, it is:
(a) 1 molal (b) 10 molal
(c) 50 molal (d) 500 molal

14. Resultant molarity of H^+ ion in a mixture of 100 mL of 0.1 M H_2SO_4 and 200 mL of 0.1 H_3PO_3 is:
(a) 0.1 M (b) 0.2 M
(c) 0.267 M (d) 0.133 M

15. To prepare a solution that is 0.50 M KCl starting with 100 mL of 0.40 M KCl:
(a) add 0.75 g KCl
(b) ad 20 mL of water
(c) add 0.10 mol KCl
(d) evaporate 10 mL water

16. The molality of a H_2SO_4 solution is 9. The weight of the solute in 1 kg H_2SO_4 solution is:
(a) 900.0 g (b) 469 g
(c) 882.0 g (d) 9.0 g

17. Number of moles of NH_3 formed when 0.535 g of NH_4Cl is completely decomposed by NaOH, is:

$$NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$$

(a) 0.01 mol (b) 5.35 mol
(c) 1.7 g (d) 0.17 mol

18. 10 L of hard water with temporary hardness [of $Ca(HCO_3)_2$] required 0.56 g of lime:

$$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$$

Temporary hardness in terms of ppm of $CaCO_3$ is:

(a) 56 (b) 1/2
(c) 100 (d) 200

19. A mixture of NaI and NaCl on reaction with H_2SO_4 gave Na_2SO_4 equal to the weight of original mixture taken. The percentage of NaI in the mixture is

(a) 82.38 (b) 26.38
(c) 62.38 (d) 28.38

20. 2.6 g of a mixture of calcium carbonate and magnesium carbonate is strongly heated to constant weight of 1.3 g. The atomic weights of calcium and magnesium are 40 and 24 respectively. State which of the following weights expresses the weight of calcium carbonate in the original mixture?

(a) 980 mg (b) 400 mg
(c) 1.75 g (d) 0.74 g

21. The amount of zinc required to produce 224 mL of H_2 at STP on treatment with dil. H_2SO_4 will be

(a) 0.65 g (b) 6.5 g
(c) 65 g (d) 0.065 g

22. 10 g of a piece of marble was put into excess of dilute HCl acid. When the reaction was complete, 1120 cm^3 of CO_2 was obtained at STP. The percentage of $CaCO_3$ in the marble is

(a) 25% (b) 50%
(c) 75% (d) 10%

23. For a given mixture of $NaHCO_3$ and Na_2CO_3, volume of given HCl required is x mL with phenolphthalein indicator and further y mL required with methyl orange indicator. Hence, volume of HCl for complete reaction of $NaHCO_3$ is:

(a) 2x (b) $\frac{x}{2}$
(c) y (d) (y – x)

24. A solution of 10 mL $\frac{M}{10}$ $FeSO_4$ was titrated with $KMnO_4$ solution in acidic medium. The amount of $KMnO_4$ used will be:

(a) 5 mL of 0.1 M (b) 10 mL of 0.1 M
(c) 10 mL of 0.5 M (d) 10 mL of 0.02 M

25. The normality of 10% (weight/volume) acetic acid is

(a) 1 N (b) 10 N
(c) 1.7 N (d) 0.83 N

26. 100 mL of 0.3 N HCl is mixed with 200 mL of 0.6 N H_2SO_4 The final normality of the resulting solution will be

(a) 0.1 N (b) 0.2 N
(c) 0.3 N (d) 0.5 N

27. In the reaction,

$$4\,NH_3\,(g) + 5O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O\,(l),$$

when 1 mole of ammonia and 1 mole of O_2 are made to react to completion

(a) 1.0 mole of H_2O is produced
(b) 10 mole of NO will be produced
(c) all the oxygen will be consumed
(d) all the ammonia will be consumed.

28. To neutralize 100 mL 0.1 M H_2SO_4. NaOH required is:

(a) 40 g (b) 80 g
(c) 0.4 g (d) 0.8 g

29. A gaseous alkane is exploded with oxygen. The volume of O_2 for compete combustion to CO_2 formed is in the ratio of 7 : 4. Deduce molecular formula of alkane.

(a) C_2H_6 (b) CH_4
(c) C_3H_8 (d) none of these

30. The hourly energy requirement of an astronaut can be satisfied by the energy released when 34 g of sucrose are burnt in his body. How many g of oxygen would be needed to be carried in space capsule to meet his requirement for one day?

(a) 916.2 g (b) 91.62 g
(c) 8.162 g (d) 9.162 g

31. 10 mL of a solution of H_2O_2 labelled '10 volume' just decolorises 100 mL of potassium permanganate solution acidified with dilute H_2SO_4. Calculate the amount of potassium permanganate in the given solution.

(a) 0.1563 g (b) 0.563 g
(c) 5.63 g (d) 0.256 g

32. If 0.5 mole of $BaCl_2$ is mixed with 0.2 mol of Na_3PO_4, the maximum amount of $Ba_3(PO_4)_2$ that can be formed is:

(a) 0.7 mol (b) 0.5 mol
(c) 0.2 mol (d) 0.1 mol

33. It takes 0.15 mole of ClO^- to oxidize 12.6 g of chromium oxide of a specific formula to $Cr_2O_7^{2-}$.

ClO^- became Cl^-. The formula of the oxide is (atomic weight Cr = 52, O = 16).

(a) CrO_3 (b) CrO_2
(c) CrO_4 (d) CrO

34. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. This solution is completely neutralised by 26.7 mL of 0.4 N NaOH. The percentage of free SO_3 in the sample is

(a) 30.6% (b) 40.6%
(c) 20.6% (d) 50%

35. 34 g of hydrogen peroxide is present in 1120 mL of solution. This solution is called

(a) 10 volume solution (b) 20 volume
(c) 30 volume (d) 32 volume

36. 50 mL of a solution containing 1 g each of Na_2CO_3, $NaHCO_3$ and NaOH was titrated with N–HCl. What will be the titre reading when only phenolphthalein is used as indicator?

(a) 35 mL (b) 32.5 mL
(c) 24.5 mL (d) 34.4 mL

ANSWER KEYS

1. (a)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (c)	**6.** (a)	**7.** (a)	**8.** (d)	**9.** (c)	**10.** (d)
11. (b)	**12.** (b)	**13.** (d)	**14.** (b)	**15.** (a)	**16.** (b)	**17.** (a)	**18.** (d)	**19.** (d)	**20.** (d)
21. (a)	**22.** (b)	**23.** (d)	**24.** (d)	**25.** (c)	**26.** (d)	**27.** (c)	**28.** (d)	**29.** (a)	**30.** (a)
31. (b)	**32.** (d)	**33.** (b)	**34.** (c)	**35.** (a)	**36.** (d)				

HINTS AND EXPLANATIONS

1. (a) Mole of

$$H_2XO_4 = \frac{0.1254}{M_x + 66} [M_x = \text{Atomic mass of x}]$$

'n' factor of $H_2XO_4 = 2$

[$\because$ H_2XO_4 is dibasic acid]

$$\therefore \quad 2.56 \times 10^{-3} = \frac{0.1254}{M_X + 66} \times 2$$

$$M_x = 31.96 \text{ g/mol} = 32 \text{ g/mol}$$

2. (b) Mass of HCO_3^- in 1 kg or 10^6 mg water = 244 mg

$$\text{Millimoles of } HCO_3^- = \frac{244}{61} = 4$$

$$2HCO_3^- + CaO \longrightarrow CaCO_3 + H_2O + CO_2 + 2e^-$$

millimoles of CaO = 2

mass of CaO = 56 × 2 = 112 mg

3. (c) Meq. of NaOH = 100 × 0.5 = 50

$$\text{Meq. of HCl} = \frac{1}{5} \times 100 = 20$$

$$\text{Meq. of } H_2SO_4 = \frac{1}{10} \times 100 = 10$$

Total meq. of acid = 20 + 10 = 30

Total meq. of NaOH = 50

$\therefore$ meq. of NaOH left = 50 – 30 = 20

4. (a) Molecular mass of chloride of metal = weight of 22,400 mL vapour of metal at STP

$$= \frac{0.72 \times 22,400}{100} = 161.28\text{g}$$

100 g of metal chloride contains = 65.5 g chloride

$$\therefore \quad 161.28 \text{ g metal chloride contains} = \frac{65.5 \times 161.28}{100} = 105.6\text{g}$$

Therefore, the number of mole of chlorine atoms per mole of metal chloride

= 105.6/35.5 = 3

Hence, the molecular formula of metal chloride is MCl_3.

5. (c) SO_3^{2-} get oxidised and its 'n' factor is 2

The metal must have been reduced

Applying the law of equivalence,

50 × 0.1 × (3 – n) = 25 × 0.1 × 2

6. (a) Molecular weight of metal chloride = 50 × 2 = 100
Let metal chloride be MCl_n then,
Eq. of metal = eq. of chloride, or $\frac{29}{E} = \frac{71}{35.5}$

$\therefore$ $E = \frac{29}{2}$

Now a + 35.5n = 100

or n.E + 35.5n = 100

n = 2

Therefore, a = 2 × E = 2 × 29/2 = 29

7. (a) Mole = 3

Weight of solvent = 1000g

$\therefore$ Weight of solution = 100 + 3 × 40 = 1120g

$\therefore$ Volume of solution = $\frac{1120}{1.110}$ml

$\therefore$ $M = \frac{3}{\frac{1120}{1.110 \times 1000}} = 2.97$

8. (d) The mass of O atoms = 1.16 – 1.00 = 0.160g

Number of moles of O atom = $\frac{0.160}{16} = 0.01$

In X_2O_3,

$\frac{\text{No. of moles of X}}{\text{No. of moles of O}} = \frac{2}{3}$

Number of moles of,

$X = \frac{2}{3} \times 0.01 = \frac{0.02}{3} = 0.00666$

Atomic weight of,

$X = \frac{\text{mass in g}}{\text{no. of moles}} = \frac{1.0}{0.00666} = 150$

9. (c) In $Ba(NO_3)_2$, the molar ratio of $Ba(NO_3)_2$ to NO_3^- is 1 : 2. Therefore, the molarity of the $Ba(NO_3)_2$ solution is $\frac{1}{2} \times 0.080 = 0.040M$.

10. (d) 71 g of Cl_2 = 1 mol = 6.02×10^{23} x 2 atoms

48 g Mg = 2 moles = 2 x 6.02×10^{23} atoms

127 g I_2 = 0.5 mol = 3.01×10^{23} atoms

4 g H_2 = 2 moles = 2 x 6.02×10^{23} atoms

11. (b) 7 gN_2 = 7/28 mol = 0.25 mol, 2 g H_2 = 2/2 = 1 mol
16 g NO_2 = 16/45 mol, 16 g O_2 = 16/32 mol = 0.5 mol

12. (b) One molal urea solution means 1 kg water has 60 g urea. Thus, total mass of one molal solution = 1060 g

1060 g solution has urea = 60 g

1000 g solution has urea = $\frac{60 \times 1000}{1060} = 56.6$ g

13. (d) 98% by weight of solution means H_2SO_4 = 98 g = 1 mol

$H_2SO_4 + H_2O$ (solution) = 100 g

$\therefore$ $H_2O = 2$ g = 0.002 kg

$\therefore$ Molality = conc. in mol $kg^{-1} = \frac{1}{0.002} = 500$ molal

Thus, (d)

14. (b) H^+ (in H_2SO_4-a dibasic acid) = 0.2 M

H^+ (in H_3PO_3-a dibasic acid) = 0.2 M

$\text{Total } [H^+] = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} = \frac{100 \times 0.2 + 200 \times 0.2}{300}$

= 0.2 M

Thus, (b)

15. (a) Increase in molar concentration = 0.1 M

= 0.01 mol in 100 mL

= 0.745 g KCl in 100 mL

16. (b) 9 molal H_2SO_4 = 9 × 98 g in 1000 g H_2O

= 882 g H_2SO_4 in 1882 g H_2SO_4 solution

= $\frac{882}{1882}$ × 1000 g H_2SO_4 in 1 kg solution = 469 g

Thus, (b)

18. (d) $Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$

56 g 2 x 100 g

0.56 g CaO = 2 g $CaCO_3$ in 10 L H_2O

10 L (= 10^4 mL) hard water has $CaCO_3$ = 2 g

$\therefore$ 10^6 mL hard water has $CaCO_3$ = 200 g

Thus, hardness part per million (in ppm) of $CaCO_3$ is = 200

Thus, (d)

19. (d) Suppose weight of original mixture = 1 g and NaI present = x g. Then NaCl = (1 – x) g

$$\underset{2(23+127)=300\,g}{2\,NaI} + H_2SO_4 \longrightarrow \underset{46+32+64=142\,g}{Na_2SO_4} + 2HI$$

x g NaI = $\frac{142}{300}$ × x g Na_2SO_4 = 0.47 x g

$$\underset{2\times 58.5=117\,g}{2\,NaCl} + H_2SO_4 \longrightarrow \underset{142g}{Na_2SO_4} + 2HCl$$

$(1-x)$ g NaCl $\equiv \frac{142}{117} \times (1-x)$ g $Na_2SO_4 = 1.21$ $(1-x)$ g

$\therefore$ $0.47x + 1.21 + 1.21x = 1$

or $0.74x = 0.21$

or $x = 0.2838$ or 28.38 %

20. (d) Suppose weight of $CaCO_3 = x$ g. Then,

$MgCO_3 = (2.6 - x)$ g

$\underset{100g}{CaCO_3} \longrightarrow \underset{56g}{CaO} + CO_2$

x g $\longrightarrow 0.56x$ g

$\underset{84g}{MgCO_3} \longrightarrow \underset{40g}{MgO} + CO_2$

$(2.6-x)$ g $\longrightarrow \frac{40}{84}(2.6-x)$ g

$0.56x + \frac{40}{84}(2.6-x) = 1.3$ (Given)

$47.04x + 104 - 40x = 109.2$

$7.04x = 5.2$ or $x = 0.74$ g

21. (a) $\underset{65g}{Zn} + H_2SO_4 \longrightarrow ZnSO_4 + \underset{22400\,cc}{H_2}$

224 cc $H_2 = 0.65$ g Zn

22. (b) $\underset{100\,g}{CaCO_3} + 2HCl \rightarrow CaCl_2 + H_2O + \underset{\substack{22400\,cc\\ as\ STP}}{CO_2}$ 1120 cc of CO_2 are obtained from pure $CaCO_3$

$= \frac{100}{22400} \times 1120 = 5$ g.

Percentage of $CaCO_3 = \frac{5}{10} \times 100 = 50\%$

23. (d) Methyl orange indicates complete neutralization of Na_2CO_3 and $NaHCO_3$ while phenolphthalein indicates only 50% reaction of Na_2CO_3 to $NaHCO_3$ stage only.

Let volume of given HCl required for complete neutralization of,

$NaHCO_3 = V_1$

and for

$Na_2CO_3 = V_2$

For phenolphthalein indicator (50% Na_2CO_3)

$= \frac{V_2}{2} = x$

For methyl orange (further titration)

$= \frac{V_2}{2} + V_1 = y = x + V_1 = y$

Volume for $NaHCO_3$, $V_1 = (y - x)$ mL.

Thus, (d)

24. (d) $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$

$$\frac{2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5}{2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow Products}$$

$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$

$(KMnO_4)$ $(FeSO_4)$

$M_1V_1 = \frac{n_1}{n_2}M_2V_2 = \frac{2}{10} \times 10 \times \frac{1}{10} = \frac{1}{5}$

For (d), $M_1V_1 = 0.02 \times 10 = \frac{1}{5}$

25. (c) 10% wt./vol means 10 g in 100 c.c.

Eq. wt. of $CH_3COOH = 60$

$\therefore$ Normality $= \frac{10}{60} \times \frac{1000}{100} \approx 1.7$ N

26. (d) 100 mL of 0.3 N HCl contains HCl = 0.03 g eq.

200 mL of 0.6 N H_2SO_4 contains H_2SO_4

$= \frac{0.6}{1000} \times 200 = 0.12$ g eq.

Total g eq. = 0.15, Total volume = 300 mL

Finally normality $= \frac{0.15}{300} \times 1000 = 0.5$

Alternatively, $N_1V_1 + N_2V_2 = N_3V_3$ i.e.,

$0.3 \times 100 + 0.6 \times 200 = N_3 \times 300$

or $0.3 + 1.2 = 3N_3$

or $N_3 = 1.5/3 = 0.5$

27. (c) 4 moles of NH_3 combine with 5 moles of O_2. One mole of NH_3 requires 5/4 mole of O_2.

28. (d) 100 mL of 0.1 M $H_2SO_4 = 0.98$ g H_2SO_4

$\underset{2(40)g}{2NaOH} + \underset{98\,g}{H_2SO_4} \rightarrow Na_2SO_4 + 2H_2O$

$\therefore$ 0.98 g H_2SO_4 will neutralize NaOH = 0.80 g

$\rightarrow$ Eudiometric Analysis

29. (a) Let formula of alkane be C_nH_{2n+2}

$C_nH_{2n+2} + \left[n + \frac{n+1}{2}\right] O_2 \rightarrow nCO_2 + (n+1)H_2O(l)$

Given $\frac{\text{Volume of } O_2 \text{ used}}{\text{Volume of } CO_2 \text{ formed}} = \frac{7}{4}$

$\therefore$ $\frac{n(n+1)/2}{n} = \frac{7}{4}$

$\therefore$ $n = 2$

$\therefore$ Alkane is C_2H_6

30. (a) $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O$

1 mole of starch requires 12 mole of oxygen

$\therefore$ $\frac{34}{342}$ mole of starch requires $\frac{34}{342} \times 12 \times 32 \times 24 =$ 916.2 g

31. (b) $2H_2O_2 \longrightarrow 2H_2O + O_2$

22400 mL of O_2 evolved from 68 g of H_2O_2

$\therefore$ 10 mL of O_2 is evolved from $\frac{680}{22400}$ g of H_2O_2

Hence, 1 mL of H_2O_2 contain $\frac{0.0303}{34}$ mol = 0.00178 equivalent 10 mL of H_2O_2 therefore 0.0178 equivalents which will be present in 100 mL of $KMnO_4$ solution.

Amount of $KMnO_4$ in given sample

$= \frac{158}{5} \times 0.0178 = 0.563$ g

32. (d) Let us first solve this problem by writing the complete balanced reaction.

$$3BaCl_2 + 2\,Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 \downarrow + 6NaCl$$

We can see that the moles of $BaCl_2$ used is $\frac{3}{2}$ times the moles of Na_3PO_4. $\therefore$ to react with 0.2 mol of Na_3PO_4, the moles of $BaCl_2$ required would be $0.2 \times \frac{3}{2} = 0.3$. Since $BaCl_2$ is 0.5 mol, we can conclude that Na_3PO_4 is the limiting reagent. Therefore, moles of $Ba_3(PO_4)_2$ formed is $0.2 \times \frac{1}{2} = 0.1$ mol.

Alternatively,

We can use the concept of equivalents to arrive at the answer. $BaCl_2$ and Na_3PO_4 must be reacting without undergoing any change in oxidation state since in $Ba_3(PO_4)_2$ the oxidation states of Ba, P and O remain fixed at +2, +5 and –2 respectively and the other product is expected to be NaCl.

Equivalents of $BaCl_2 = 0.5 \times 2$ (Calculate 'n' factor as number of moles of cation in 1 mole of substance × oxidation state of each cation).

Equivalents of $Na_3PO_4 = 0.2 \times 3 = 0.6$

Therefore, Na_3PO_4 is the limiting reagent.

$\Rightarrow$ Equivalents of $Ba_3(PO_4)_2$ formed = 0.6

'n' factor of $Ba_3(PO_4)_2 = 6$ ($\because$ 'n' factor of Na_3PO_4 is 3, $\therefore$ Na_3PO_4 and $Ba_3(PO)_4$ will be in the molar ratio of 2:1) $\therefore$ Moles of $Ba_3(PO_4)_2 = \frac{0.6}{6} = 0.1$

$\therefore$ (d)

33. (b) 'n' factor of ClO^- is 2 ($Cl^{+1} \rightarrow Cl^{-1}$)

$\therefore$ Equivalents of $ClO^- = 0.15 \times 2 = 0.3$

If the molecular weight of the chromium oxide is M, and the oxidation state of chromium in it is x. Then equivalents of chromium oxide is,

$(6 - x) \times \frac{12.6}{M}$ (number of chromium atoms in the oxide is 1 $\because$ all the choices have 1 Cr per molecule)

$\therefore$ $(6-x) \times \frac{12.6}{M} = 0.3$

$\frac{6-x}{M} = \frac{0.3}{12.6}$ or $\frac{M}{6-x} = \frac{12.6}{0.3}$

Put each choice and find out the correct result. Choice (a) and (c) can be ignored (because oxidation state of Cr is +6 and +8 respectively. The later is an impossible oxidation state of Cr).

34. (c) Meq. of H_2SO_4 + Meq. of SO_3 = Meq. of NaOH

$\therefore$ $\frac{(0.5-x)}{98/2} \times 1000 + \frac{x}{80/2} \times 1000 = 26.7 \times 0.4$

$\therefore$ $x = 0.103$

$\therefore$ % of $SO_3 = \frac{0.103}{0.5} \times 100 = 20.6\%$

35. (a) Amount of H_2O_2 in one mL = $\frac{34}{1120}$ g

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

$\because$ 34 g of H_2O_2 gives 16 g or 11200 mL of O_2

$\therefore$ $\frac{34}{1120}$ g $H_2O_2 = \frac{11200}{34} \times \frac{34}{1120} = 10$ mL O_2

$\therefore$ Volume strength of $H_2O_2 = 10$ volume

36. (d) At the end point using phenolphthalein as indicator uses complete NaOH and $\frac{1}{2}$ Meq. of Na_2CO_3.

$\therefore$ Meq. of NaOH + $\frac{1}{2}$ meq. of Na_2CO_3 = Meq. of HCl

$\frac{1}{40} \times 1000 + \frac{1}{2} \times \frac{1}{106} \times 2 \times 1000 = V \times 1$

$\therefore$ $V = 34.4$ mL

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. For the following balanced redox reaction,
$2MnO_4^- + 8H^+ + Br_2 \rightleftharpoons 2Mn^{+2} + 2BrO_3^- + 2H_2O$
If the molecular wt. of MnO_4^-, Br_2 be M_x, M_y respectively, then
(a) equivalent wt. of MnO_4^- is Mx/5
(b) equivalent wt. of Br_2 is My/10
(c) the n-factor ratio of Mn^{+2} to BrO_3^- is 1: 1
(d) none of these

2. When a mixture of Cu_2S and CuS is titrated with $Al(MnO_4)$ in acidic medium, then the oxidation product of Cu_2S and CuS are Cu^{+2} SO_2. If the molecular weight of Cu_2S, CuS and $Al(MnO_4)_3$ be M, M' and M" respectively, then which of the following statement are correct?
(a) Equivalent weight of Cu_2S is $\frac{M}{8}$
(b) Equivalent weight of CuS is M'/5
(c) Equivalent weight of $Al(MnO_4)_3$ is M"/5
(d) Equivalent weight of $Al(MnO_4)_3$ is M"/5.

3. For the balanced redox reaction a NO_3^- + b As_2S_3 + $4H_2O \longrightarrow$
x AsO_4^{-3} + yNO + z $3SO_4^{-2}$ + 8H which of the following statements are correct?
(a) equivalent wt. of As_2S_3 is M/28 where M is molecular wt. of As_2S_3
(b) the value of a : b = 28 : 3
(c) The value of $\frac{a+2b}{x+y}$ is 1
(d) The value of $\frac{z-x}{3}$ is 1

4. When non-stoichiometric compound $Fe_{0.95}O$ is heated in presence of oxygen, then it converts into Fe_2O_3, then which of the following statements are correct?
(a) Equivalent weight of $Fe_{0.95}O$ is $\frac{M}{0.85}$ where M is molecular weight of $Fe_{0.95}O$.
(b) The number of moles of Fe^{+3} and Fe^{+2} 1 moles $Fe_{0.95}O$ and 0.1 and 0.85 respectively.
(c) The numebr of moles of Fe^{+3} and Fe^{+2} in 1 mole of $Fe_{0.95}O$ are 0.85 and 0.10 respectively.
(d) The % composition of Fe^{+2} and Fe^{+3} in the non stoichiometric compound is 89.47% and 10.53% respectively.

5. When FeS_2 is oxidised with sufficient O_2, then its oxidation product is found to be Fe_2O_3 and SO_2, if the molecular weight of FeS_2, Fe_2O_3 and SO_2 are M, M' and M", then which of the following statements are correct?
(a) Equivalent wt. of FeS_2 is M/11
(b) The molar ratio of FeS_2 to O_2 is 4 : 11
(c) The molar ratio of FeS_2 to O_2 is 11 : 4
(d) The molar ratio of Fe_2O_3 and SO_2 is 1 : 4

6. 40 g NaOH, 106 g Na_2CO_3 and 84 g $NaHCO_3$ is dissolved in water and the solution is made 1 litre. 20 mL of this stock solution is titrated with 1N HCl, hence which of the following statements are correct?
(a) The titre reading of HCl will be 40 mL. if phenolphthalein is used indicator from the very beginning.
(b) The titre reading of HCl will be 60 mL if phenolphthalein is used indicator from the very beginning.
(c) The titre reading of HCl will be 40 mL if the methyl orange is used indicator after the 1st end point.
(d) The titre reading of HCl will be 80 mL, if methyl orange is used as indicator from the very beginning.

7. 150 mL $\frac{M}{10}$ $Ba(MnO_4)_2$ in acidic can oxidise completely
(a) 150 mL 1 M Fe^{+2}
(b) 50 mL 1M $FeCrO_4$
(c) 75 mL 1 M $C_2O_4^{-2}$ ions
(d) 25 mL 1 M $K_2Cr_2O_7$ solution.

8. $\begin{matrix}COOH\\|\\COOH\end{matrix}$ and $\begin{matrix}COOK\\|\\COOH\end{matrix}$ behave as acid are well as reducing agent. Then which of the following are the correct statements regarding $\begin{matrix}COOH\\|\\COOH\end{matrix}$ and $\begin{matrix}COOK\\|\\COOH\end{matrix}$?
(a) When $\begin{matrix}COOH\\|\\COOH\end{matrix}$ and $\begin{matrix}COOK\\|\\COOH\end{matrix}$ behaves as reducing agent, then its equivalent weights are equal to half of its molecular weight respectively?
(b) 1000 mL of 1 N solution of each is neutralised by 1000 mL 1N $Ca(OH)_2$

(c) 1000 mL of 1M soltuion is neutralised by 1000 mL of 1 M $Ca(OH)_2$

(d) 1000 mL or 1M solution is neutralised by 200 mL 2 M of $KMnO_4$ in acidic medium.

9. For the reaction

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 + 2H_2O$$

1 mole 1 mole

then which of the following statements are correct?

(a) the equivalent weight of H_3PO_4 is 49.

(b) the resulting solution is neutralized by 1 mole of KOH

(c) 1 mole of H_3PO_4 is completely neutralized by 1.5 mole of $Ca(OH)_2$

(d) None

10. When FeS_2 is oxidised with sufficient O_2, then its oxidation product is found to be Fe_2O_3 and SO_2, if the molecular weight of FeS_2, Fe_2O_3 and SO_2 are M, M' and M", then which of the following statements are correct?

(a) Equivalent wt. of FeS_2 is M/11

(b) The molar ratio of FeS_2 to O_2 is 4 : 11

(c) The molar ratio of FeS_2 to O_2 is 11 : 4

(d) The molar ratio of Fe_2O_3 and SO_2 is 4 : 1

11. Which of the following weighs equal to 32 g?

(a) 1 mole of sulphur atoms

(b) 1 mole of oxygen atoms

(c) 1 mole of carbon dioxide

(d) 22.4 L of oxygen molecule at S.T.P.

SWER KEYS

1. (a, b, c) **2.** (a, d) **3.** (a, b, c, d) **4.** (a, b, d) **5.** (a, b) **6.** (a, c) **7.** (a, b, c, d) **8.** (a, b, d)
9. (a, b, c) **10.** (a, b) **11.** (a, d)

COMPREHENSION BASED QUESTION

COMPREHENSION-I

The percentage labelling of oleum is a unique process by means of which, the percentage composition of H_2SO_4, SO_3 (free) and SO_3 (combined) is calculated.

Oleum is nothing but it is a mixture of H_2SO_4 and SO_3 i.e., $H_2S_2O_7$, which is obtained by passing

SO_3 in solution of H_2SO_4. In order to dissolve free SO_3 in oleum, dilution of oleum is done, in which oleum converts into pure H_2SO_4. It is shown by the reaction as under:

$$H_2SO_4 + SO_3 + H_2O \longrightarrow 2\,H_2SO_4(\text{pure})$$

or, $$SO_3 + H_2O \longrightarrow H_2SO_4(\text{pure})$$

When 100 g sample of oleum is diluted with desired weight of H_2O (in g), then the total mass of pure H_2SO_4 obtained after dilution is known as percentage labelling in oleum.

For example, if the oleum sample is labelled as "109% H_2SO_4" it means that 100 g of oleum on dilution with 9 g of H_2O provides 109 g pure H_2SO_4, in which all free SO_3 in 100 g of oleum is dissolved.

Answer the following questions on the basis of the above write up:

1. For 109% labelled oleum if the number of moles of H_2SO_4 and free SO_3 be x and y respectively, then what will be the value of $\frac{x+y}{x-y}$?

(a) 1 (b) 18

(c) $\frac{1}{3}$ (d) 9·9

2. In the above question number 1, what is the percentage of free SO_3 and H_2SO_4 in the oleum sample respectively?

(a) 60%, 40% (b) 30%, 70%

(c) 85%, 15% (d) 40%, 60%.

3. In the above question number 1, what will be the percentage of combined SO_3 in the given oleum sample?

(a) 20% (b) 30%

(c) 48.98% (d) 51%

4. What volume of 1 M NaOH (in mL) will be required to react completely with H_2SO_4 and SO_3 in 109% labelled oleum?
   (a) 250 mL (b) 1612 mL
   (c) 750 mL (d) 1800 mL

5. What volume of 10 M NaOH (in mL) will be required to react completely with free SO_3 in 118% labelled oleum sample?
   (a) 500 mL (b) 200 mL
   (c) 400 mL (d) 600 mL

6. For "118% H_2SO_4" labelled oleum, if the number of moles of free SO_3, number of moles of H_2SO_4 and number of moles of H_2O be x, y and z respectively, then what will be value of $x + y + z$?
   (a) 3.4 (b) 3.2
   (c) 4.2 (d) 2.2

7. A 10 g sample of fuming sulphuric acid containing H_2SO_4, SO_3 and SO_2 undergoes complete neutralisation wirn 206.25 mL of 1M NaOH solution. What will be volume of NaOH (in mL) required to react completely with H_2SO_4, assuming that the sample shows the presence of 2% of SO_2?
   (a) 70 mL (b) 50 mL
   (c) 40 mL (d) 89.79 mL

8. In the question number 7, what will be the percentage by weight of H_2SO_4 in the sample?
   (a) 30% (b) 40%
   (c) 25% (d) 44%

9. In above question number 7, what will be the volume of 1 M NaOH (in mL) consumed with SO_3?
   (a) 71 mL (b) 112 mL
   (c) 85 mL (d) 122.44 mL

10. In the above question number 7, what will be the percentage of the combined SO_3 by weight?
    (a) 45% (b) 55%
    (c) 65% (d) 35.92%

COMPREHENSION-II

Iodine titrations: Compounds containing iodine are widely used in titrations, commonly known as iodine titration. It is of two kinds:

(i) lodometric titrations
(ii) lodimetric titrations.

(i) **lodometric titrations:** It is nothing but an indirect method of estimating the iodine. In this type of titration, an oxidising agent is made to react with excess of KI, in acidic medium or, basic medium in which I^- oxidises into I_2. Now the liberated I_2 can be titrated with $Na_2S_2O_3$ solution.

$$KI \xrightarrow{\text{Oxidising agent}} I_2 \xrightarrow{Na_2S_2O_3/H^+} I^- + Na_2S_4O_6$$

Although solid I_2 is black and insoluble in water, but it converts into soluble I_3 ions

$$I_2(s) + I^- = \rightleftharpoons I_3^-$$

black dark brown

Starch is used as indicator near the end point or equivalence point. Even small amount of I_2 molecules, gives blue colour with starch. The completion of the reaction can be detected when blue colour disappears at the and point. Iniodimetric titration, the strength of reducing agent is determined by reacting it with I_2.

Answer the following questions on the basis of above write up:

11. When 79.75 g of $CuSO_4$ sample containing inert impurity is reacted with KI, the liberated I_2 is reacted with 50 mL (1M) $Na_2S_2O_3$ in basic medium, where it oxidises into SO_4^{-2} ions, and I_2 reduces into I^-, then what will be the percentage purity of $CuSO_4$ in sample?
    (a) 60% (b) 80%
    (c) 50% (d) 95%

12. When 214 g of KIO_3 reacts with excess of Kl in presence of H^+, then it produces I_2. Now I_2 is completely reacted with 1 M $Na_2S_2O_3$ solution in basic medium, where it converts into SO_4^{-2} ions. Then what volume of $Na_2S_2O_3$ is needed to react the end point of the reaction?
    (a) 500 mL (b) 800 mL
    (c) 1500 mL (d) 750 mL

13. A solution containing Cu^{+2} and $C_2O_4^{-2}$ ions which on titration with $\frac{M}{10}KMnO_4$ requires 50 mL. The resulting solution is neutralized with K_2CO_3, then treated with excess of KI. The liberated I_2 required 25 mL $\frac{M}{10}$ $Na_2S_2O_3$ in acidic solution, then what is the difference of the number of m mole of Cu^{+2} and $C_2O_4^{-2}$ ions in the solution?
    (a) 40 (b) 10
    (c) 30 (d) 50.

14. When 1.66 g of KI is reacted with excess of KIO_3 in presence of 6N HCl, then ICl is produced. The amount of KIO_3 reacted and the ICl formed are respectively,
    (a) 4×10^{-2} mole, 3×10^{-3} mole
    (b) 1.5×10^{-2} mole, 5×10^{-3} mole

(c) 5×10^{-2} mole, 1.5×10^{-3} mole
(d) 5×10^{-3} mole, 1.5×10^{-2} mole

15. In order to estimate 0_3 in the air, 22.4 L of air at NTP, is passed through acidifi d KI solution where O_2 is evolved and I^- is oxidised to I_2. The liberated I_2 required 200 mL $\frac{M}{10}$ $Na_2S_2O_3$ in acidic medium, then what will be the % composition of O_3 by volume in the sample?
(a) 50% (b) 10%
(c) 0.1% (d) 1%

COMPREHENSION-III

Indicators are weak organic acids or bases which show completion of reaction (end point of reaction) by changing its colour, which is accompanied by the structural changes i.e., benzenoid structure into quinonoid structure. Namely we use two indicators, i.e., phenolphthalien and methyl orange.

Phenolphthalein acts as an indicator only in weakly basic madium by showing pink colour, but not in acidic medium. In basic medium, up to bicarbonate stage i.e., first end point, phenolphthalein acts indicator. Methyl orange acts as indicator in acidic medium as well as in basic medium. The volume of externally added acid (HCl) or base (NaOH) consumed in basic or acidic solution is respectively known as titre readings of HCl and NaOH.

(i) Phenolphthalein and metyl orange as indicator:
When volume of 1N HCl is used at different end point of the reactions:

$$\left.\begin{array}{l}\text{Step(i)}\ NaOH + HCl \rightarrow NaCl + H_2O \\ \text{Step(ii)}\ Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl\end{array}\right] \text{First endpoint}$$

$$\left.\text{Step(i)}\ NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O\right] \text{Second end point}$$

Phenolphthalium acts as indicator up to first end point i.e., stage (i) and (ii) of the reaction. Methyl orange acts as indicator up to first end point as well as in second end point also. i.e., stages (i) and (ii) as well as in step (iii) also.

(ii) **Methyl orange as indicator,**
When the volume of 1N NaOH is used in the following titrations;

(i) $H_3PO_2 + NaOH \longrightarrow NaH_2PO_2 + H_2O$
(Colour change)

(ii) $H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_3 + 2H_2O$
(Colour change)

(iii) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$
(Colour change)

(iii) **Phenolphthalein as indicator**
When the volume of 1M NaOH is used in the following titraton:

(i) $H_3PO_2 + NaOH \longrightarrow NaH_2PO_2 + H_2O$
(Colour change)

(ii) $H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_3 + 2H_2O$
(Colour change)

(iii) $H_3PO_4 + 3\ NaOH \longrightarrow Na_3PO_4 + 3H_2O$
(Colour change)

(iv) **Phenolphthalein and methyl orange as indicator** (for mixture of acids H_3PO_4 and HIO_3). It is titrated with 1N NaOH solution. H_3PO_4 neutralises in three steps
(a) ***M.O. as indicator***

(i) $HIO_3 + NaOH \longrightarrow NaIO_3 + H_2O$
(Color change)

(ii) $H_3PO_4\ NaOH \longrightarrow NaH_2PO_4 + H_2O$
(Colour change)

(b) ***Phenolphthalein as indicator***

(i) $HIO_3 + NaOH \longrightarrow NaIO_3 + 2H_2O$
(Colour change)

(ii) $H_3PO_4 + 2\ NaOH \longrightarrow Na_2HPO_4 + 2H_2O$
(Colour change)

(v) ***The certain weights of acids and bases have been taken in data as under:***

(a) Acids	is weight (in g) taken
H_3PO_2	66
H_3PO_4	82
H_3PO_4	98
HIO_3	178
(b) Bases	Its weight (in g) in 1 litre solution
NaOH	40
$NaHCO_3$	40
Na_2CO_3	40

16. What will be the titre readings of standard HCl solution, if 50 mL basic solution i.e., solution of NaOH, Na_2CO_3 and $NaHCO_3$ is titrated with HCl in presence of only phenolphthalein indicator from the very beginning?
(a) 45 mL (b) 34.4 mL
(c) 55 mL (d) 68.8 mL

17. What will be the titre readings of HCl in 50 mL of basic solution only if only methyl orange is used as indicator from the very beginning?
(a) 60 mL (b) 55.8 mL
(c) 40 mL (d) 111.5 mL

18. What will be the titre readings of HCl in 25 mL of basic solution, if onlymethyl orange is used as indicator after the first end point with pehnolphthalein?
(a) 50 mL (b) 42.6 mL
(c) 46.2 mL (d) 21.3 mL

19. What will be total numbers of mmole of HCl consumed in 50 mL solution during in 50 mL solution entire titration?
(a) 70 (b) 60
(c) 111.5 (d) 55.8

20. What volume (in mL) of standard solution NaOH will be consumed for reaction with H_3PO_3, H_3PO_2 and while phenolphthalein acts as indicator?
(a) 1000 mL (b) 3000 mL
(c) 4000 mL (d) 6000 mL

21. What volume (in mL) of standard soltuion NaOH will be consumed for reaction with H_3PO_3, H_3PO_2 and H_3PO_4, while methyl orange acts as indicator?
(a) 1000 mL (b) 3000 mL
(c) 2000 mL (d) 5000 mL

22. What will be the litre readings of NaOH (in mL) of standard solution NaOH, for reaction with HIO_3 and H_3PO_4 while phenolphthalein will act as indicator?
(a) 1000 mL (b) 2000 mL
(c) 1500 mL (d) 3000 mL

ANSWER KEYS

1. (d)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (b)	**6.** (d)	**7.** (d)	**8.** (d)	**9.** (b)	**10.** (d)
11. (b)	**12.** (d)	**13.** (b)	**14.** (b)	**15.** (d)	**16.** (d)	**17.** (d)	**18.** (d)	**19.** (c)	**20.** (a)
21. (c)	**22.** (d)								

HINTS AND EXPLANATIONS

COMPREHENSION-I

1. (d) 109% labelled oleum will contain 9 g H_2O, 40 g free SO_3, 6 g H_2SO_4

$$40\text{ g(free)}SO_3 = \frac{1}{2}\text{ mole } SO_3\text{(free)} = y$$

$$60\text{ g }(H_2SO_4) = \frac{60}{98} = x \text{ mole } H_2SO_4 = x$$

$$\Rightarrow \quad \frac{x+y}{x-y} = 9.9$$

2. (d) In 100 g oleum sample,
wt. of SO_3 = 40 g
wt. of H_2SO_4 = 60 g
% of SO_3 = 40% and
% of H_2SO_4 = 60 %

3. (c) $\because$ 98 g H_2SO_4 contains 80 g SO_3

$$\therefore \quad 60\text{ g } H_2SO_4 \text{ contains} = \frac{80\times 60}{98}\text{ g } SO_3$$

$$= 48.98\text{ g } SO_3$$

% of combined SO_3 in oleum = 48.98%.

4. (b) Use, m eq. of NaOH = m eq. of SO_3 + m eq. of H_2SO_4.

5. (b) 118% labelled oleum sample contains 80 g SO_3 i.e., 1 mole of SO_3
Let the volume of NaOH = y mL, then

$$y \times 10 \times 1 = \text{m eq of } SO_3 \text{ (n f = 2)}$$

$$= 1 \times 2 \times 1000$$

$$y = 200 \text{ mL}$$

6. (d) 118% labelled oleum sample will contain
18 g H_2O = 1 mole H_2O = 2 moles
80 g SO_3 = 1 mole SO_3 = x moles

$$20\text{ g } H_2SO_4 = \frac{20}{98}\text{ moles of } H_2SO_4$$

$$= y \text{ mole}$$

7. (d) Wt. of SO_2 in the sample = $\frac{10\times 2}{100} = 0.2$g
Now wt. of $SO_3 + H_2SO_4$ = 9.8 g
Now, apply the law of equivalence.

8. (d) Let the wt. of H_2SO_4 in the sample be x g, then from law of equivalence,

m eq. of H_2SO_4 + m eq. of SO_2

reacted reacted

= total m eq. of NaOH – m eq. of NaOH reacted with SO_2.

$\Rightarrow \frac{x}{98} \times 2 \times 1000 + \frac{(9.8-x)}{80} \times 2$

= total m eq. of NaOH – m eq. of SO_2.

$\Rightarrow$ x = 4.4 g

% of H_2SO_4 by wt. = $\frac{4.4}{10} \times 100 = 44\%$

9. (b) $\because$ wt. of SO_3 in the mixture

= 9.8 – 4.4 = 5.4 g

n-factor of SO_3 = 2

Now, apply m eq. of SO_3 = m eq. of NaOH

then find volume

10. (d) % of combined SO_3 by wt.

$= \frac{80}{98} \times 44\% = 35.92\%$

COMPREHENSION-II

11. (b) m eq. of $CuSO_4$ reacted

= m eq. of $Na_2S_2O_3$ reacted (n-f = 8)

$= 50 \times 1 \times 8 = 400$

% Purity of $CuSO_4$

$= \frac{400}{\text{Original in eq. of } CuSO_4} \times 100 = 80\ \%$

12. (d) 214 g KIO_3 = 1 mole of KIO_3

= 3 mole of I_2 (in the balanced chemical reaction)

= 6 eq. of I_2 (n f = 2)

= 6000 m eq. of I_2

Let the vol. of $Na_2S_2O_3$ = x mL, then

$(x \times 1) \times 8 = 6000$

x = 750 mL.

13. (b) m mole of $KMnO_4$ used = $50 \times \frac{1}{10} = 5$

m eq. of $KMnO_4$ used (n f = 5)

= 25 m eq. of $C_2O_4^{-2}$

m mole of $C_2O_4^{-2}$ (n = 2) = $\frac{25}{2} = 12.5$

m eq. of $Na_2S_2O_3$ = 2.5 m eq. of Cu^{+2} (n = 1)

$\because$ m eq. of Cu^{+2}(n = 1) = 2.5

Difference in number of m moles of Cu^{+2} and $C_2O_4^{-2}$ = 12.5 – 2.5 = 10

15. (d) $\because$ n-factor of O_3 = 2

$\therefore$ m eq. of $Na_2S_2O_3$ = m eq. of I_2 = m eq. of F^-

= m eq of O_3 reacted

$= 200 \times \frac{1}{10} \times 1 = 20$

$\because$ m mole of O_3 (n f = 2) = 10

$\therefore$ Mole of $O_3 = 10^{-2}$

% composition of O_3 by volume in air

$= \frac{\text{mole of } O_3}{\text{mole of air}} \times 100 = \frac{10^{-2}}{1} \times 100 = 1\%$

16. (d) Let the number of m moles of NaOH and Na_2CO_3 in 50 mL solution are x and y respectively.

Then, $x = \frac{2}{40} \times 1000 = 50$

$y = \frac{2}{106} \times 1000 = 18.8$

$\because$ n-factor of NaOH = 1,

n-factor of Na_2CO_3 = 1,

$\therefore$ m eq. of NaOH + m eq. of Na_2CO_3 = m eq. of NaOH

$\Rightarrow$ x + y = V mL × 1 N,

When V mL is the volume of HCl used.

Then, V = 68.8 mL

17. (d) Let the number of m moles of $NaHCO_3$ = Z in 50 mL solution

Then, $Z = \frac{2}{84} \times 1000$

When M.O. is added from the very beginning then x + 2y + z = m eq. of HCl used

$\frac{2}{40} \times 1000 + 2 \times \frac{2}{106} \times 1000 + \frac{2}{84} \times 1000$

Where V(mL) is the volume of HCl used.

Then, V = 50 + 37.6 + 23.8

= 111.5 mL

18. (d) When M.O. is used after the 1st end point in 25 mL solution, then,

$\frac{y}{2} + \frac{z}{2}$ = m eq. of HCl $\frac{1}{2} \times \frac{2}{100} \times 1000 + \frac{1}{2} \times \frac{2}{84} \times 1000$ = V mL × 100

$\Rightarrow \frac{1000}{106} + \frac{1000}{84} = V$

$\Rightarrow$ V = 9.43 + 11.9 = 29.33 mL.

19. (c) Let the volume NaOH be V mL, then m eq. of acids mixture = m eq. of NaOH

$\Rightarrow$ $(1 \times 1000) + (1 \times 1000) \times 2$
$+ (1 \times 1000) \times 3 = V\ mL \times 100$

$\Rightarrow$ $V = 6000\ mL$

22. (d) Let the volume of NaOH (in mL) = V
Then, m eq. of HIO_3 + m eq. of H_3PO_4
= m eq. of NaOH
$(1 \times 1000) \times 1 + (1 \times 1000) \times 2$
$= V\ mL \times 100$

$\Rightarrow$ $V = 3000\ mL$

MATCH THE COLUMN TYPE QUESTIONS

1.

Column-I	**Column-II (volume of x)**
(i) $2H_2 + O_2 \rightarrow 2H_2O$ 1 g 1 g x g	(a) 0.56 g
(ii) $N_2 + 3H_2 \rightarrow 2NH_3$ 1 g 1 g x g	(b) 1.333 g
(iii) $CaCO_3 \rightarrow CaO + CO_2$ 1 g x g	(c) 1.125 g
(iv) $2H_2 + C \rightarrow CH_4$ 1 g 1 g x g	(d) 1.214 g

ANSWER KEYS

1. (i) –c, (ii) –d, (iii) –a, (iv) –b

TRUE/FALSE TYPE QUESTIONS

1. If 1 mol of H_2 is taken out from 2 g H_2, 1 g H_2 is left.

2. In the reaction between 2 g H_2 and 3 g O_2, H_2 is the limiting reactant and O_2 is in excess.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

3. Equivalent weight of MnO_4^- when it changes to MnO_2 in concentrated basic medium is one-fifth of molar mass.

4. In a mixture containing 1 g benzene (C_6H_6) and 1 g toluene ($C_6H_5CH_3$), the mole fraction of two liquids is the same.

5. The strength of a solution (gL^{-1}) = Normality × eq. wt.

ANSWER KEYS

1. F **2.** F **3.** F **4.** F **5.** T

HINTS AND EXPLANATIONS

4. 1 g benzene and 1 g toluene have different number of moles

ASSERTION/REASON TYPE QUESTIONS

Instructions: In the following questions, an Assertion (A) is given followed by a Reason (R). Mark your responses from the following options.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'
(b) Both Assertion and Reason are true and Reason is not the correct explanation of 'Assertion'
(c) Assertion is true but Reason is false
(d) Assertion is false but Reason is true

1. **Assertion:** For the redox reaction
$Cu_2S \longrightarrow CuO + SO_2$,
y mole Cu_2S is equal to 8y equivalents of Cu_2S
Reason: Since the n-factor of Cu_2S is 8 and number of equivalents = n-factor × number of moles.
2. **Assertion:** Oxidation number of a bonded atom represents its valency.
Reason: Valency is the number of coralent bonder attached to any covalent bonds atom.
3. **Assertion:** The number of moles of $KMnO_4$ that will be needed to react with 1 mole of HCN (While HCN oxidises into CO_3^{-2} and NO_3^-) in acidic medium is 0.5.
Reason: Because the n-factor of $KMnO_4$ in acidic medium is 5 and the n-factor of HCN is 10. So, molar ratio of $KMnO_4$ to HCN is 1 : 2.
4. **Assertion:** A bottle is labelled as "10V" of H_2O_2. So, its percentage strength is 5%.
Reason: % Strength of H_2O_2 is nothing but it is the number of grams of H_2O_2 in 100 mL solution of H_2O_2 and it is related with volume strength as under 1 "Vol" of H_2O_2= 0.303%.
5. **Assertion:** When a 20 mL of mixture (whose one litre contain x m mole, y m mole and z m mole of NaOH, Na_2CO_3 and $NaHCO_3$ respectively), is treated with 1 N HCl in presence of methyl orange indicator from the very beginning, then the total used volume of HCl is,
$$\frac{x}{100}+\frac{2y}{100}+\frac{z}{100}\ mL$$
Reason: Because the n-factor of Na_2CO_3 reacting with HCl is 1 and total m eq's of HCl used is equal to total m eq's of bases reacted.

ANSWER KEYS

1. (a) 2. (d) 3. (a) 4. (d) 5. (a)

SUBJECTIVE QUESTIONS

1. A sample of $CaCO_3$ and $MgCO_3$ weighed 2.21 g is ignited to constant weight of 1.152 g . What is the composition of the mixture. Also calculate the volume of CO_2 evolved at 0°C and 76 cm of pressure.
2. A mixture of FeO and FeO_3 when heated in air to constant weight gains 5% in weight. Find out composition of mixture.
3. Calculate the weight of FeO from 2 g VO and 5.75 g of Fe_2O_3. Also report the limiting reagent.
$$VO + Fe_2O_3 \longrightarrow FeO + V_2O_5$$
4. A mixture of KBr, NaBr weighing 0.56 g was treated with aqueous solution of Ag^+ and the bromide ion was recovered as 0.97 g of pure AgBr. What was the weight of KBr in the sample?

5. In a gravimetric determination of P of an aqueous solution of dihydrogen phosphate in $H_2PO_4^-$ is treated with a mixture of ammonium and magnesium ions to precipitate magnesium ammonium phosphate $Mg(NH_4)PO_4.6H_2O$. This is heated and decomposed to magnesium pyrophosphate. $Mg_2P_2O_7$ which is weighed. A solution of $H_2PO_4^-$ yielded 1.054 g of ($Mg_2P_2O_7$) which is weighed. What weight of NaH_2PO_4 was present originally?

HINTS AND EXPLANATIONS

1. $CaCO_3 \longrightarrow CaO + CO_2$
x g

$MgCO_3 \longrightarrow MgO + CO_2$
y g

$\therefore$ $(x + y) = 2.21$ g ...(1)

$\because$ 100 g of $CaCO_3$ gives 56 g of CaO

$\therefore$ x g of $CaCO_3 \equiv \frac{56}{100} \times (x)$g CaO

Similarly, 84 g of $MgCO_3$ gives 40 g of MgO

$\therefore$ y g of $MgCO_3 = \frac{40 \times (y)}{84}$ g

$\therefore$ Wt. of residue $= \frac{56x}{100} + \frac{40y}{84} = 1.152$ ...(2)

Solving equations (1) and (2)

$x = 1.19$ g

$y = 1.02$ g

Mole of CO_2 formed = Mole of $CaCO_3$ + Mole of $MgCO_3$

$= \frac{1.19}{100} + \frac{1.02}{84} = 0.0241$

$\therefore$ Volume of CO_2 at STP = 0.0421 × 22.4 litre = 539.8 mL

2. $2FeO + \frac{1}{2}O_2 \longrightarrow Fe_2O_3$

$2Fe_3O_4 + \frac{1}{2}O_2 \longrightarrow 3Fe_2O_3$

Let, weight of FeO = x

Weight of Fe_3O_4 = y

$\therefore$ $x + y = 100$ ...(1)

$\because$ 2×72 g of FeO give $Fe_2O_3 = 160$ g

$\therefore$ x g FeO gives $Fe_2O_3 = \frac{160 \times (x)}{144}$ g

2×232 g of Fe_3O_4 gives $Fe_2O_3 = 3 \times 160$ g

$\therefore$ y g Fe_3O_4 gives $Fe_2O_3 = \frac{3 \times 160 \times y}{2 \times 232}$ g

$\therefore$ $\frac{160x}{144} + \frac{3 \times 16 \times y}{464} = 105$ ...(2)

Solving equation (1) and (2)

$x = 20.25$ g

$y = 79.95$ g

3. Balanced equation

$2VO + 3Fe_2O_3 \longrightarrow 6FeO + V_2O_5$

Moles before reaction $\frac{2}{67}$ $\frac{5.75}{160}$

$= 0.0298$ 0.0359 0 0

Moles after reaction (0.0298 – 0.0359)

0 $\left(\frac{6}{3} \times 0.0359\right)$ $\left(\frac{1}{3} \times 0.0359\right)$

As 2 mole of VO react with 3 mole of Fe_2O_3

$\therefore$ 0.0298 g mole of VO = $\frac{3}{2} \times 0.0298 = 0.0447$ mole of Fe_2O_3

Moles of Fe_2O_3 available = 0.0359 only

Hence, Fe_2O_3 is the limiting reagent

Mole of FeO formed = $\frac{6}{3} \times 0.0349$

$\therefore$ Weight of FeO formed = $0.0359 \times 2 \times 72 = 5.17$ g

$\left(\frac{n_{FeO}}{n_{Fe_2O_3}} = \frac{6}{3}\right) \Rightarrow n_{FeO} = \frac{6}{3} \times n_{Fe_2O_3}$

$W_{FeO} = \frac{6}{3} \times n_{Fe_2O_3} \times M_{Fe_2O_3}$

4. $KBr + NaBr + Ag^+ \longrightarrow AgBr$

a g (0.56 – a) g 0.97 g

Applying POAC for Br atoms

Moles of Br in KBr + moles of Br in NaBr = moles of Br in AgBr

or $1 \times$ moles of KBr + $1 \times$ moles of NaBr = $1\times$ moles of AgBr

$\Rightarrow \quad \frac{a}{119} + \frac{(0.56 - a)}{103} = \frac{0.97}{188}$ ($M_{KBr} = 199$, $M_{NaBr} = 103$, $M_{AgBr} = 188$)

$\therefore$ $a = 0.1332$ g

Percentage of KBr in the sample = $\frac{0.1332}{0.560} \times 100 = 23.78$

5. $NaH_2PO_4 + Mg^{2+} + NH_4^+ \longrightarrow Mg(NH_4)PO_4.6H_2O \xrightarrow{\Delta} Mg_2P_2O_7$

As P atoms are conserved, apply POAC for P atoms, moles of P in NaH_2PO_4 = moles of P in $Mg_2P_2IO_7$

$\Rightarrow$ $1 \times$ moles of $NaH_2PO_4 = 2 \times 2$ moles of $Mg_2P_2O_7$

$\therefore \quad \frac{W_{NaH_2PO_4}}{M_{NaH_2PO_4}} = 2 \times \frac{W_{Mg_2P_2O_7}}{M_{Mg_2P_2O_7}} \Rightarrow \frac{W_{NaH_2PO_4}}{120} = 2 \times \frac{}{222}$

$\Rightarrow \quad \frac{W_{NaH_2PO_4}}{120} = 2 \times \frac{1.054}{222}$

$\therefore \quad W_{NaH_2PO_4} = 1.14$ g

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

1. H_2O_2 acts as both oxidising as well as reducing agent . Its product is H_20, when acting as an oxidising agent and its product is O_2 when it acts as a of reducing agent. The strength of '10\P means one liter of H_20_2 solution on decomposition at S.T.P. condition liberates 10 liters of oxygen gas $(H_2O \rightarrow H_2O + \frac{1}{2}O_2)$ 15 gm $MnO_4)_2$ sample containing inert impurity is completely reacting with 100 ml of '11.2 V' H_20_2, then what will be the % purity of Ba $(Mn0_4)_2$ in the sample?
(Atomic mass Ba = 137, Mn = 55)
(a) 5% (b) 10%
(c) 50% (d) none

2. 1.2 gm of carbon is burnt completely in oxygen (limited supply) to produce CO and CO_2. This mixture of gases is treated with solid 1_20_5 (to know the amount of CO produced), the liberated iodine required 120 ml of 0.1 M hypo solution for complete titration. The % of carbon converted into CO is:
(a) 60% (b) 100%
(c) 50% (d) 30%

3. In what ratio should a 15% solution of acetic acid be mixed with a 3% solution of the acid to prepare a 10% solution (all percentages are mass/ percentages):
(a) 7 : 3 (b) 5: 7
(c) 7 : 5 (d) 7 : 10

4. 105 ml of pure water at 4°C saturated with NH_3 gas yielded a solution of density 0.9 g/ml, containing 30% NH by mass. Find the volume of resulting NH_3 solution.
(a) 66.67 ml (b) 166.67 ml
(c) 133.33 ml (d) 266.67 ml

5. The equivalent mass of H_3BO_3 (M = Molar mass of H_3BO_3) in its reaction with NaOH to from $Na_2B_4O_7$ is equal to
(a) M (b) $\frac{M}{2}$
(c) $\frac{M}{4}$ (d) $\frac{M}{6}$

6. x gram of pure As_2S_3 is completely oxidized to its respective highest oxidation states by 50 ml of 0.1 M hot acidified $KMnO_4$. Then x mass of As_2S_3 taken is: (Molar mass of As_2S_3 = 246)
(a) 22.4 g (b) 43.92 g
(c) 64.23 g (d) None

7. The number of moles of ferrous oxalate oxidized by one mole of $KMnO_4$ is
(a) $\frac{5}{2}$ (b) $\frac{2}{5}$
(c) $\frac{3}{5}$ (d) $\frac{5}{3}$

8. How many moles of $KMnO_4$ are needed in a mixture of 1 mole of each $FeSO_4$ & FeC_2O_4 in acidic medium
(a) $\frac{4}{5}$ (b) $\frac{5}{4}$
(c) $\frac{3}{4}$ (d) $\frac{5}{3}$

9. In the reaction
$Na_2S_2O_3 + 4C1_2 + 5H_2O \rightarrow Na_2SO_4 + H_2S0_4 + 8HCI$
the equivalent weight of $Na_2 S_2O_3$ will be
(a) M/4 (b) M/8
(c) M/1 (d) W/2
(M = molecular weight of $Na_2S_20_3$)

10. Which of the following equations is a balanced one
(a) $5BiO_3 + 22H^+ + 2M^{n2+} \rightarrow 5BiO^{3+} + 7H_2O + 2MnO^-_4$
(b) $5BiO_3 + 14H^+ + Mn^{2+} \rightarrow 5BiO^{3+} + 7H_2O + 2MnO4^-_4$
(c) $261O_3 + 4H^+ + 2M^{n2+} \rightarrow 6Bi^{3+} + 2H_2O + MnO4^-_4$
(d) $6BiO_3 + 12H^+ + 2Mn^{2+} \rightarrow 6Bi^{3+} + 6H_2O + 2MnO4^-_4$

11. The following equations are balanced atomwise and chargewise.
(i) $Cr_2O_7^{2-} + 8H^+ + 2H_2O_2 \rightarrow 2Cr^{3+} + 7H_2O + 2O_2$
(ii) $Cr_2O_7^{2-} + 8H^+ + 5H_2O_2 \rightarrow 2Cr^{3+} + 9H_2O + 4O_2$
(iii) $Cr_2O_7^{2-} + 8H^+ + 7H_2O_2 \rightarrow 2Cr^{+} + 11H_2O + 5O_2$

The precise equations representing the oxidation of H_2O_2 is/are
(a) (i) only
(b) (ii) only
(c) (iii) only
(d) all the three

12. An excess of NaOH was added to 100 mL of a ferric chloride solution. This caused the precipitation of 1,425 g of $Fe(OH)_3$. Calculate the normality of the ferric chloride solution
(a) 0.20 N
(b) 0.50 N
(c) 0.25 N
(d) 0.40 N

13. In the reaction $CrO_5 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + O_2$ how many moles of O_2 will one mole of CrO_5 liberate.
(a) 5/2
(b) 5/4
(c) 9/2
(d) none of these

14. 0.4g of a polybasic acid H_nA (all the hydrogens are acidic) requires 0.5 g of NaOH for complete neutralization. The number of replaceable hydrogen atoms in the acid and the molecular weight of 'A' would be: (Molecular weight of the acid is 96 gms.)
(a) 1, 95 (b) 2, 94
(c) 3, 93 (d) 4,92

15. 25.0 g of $FeSO_4.7H_2O$ was dissolved in water containing dilute H_2SO_4, and the volume was made up to 1.0 Litre 25.0 mL of this solution required 20 mL of an N/10 $KMnO_4$ solution for complete oxidation. The percentage of $FeSO_4.7H_20$ in the acid solution is
(a) 78% (b) 98%
(c) 89% (d) 79%

16. 1.0 mol of Fe reacts completely with 0.65 mol of O_2 to give a mixture of only FeO and Fe_2O_3. The mole ratio of ferrous oxide to ferric oxide is
(a) 2 : 2 (b) 4 : 2
(c) 1 : 2 (d) 2 : 7

17. 25 mL of a solution containing HCl and H_2SO_4 required 10 mL of 1 N NaOH solution for neutralization. 20 mL of the same acid mixture, on being treated with an excess of $AgNO_3$ gives 0.1425 g of AgCf. The normality of the HC and the normality of the H_2SO_4 are respectively
(a) 0.40 N and 0.05 N
(b) 0.05 N and 0.25 N
(c) 0.50 N and 0.25 N
(d) 0.40 N and 0.5 N

18. If 10 gm of V_20_5 is dissolved in acid and is reduced to V^{2+} by zinc metal, how many moles of I_2 could be reduced by the resulting solution if it is further oxidized to $V0^{2+}$ ions?
[Assume no change in state of Zn^{2+}ions] (V = 51, 0 = 16, I = 127):
(a) 0.11 mole of 1_2
(b) 0.22 mole of 1_2
(c) 0.055 mole of 1_2
(d) 0.44 mole of 1_2

19. 0.70 g of mixture $(NH_4)_2\ SO_4$ was boiled with 100 mL of 0.2 N NaOH solution till all the $NH_3(g)$ evolved and get dissolved in solution itself. The remaining solution was diluted to 250 mL. 25 mL of this solution was neutralized using 10 mL of a 0.1 N H_2SO_4 solution. The percentage purity of the $(NH_4)_2$ SO sample is
(a) 94.3
(b) 50.8
(c) 47.4
(d) 79.8

20. A mixed solution of potassium hydroxide and sodium carbonate required 15 ml. of an N/20 HCI solution when titrated with phenolphthalein as an indicator. But the same amount of the solution when titrated with methyl orange as an indicator required 25 mL of the same acid. The amount of KOH present in the solution is
(a) 0.014g
(b) 0.14g
(c) 0.028g
(d) 1.4g

21. The percentage of copper in a copper(II) salt can be determined by using a thiosulphate titration. 0.305 gm of a copper(II) salt was dissolved in water and added to, an excess of potassium iodide solution liberating iodine according to the following equation

$$2Cu^2\ (aq) + 4I^-\ (aq) \quad 2CuI(s) + I_2(aq)$$

The iodine liberated required 24.5cm^3 of a 0.100 mole dm^{-3} solution of sodium thiosulphate

$$2S_2O_3^{2-}\ (aq) + I_2(aq) \rightarrow 2I^-\ (aq) + S_4O_6^{2-}\ (aq)$$

the percentage of copper, by mass in the copper (ll) salt is. [Atomic mass of copper = 63.5]
(a) 64.2 (b) 51.0
(c) 48.4 (d) 25.5

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

22. There are two samples of CI having polarity 1M and 0.25 M. Find the volume of these samples taken in order to prepare the 0.75 M HCI solution. (Assume no water is used)

(a) 20 ml, 10 ml (b) 100 ml, 50 ml

(c) 40 ml, 20 ml (d) 50 ml, 25 ml

23. If 100 ml of 1M H_2SO_4 solution is mixed with 100 ml of 98%(wlw) H_2SO_4 solution (d = 0.1 gml) then:

(a) concentration of solution remains same

(b) volume of solution become 200 ml

(c) mass of H_2SO_4 in the solution is 98 gm

(d) mass of H_2SO_4 in the solution is 19.6 gm

24. Choose the correct statement :

(a) 2 mole of MnO_4^- ion can oxidized 5 moles of Fe^2 ion in acidic medium

(b) 2 mole of $Cr_2O,^{2-}$ ion can oxidized 6 moles of Fe^2 ion in acidic medium

(c) 2 mole of Cu_2S can be oxidized by 2.6 moles of MnO4 ion in acidic medium

(d) 2 mole of Cu_2S can be oxidized by 2.33 moles of $Cr_2O,^{2-}$ ion in acidic medium

25. 0.1 M solution of KI reacts with excess of H_2SO_4 and and KIO_3 solutions. According to equation $5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$; which of the following statement is correct

(a) 200 ml of the KI soluition react with 0.004 mole KIO_3

(b) 200 ml of the KI solution reacts with 0.006 mole of H_2SO_4

(c) 0.5 litre of the KI solution produced 0.005 mole of I_2

(d) Equivalent weight of KIO_3 is equal to $\left(\frac{\text{Molecular Weight}}{5}\right)$

ASSERTION/REASON TYPE QUESTIONS

26. KIO_3 reacts with KI to liberate iodine and the liberated iodine is titrated with standard hypo solution. The reactions are

- $IO_3^- + I^- \rightarrow I_2$ **(valency factor = 5/3)**
- $I_2 + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + I^-$ **(valency factor = 2)**

meq of hypo = meq of I_2 = meq of IO_3^- + meq of I^-

$\therefore$ IO_3^- react with I^-

$\Rightarrow$ meq of IO_3^- = meq of I^-

Statement-1: meq of hypo = 2 x meq of IO_3^-

Statement-2: valency factor of I_2 in both the equations are different therefore, we cannot equate milliequivalents in sequence

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-2.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-2.

(c) Statement-1 is True, Statement-2 is False.

(d) Statement-1 is False, Statement-2 is True.

27. Statement-1: One mole of SO_2 contains double the number of molecules present in one mole of O_2.

Statement-2: Molecular weight of SO_2 is double to that of O_2.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-2.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-2.

(c) Statement-1 is True, Statement-2 is False.

(d) Statement-1 is False, Statement-2 is True

28. Statement-1: The ratio by volume of gaseous reactants **and products are in agreement** with their molar ratio.

Statement-2: Volume of a gas is inversely proportional to **the number of moles of a gas.**

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-2.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-2.

(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

29. **Statement-1:** In the titration of Na_2CO_3 with HCI using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.
Statement-2: Two mole of HCI are required for the complete **neutralization of one mole of** Na_2CO_3.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-2.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-2.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

TRUE AND FALSE TYPE QUESTIONS

30. The reaction $2H_2O_2 -> 2H_2O + O_2$ is not an example of a redox reaction.

31. In a reaction H_2MoO_4 is changed to MoO_2+. In this case, H_2MoO_4 acts as a reducing agent.

32. The equivalent mass of $K_2Cr_2O_7$ in acidic medium is molar mass divided by two.

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

632 g of sodium thiosulphate ($Na_2S_2O_3$) reacts with copper sulphate to form cupric thiosulphate which is reduced by sodium thiosulphate to give cuprous compound which is dissolved in excess of sodium thiosulphate to form a complex compound sodium cuprothiosulphate ($Na_4[Cu_6(S_2O_3)_5]$).

$$CuSO_4 + Na_2S_2O_3 \rightarrow CuS_2O_3 + Na_2SO_4$$
$$2CuS_2O_3 + Na_2S_2O_3 \rightarrow Cu_2S_2O_3 + Na_2S_4O_6$$
$$3Cu_2S_2O3 + 2Na2S_2O_3 \rightarrow Na_4[Cu_6(S_2O_3)_5]$$
Sodium cuprothiosulphaté

In this process, 0.2 mole of sodium cuprothiosulphate is formed. (O = 16, Na = 23, S = 32)

Now answer the following questions.

33. The average oxidation states of sulphur in $Na_2S_2O_3$ and $Na_2S_4O_6$ are respectively.
(a) +5 & +2 (b) +2 & +2.5
(c) +5 & 2.5 (d) +2 & +4

34. Moles of sodium thiosulphate reacted and unreacted after the reaction are respecticvely.
(a) 3 & 2 (b) 2 & 3
(c) 2.2 & 1.8 (d) 1.8 & 2.2

35. If instead of given amount of sodium thiosulphate, 2 moles of sodium thiosulphate along with 3 moles of Cu SO_4 were taken initially. Then moles of sodium cuprothiosulphate formed is
(a) 0 (b) 1
(c) 1.5 (d) 2

COMPREHENSION-2

We know that balancing of a chemical equation is entirely based on law of conservation of mass. However, the concept of Principle of Atom Conservation (POAC) can also be related to law of conservation of mass in a chemical reaction. So, POAC can also act as a technique for balancing a chemical equation. For example, for a reaction

$$2AB_3 \rightarrow AB + C_2$$

On applying POAC for, B & C and relating the 3 equations, we get: $\frac{n_{ABC_3}}{2} = \frac{n_{AB}}{2} = \frac{n_{C_2}}{3}$ (n_x: number of moles of X)

Thus, the coefficients of ABC_3, AB & C_2 in the balanced chemical equation will be 2, 2 & 3 respectively and the balanced chemical equation can be represented as

$$ABC_3 \rightarrow AB + 3C_2$$

Now answer the following questions.

36. Which of the following relation is correct regarding the numerical coefficients p, q, r in the balanced chemical equation:

$$\mathbf{p}A + \mathbf{q}B_2 \rightarrow \mathbf{r}A_2B_5$$

(a) 2p = r (b) q = 1.25 p
(c) r = 2q (d) q = 0.8p

37. If the weight ratio of C and O_2 present is 1 : 2 and both of reactants completely consume and form CO and CO_2 and we will obtain a gasous mixture of CO

and CO_2. What would be the weight ratio of CO and CO_2 in mixture.

(a) 11 : 7 (b) 7 : 11

(c) 1 : 1 (d) 1 : 2

38. If the atomic masses of X and Y are 10 & 30 respectivetly, then the mass of XY_3 formed when 120 g of $\mathbf{Y_2}$ reacts completely with X is:

Reaction $X + Y_2 \rightarrow XY_3$

(a) 133.3 g (b) 200 g

(c) 266.6 g (d) 400 g

COMPREHENSION-3

Oleum is considered as a solution of SO_3 in H_2SO_4, which is obtained by passing $8O_3$ in solution of H_2SO_4. When 100 g sample of oleum is diluted with desired weight of H_2O then the total mass of H_2SO_4 obtained after dilution is known as percentage labelling in oleum.

For example, a oleum bottle labelled as '109% H_2SO_4' means that 109 g total mass of pure H_2SO_4 will be formed when 100 g of oleum is diluted by 9 g of Hp which combines with all the free $8O_3$ to form H_2SO_4 as

$$SO_3 + H_2O \rightarrow + H_2SO_4.$$

39. What is the percentage of free SO_3 in an oleum that is labelled as '104.5% H_2SO_4'?

(a) 10 (b) 20

(c) 40 (d) Noneof these

40. If excess water is added into a 100 g bottle sample labelled as '112% H_2SO_4' and is reacted with 5.3 g Na_2CO_3, then find the volume of CO_2 evolved at 1 atm pressure and 300 k temperature after the completion of the reaction: [R = 0.0821 Litre atom mol^{-1} K^{-1}]

$$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + H_2O + CO_2$$

(a) 2.46 L (b) 24.6 L

(c) 1.23 L (d) 123

41. 1 g of oleum sample is diluted with water. The solution required 54 ml of 0.4 N NaOH for compete neutralization.The percentage of free SO_3 in the sample is :

(a) 74 (b) 26

(c) 20 (d) None of these

COMPREHENSION-4

Volumetric analysis is based on the principle of equivalence a that minloces lead in the ratio of their equivalents. At the equivalence point of the reaction, involving the reactants A and B:

Number of gram equivalents of A = Number of gram equivalents of B.

If V_A ml of solution A having normality N_A reacts just completely with V_B ml of solution B having normality N_B then

$$\frac{N_A V_A}{1000} = \frac{N_B V_B}{1000}; N_A V_A = N_B V_B \quad \ldots (i)$$

Equation (1), called normality equation is very useful in numerical of volumetric analysis. Equivalent masses of different substances:

Basically the equivalent mass of a substance is defined as the pads by seam, which combines with or displace 1.0078 parts (≈1part) by mass of hydrogen, 8 parts by mansetaisiosaid 35.5 parts by mass of chlorine.

Mass of a substance expressed in grams equal to its equivalent mass is' gram equivalent mass. Equivalent mass of a substance is not constant but depends upon the mass of the substance participates.

Equivalent mass of an acid in acid-base reaction is its mass in grams with replaceable Fi ions (= 1.0078 g ≈ 1 g). On the other hand, equivalent mass of a bagels contains 1 mole of replaceable OH^- ions. 1 g equivalent mass each of an acid and base an ionclinegins saint and 1 mole of water (= 18 g).

Equivalent mass of an oxidizing agent is its mass which gains 1 mole at ellecism, it can be obtained by dividing the molecular mass or formula mass by the total decrease in addition of one or more elements per molecule.

On the other hand, equivalent mass of a **reducing agent** is the mass of the substance which loses 1 mole of electorns. It can be calculated by dividing the molecular or formula mass of the subtance by the total increase in oxidation number of one or more elements per molecular or formula mass.

42. How many grams of phosphoric acid (H_3PO_4) would be required to neutralize 58 g of magnesium hydroxide?

(a) 65.3 g (b) 70.2 g

(c) 85.0 g (d) 112.0 g

43. Which of the following solutions, when mixed with 100 ml of 0.05 M NaOH, will give a neutral solution?

(a) 100 ml of 0.1 M H_2SO_4

(b) 50 ml of 0.05 M H_2SO_4

(c) 100 ml of 0.05 M CH_3 COOH

(d) None of these

44. 100 ml of 0.1 M H_3 PO_2 is titrated with 0.1 M NaOH. The volume of NaOH needed will be

(a) 300 ml (b) 200 ml

(c) 100 ml (d) None of these

45. 9.8 g of an acid on treatment with excess of an alkali forms salt along with 3.6 g of water. What is the equivalent mass of the acid?

(a) 98.0 g (b) 49.0 g

(c) 24.5 g (d) 73.5 g

MATCH THE COLUMN TYPE QUESTIONS

46.

Column-I (Reactions)	**Column-II (Information conveyed by the reactions)**
(a) Complete reaction of Cuprous Sulphide with acidified Potassium permanganate solution producing a gas which turns lime water milky.	(p) Gases evolved do not have their constituent elements in their maximum possible oxidation states
(b) Reaction of Hydrochloric acid with Potassium dichromate solution Producing a gas necessary for the manufacture of Bleaching Powder	(q) Greater than one mole of oxidizing agent is consumed for every mole of reducing agent.
(c) Reaction of Iron pyrites (FeS_2)with Oxygen gas producing a gas having bent shape	(r) The element in oxidant, which undergoes change in oxidation number, is in its maximum possible oxidation state.
(d) Complete reaction of Ferrous oxalate with acidified Potassium dichromate solution producing a gas isoelectronic and isostrural with nitrous oxide.	(s) Moles of reductant consumed is ten times greater than the moles of oxidant consumed.

47. Match the column

Column-I	**Column-II**
(a) $CaCO_3 + H_3PO_4 \rightarrow Ca_3(PO_4)_2 + CO_2 + H_2O$	(p) 1 mole of oxidizing agent gains more electrons than lost by 1 mole of reducing Agent.
(b) $MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$	(q) No change in oxidation number of any element takes place.
(c) $Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4$	(r) All elements (except oxygen) are in their maximum oxidation states on the reactant side.
(d) $H_2O + F_2 \rightarrow HF + O_2$	(s) Number of moles of oxidizing agent consumed is less than number of moles of reducing agent.

48. [H = 1, C = 12, O = 16, Na = 23, P = 31, S = 32]

Column-I	**Column-II**
(a) 4.1 g H_2SO_3	(p) 200 ml of 0.5 N NaOH is used for complete neutralization
(b) 4.9 g H_3PO_4	(q) 200 millimoles of oxygen atoms
(c) 4.5 g oxalic acid ($H_2C_2O_4$)	(r) Central atom has its highest oxidation number
(d) 5.3 g Na_2CO_3	(s) May react with an oxidizing agent
(e)	(t) Shape around central atom is regular

49. Match the reacting mixture in column-I with the reagent in column-II

Column-I	**Column-I**
(a) $H_2C_2O_4 + NaHC_2O_4$	(p) NaOH
(b) $naHPO_4 + NaNO_2$	(q) HCl
(c) $Fe_2(SO_4)_3 + FeC_2O_4$	(r) $KMnO_4$
(d) $FeO + Fe_2O_3$	(s) Zinc dust

50. Match the following

Column-I	**Column-II**
(a) 4.5 m solution of $CaCO_3$ density 1.45 gm/ml	(p) mole fraction of solute is 0.2
(b) 3M 100 ml H_2SO_4 mixed with 1M 300 ml H_2SO_4 solution	(q) mass of the solute is 360 gm
(c) 14.5 m solution of Ca (r) molarity = 4.5	(r)
(d) in 4 M 2 litre solution of NaOH, 40 gm NaOH is added.	(s) molarity 1.5
(e) 5m (molal) NaOH solutlion	(t) 16.66% (w/w) of NaOH in solution

ANSWER KEYS

1. (c)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (a)	**6.** (b)	**7.** (d)	**8.** (a)	**9.** (b)	**10.** (b)
11. (a)	**12.** (d)	**13.** (d)	**14.** (c)	**15.** (c)	**16.** (b)	**17.** (b)	**18.** (a)	**19.** (a)	**20.** (a)
21. (b)	**22.** (a, b, c, d)	**23.** (a, b, d)	**24.** (a, b, c, d)	**25.** (a, d)	**26.** (a)	**27.** (d)	**28.** (c)	**29.** (b)	**33.** (b)
34. (c)	**35.** (a)	**36.** (b)	**37.** (b)	**38.** (a)	**39.** (b)	**40.** (c)	**41.** (b)	**42.** (a)	**43.** (b)

44. (c) **45.** (b) **46.** (a – p, q, r), (b – p, r, s), (c – p, q), (d – r). **47.** (a – q, r), (b – p, s), (c – q, r), (d – r). **48.** (a – p, s), (b, – q, r, t) ; (c – p, q, s, t), (d – r, t) **49.** (a – p, q, r), (b – p, q, r, s,), (c – r, s), (d – r, s) **50.** (a – r) ; (b – s) ; (c – p) ; (d – q, r,) (e – t)

HINTS AND EXPLANATIONS

1. (c) $N = \frac{11.2}{5.6}$

Milli equivalents $Ba(MnO_4)_2$ reacted $\Rightarrow$ equivalents of H_2O_2 reacted

$\Rightarrow 2 \times 100$

$\Rightarrow 200$ m eq^n

$\Rightarrow 0.2$ eq^n

Moles of $Ba(MnO_4)_2 \Rightarrow \frac{0.2}{10} = 0.02$

$\therefore$ wt. of $Ba(MnO_4)_2 = 0.02 \times 375.$

% purity of $Ba(MnO_4)_2 = \frac{375 \times 0.02}{15} \times 100 = 50\%$

2. (d)

	C	+ O2	$\rightarrow$	CO	+ CO_2
t = 0	0.1			–	–
t	0			x	(0.1 – x)

$5CO + I_2O_5 \rightarrow 5CO_2 + I_2$

t = 0 x x/5

moles of I_2 liberated = $\frac{1}{2}$ moles of hypo consumed = $\frac{1}{2} \times 120 \times 10^{-3} \times 0.1 = 60 \times 10^{-4}$

So, $x = 5 \times 60 \times 10^{-4} = 0.03$ moles

So, % of C forming CO = 30%.

5. (a) H_3BO_3 is a mono basic acid

So $\frac{M}{1}$ = equivalent mass

6. (b) $5As_2S_3 + 28KMnO_4 + H^+ \rightarrow 10H_3AsO_4 + 28Mn^{2+} + SO_4^{2-}$

mmoles of $KMn0_4 = 50 \times 0.1 = 5$

28 mmoles of $KMnO_4 \rightarrow 5$ Moles of As_2S_3

1 mmoles of $KMnO_4 \rightarrow 5/28$ moles of As_2S_3

Mass of $As_2S_3 = x = 246 \times \frac{5}{28}$ g = 43.92 g

7. (d) Equivalents of FeC_2O_4 = equivalents of $KMnO_4$

x (mole) $\times$ 3 = 1 $\times$ 5

$x = \frac{5}{3}$

8. (a) Equivalents of $KMnO_4$ = equivalent of $FeSO_4$ + equivalent of FeC_2O_4

$x \times 5 = 1 \times 1 + 1 \times 3$

$x = \frac{4}{5}$ mole

9. (b) $Na_{2S}^{+2}O_3 \rightarrow Na_{2S}^{+6}O_4$

see the total change in oxidation number = 4 $\times$ 2 = 8

$\therefore \quad E_{Na_2S_2O_3} = \frac{\text{mol.wt.}}{\text{V.f}} = \frac{M}{8}$

Reduction

10. (b) $BiO_3^- + Mn^{2+} \rightarrow Bi^{3+} + MnO_4^-$

Oxidation

(i) $2e + 6H^+ + BiO_3^- \rightarrow Bi^{3+} + 3H_2O$

(ii) $4H_2O + Mn^{2+} \rightarrow MnO_4^- + 8H^+ + 5e$

(i) $\times$ 5 + (ii) $\times$ 2 we get

$14\ H^+ + 5\ BiO_3^- + 5Mn^{2+} \rightarrow 5Bi^{3+} + 2MnO_4^- + 7H_2O$ is the correct balanced reaction.

12. (d) $3\ NaOH + FeCl_3 \rightarrow Fe(OH)_3 + 3NaCl$

m.e. of NaOH = me.e of $Fe(OH)_3$

$100 \times N = \frac{W}{E} \times 1000 \left(E_{Fe(OH)_3} = \frac{\text{mol.wt.}}{3} \right)$

$N = \frac{1.425 \times 10 \times 3}{107} = 0.3999 = 0.4N$

13. (d) The balance reaction is

$4CrO_5 + 2H_2SO_4 \rightarrow 2\ Cr_2(SO_4)_3 + 2H_2O + O_2$

$\therefore$ 1 mole CrO_5 can liberate only $\frac{1}{4}$ mole O_2

14. (c) Eq of Acid = Eq of Base

$$n \times \frac{0.4}{96} = \frac{0.5}{40}$$

$$n = \frac{1}{80} \times \frac{96}{0.4} = \frac{96}{32} = 3$$

$\therefore$ Wt of A = 96 – 3 = 93.

15. (c) M.e. of $FeSO_4 \cdot 7H_2O$ in 25 ml = m.e. of $KMnO_4$ used = 2 m.e.

M.e. of $FeSO_4 \cdot 7H_2O$ in 1000 ml = 80 m.e.

mass of $FeSO_4 \cdot 7H_2O$ in solution

$$= \frac{80}{1} \times 2787 \times \frac{1}{1000} = 22.24 \text{ gm}$$

$$\% \text{ of } FeSO_4 \cdot 7H_2O = \frac{22.24}{25} \times 100 = 88.96\ 89\%$$

16. (b) Let moles of FeO and Fe_2O_3 in the mixture is a and b respectively, then by POAC, we get the following two equations.

$a + 3b = 0.65 \times 2 = 1.3$ ...(i)

$a + 2b = 1$ ...(ii)

by solving (i) & (ii) we get, a : b = 4 : 3

17. (b) Let normality of HCℓ is N_1 and H_2SO_4 is N_2.

$\therefore$ M.e. of HCℓ + M.e. of H_2SO_4 = M.e of NaOH

$25 - N_1 + 25 \times N_2 = 10 \times 1$ ... (1)

$N_1 + N_2 = 0.4$ ... (1)

BY POAC

Moles of Cℓ = moles of AgCℓ

$$\frac{20 \times N_1}{1000} = \frac{0.1435}{143.05} = 10^{-3}$$

$N_1 = 0.05$ N

$N_2 = 0.35$ N

18. (a) $6e^- + 10H^+ + V_2O_5 \rightarrow 2V2^+ + 5\ H_2O$

$Zn \rightarrow Zn^{2+} + 2e^-\ 3 \times 3$

$V_2O_5 + 3\ Zn + 10\ H^+$

$\rightarrow 3\ Zn^{2+} + 2V^{2+} + 5H_2O$ ... (1)

Now $H_2O + V^{2+} \rightarrow VO^{2+} + 2H^+ + 2e^-$

$2e^- + I_2 \rightarrow 2r^-$

$V^{2+} + I_2 + H_2O \rightarrow 21^- + VO^{2+} + 2H^+$

So, we have 12 moles of V_2O_5 will reduce 2 moles of iodine

So, $\left(\frac{10}{102+80}\right) \times 2$ moles of will be reduced by given amount of V_2O_5 = 0.11 moles of 1_2

19. (a) M.e. of NH_3 = 10

m.e. of NH3 = 10

m.mole of $(NH_4)_2SO_4$ = 5

wt. of $(NH_4)_2\ SO_4$ = 5

wt. of (NH4)2 SO4 = $\frac{5}{1000} \times 132 = 0.66$ gm

% of $(NH_4)_2\ SO_4 = \frac{0.66}{0.7} \times 100 = 94.28\ \%$

20. (a) KOH + Na_2aO_3

a M.e. b.M.e.

$$a + \frac{b}{2} = 15 \times \frac{1}{20}$$

$2a + b = 1.5$ ... (i)

(in presence of phenolphthalein)

$a + b = \times \frac{1}{20} = 1.25$ ... (ii)

(in presence of Methyl orange)

by solving (i) & (ii) a = 0.25 m.e

mass of K0H = $\frac{0.25}{1000} \times 56 = 0.014$ gm

21. (b) From given reactions

mmoles of hypo = mmoles of iodine × 2

= mmoles of Cu^{2+} ions

= 24.5 × 0.1 mmoles

So, mass of copper = $24.5 \times 0.1 \times 10^{-3} \times 63.5$ gm

So, % of copper =

$$\frac{24.5 \times 0.1 \times 10^{-3} \times 63.5}{0.305} \times 100\% = 51.0\%$$

22. (a, b, c, d)

Final molarity = $\frac{V_1 \times 1 + V_2 \times 0.25}{(V_1 + V_2)}$

$0.75\ (V_1 + V_2) = V_1 + V_2 \times 0.25$

$0.75\ V_1 + 0.75\ V_2 = V_1 + V_2 \times 0.25$

$0.5\ V_2 = 0.25\ V_1$

$$\frac{V_1}{V_2} = 2$$

23. (a, b, d)

(a) Molarity of second solution is = $\frac{10 \times d \times x}{M} = 1M$

(b) Volume = 100 + 100 = 200 ml

(d) Mass of $H_2SO_4 = \frac{200 \times 1}{1000} \times 98 = 19.6$ gm.

24. (a, b, c, d)

Use equivalent of oxidising agent = equivalents of reducing agent.

25. (a, d)

$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

$$\frac{\text{moles of KI used}}{\text{moles of } KIO_3} = 5$$

Valency factor of $KIO_3 = 5$

$\therefore E_{KIO3} = \frac{\text{mol. wt.}}{5}$

27. (d) One mole of SOI_2 and O_2 have same number of molecules.

28. (c) $V \alpha n$ at same temperature and Pressure.

30. **False** It is a disproportionation reaction.

31. **False** H_2MoO_4 reduces itself therefore oxidize others and act as oxidizing agent.

32. **False** It is $\frac{\text{mol. wt.}}{6}$

34. (c) Moles of $Na_2S_2O_3$ used = 0.4 + 0.6 + 1.2 = 2.2

Moles of $Na_2S_2O_3$ left unreacted = $\frac{632}{158} - 2.2 = 1.8$

35. (a) No moles of $Na_2S_2O_3$ would remain in step (i), so further reaction will stop because $Na_2S_2O_3$ is required in excess.

36. to 38.

On applying POAC for A & B respectively, we get

$$1 \times n_A = 2 \times n_{A_2B_5} \quad \ldots (1)$$

$$2 \times n_{B_2} = 5 \times n_{A_2B_5} \quad \ldots (2)$$

By (1) & (2), $\frac{n_A}{4} = \frac{n_{B_2}}{5} = \frac{n_{A_2B_5}}{2}$

$\therefore$ Balanced equation: $4A + 5B_2 \rightarrow 2A_2B_5$

$\therefore$ q = 1.25

on applying POAC for X and Y respectively, we get

$$1 \times n_x = 1 \times n_{XY_3} \quad \ldots (3)$$

$$2 \times n_{Y_2} = 3 \times n_{XY_3} \quad \ldots (4)$$

by (3) & (4), $n_{Y_2} = 1.5 \times n_x$

from (3) and (4)

$$\frac{n_X}{2} = \frac{n_{Y_2}}{3} = \frac{n_{XY_3}}{2}$$

$\therefore$ Balanced equation:

$2X + 3Y_2 \rightarrow 2XY_3$

$n_{Y_2} = \frac{120}{60} = 2 \quad \therefore n_{XY_3} = \frac{4}{3}$

$\therefore m_{XY_3} = \frac{4}{3} \times 100 = 133.3\,g$

(2) $C + O_2 \rightarrow CO + CO_2$

W 2W x gm y gm

POAC for C POAC for O

$$\frac{w}{12} = \frac{x}{28} + \frac{y}{44} \qquad 2 \times \frac{2w}{32} = \frac{x}{28} + 2 \times \frac{y}{44}$$

$$\frac{w}{3} = \frac{x}{7} + \frac{y}{11} \quad \ldots (1)$$

$$\frac{w}{4} = \frac{x}{14} + \frac{y}{11} \quad \ldots . (2)$$

So now $\frac{3y}{11} + \frac{3x}{7} = \frac{4x}{14} + \frac{4y}{11}$

$$\frac{3y}{7} - \frac{3x}{7} = \frac{y}{11}$$

$$\frac{x}{7} = \frac{y}{11}, \frac{x}{y} = 7:11$$

39. (b) $SO_3 + H_2O \rightarrow H_2SO_4$;

18 g water combines with 80 g SO_3

$\therefore$ 4.5 g of H_2O combines with 20 g of SO_3

$\therefore$ 100 g of oleum contains 20 g of SO_3

or 20% free SO_3

40. (c) $H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + H_2O + CO_2$

Moles of CO_2 formed = moles of Na_2CO_3 reacted

(it is limiting reagent) = $\frac{5.3}{106} = 0.05$

volume of CO_2 formed at 1 atm pressure and 300 K = $0.05 \times 24.63 = 1.23$ L.

41. (b) Equivalent of H_2SO_4 + equivalent of SO_3 = equivalent of NaOH

$$\frac{x}{98} \times 2 + \frac{(1-x) \times 2}{80} = 54 \times 0.4 \times 10^{-3}$$

x = 0.74

$$\% \text{ of free } SO_3 = \frac{1 - 0.74}{1} \times 100 = 26\%$$

42. (a) $\left(\frac{W}{E}\right)_{H_3PO_4} = \left(\frac{W}{E}\right)_{Mg(OH)_2}$

$$\frac{W}{98} \times 3 = \frac{58}{58} \times 2$$

W = 65.33 gm

43. (b) Equilize the m.e. of NaOH by m.e. of acid.

44. (c) M.e. of H_3PO_2 = m.e. of NaOH
$100 \times 0.1 \times 1 = V \times 0.1$
$V = 100$ ml
H_3PO_2 is mono basic acid

45. (b) Number of moles of water produced = 0.2 moles
$\therefore$ 0.2 equivalent of acid should be reacted

$$\frac{W_{acid}}{E_{acid}} = 0.2 \Rightarrow E_{acid} = 49$$

46. (a – p, q, r), (b – p, r, s), (c – p, q), (d – r).
(a) $5Cu_2S + 8\ KMnO_4 \rightarrow Cu^{2+} + SO_2 + Mn^{2+}$
vf = 8 vf = 5
(b) $K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2\ CrCl_3 + 3Cl_2 + 7H_2O$
(c) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$
(d) $6FeC_2O_4 + 3K_2Cr_2O_7 \rightarrow Cr^{3+} + Fe^{3+} + CO_2$
Vf = 3 Vf = 6

47. (a – q, r), (b – p, s), (c – q, r), (d – r).

48. (a – p, s), (b – q, r, t); (c – p, q, s, t), (d – r, t)

(a) 4.1 gm = $\frac{4.1}{82}$ mole H_2SO_3 = 50 m mole

$2NaOH + H_2SO_3 \rightarrow Na_2\ SO_3 + 2H_2O$
m mole of NaOH requires = 2 × m mole of H_2SO_3 = 100
= m mole of NaOH present (200 ml × 0.5 N)
Highest O.N. of S = + 6

(b) 4.9 gm = $\frac{4.9}{98}$ mole = 50 m mole of H_3PO_4 = 200 m mole 'O' atom
Highest O.N. of P = + 5

(c) 4.5 gm = $\frac{4.5}{90}$ = 50 m mole of $H_2C_2O_4$ (di basic acid)
m mole of NaOH requires = 2 × 50 = 100
Highest O.N. of C = + 4

(d) 5.3 gm = $\frac{1}{20}$ mole Na_2CO_3. It does not react with NaOH and m mole of O atom = $\frac{1}{20} \times 3 = 150$

49. (a – p, q, r), (b – p, q, r, s), (c – r, s), (d – r, s)

50. (a – r); (b – s); (c – p); (d – q, r, (e – t)
(a) 4.5, H2SO4 means
4.5 moles of $CaCO_3$ is present in 1000 g solvent.
mass of solute = 4.5 × 100 = 450 g
mass of solution = 1000 ml
Hence molarity = 4.5 M

(b) $\text{Resultant molarity} = \frac{3\times100+1\times300}{400} = \frac{3}{2} = 1.5\text{M}$

(c) Mole fraction = $\frac{14.5}{14.5+55.5} = 0.2$

(d) Moles of NaOH in 2 ltr = 4 × 2 = 8 mole
moles of NaOH added = $\frac{40}{40}$ = 1 mole
$\therefore$ Molarit = $\frac{9}{2}$ = 4.5 M
mass of NaOH = 9 × 40 = 360 g

(e) % (w/w) NaOH = $\frac{5\times40}{5\times40+1000}\times100 = 16.66\%$

SUBJECTIVE TYPE QUESTIONS

1. The measured density at NTP of He is 0.1784 g/L. What is the weight of one mole of He?

Sol. One mole of He occupies 22.4 litre volume
$\because$ 1 litre volume weigh = 0.1784 g
$\therefore$ 22.4 litre volume weigh = 0.1784 × 22.4
= 4 g mol^{-1}

2. Calculate the number of moles of water in 488 g $BaCl_2 . 2H_2O$.

Sol. Mol. Wt. of $BaCl_2 . 2H_2O$ = 244 g
$\because$ 244 g $BaCl_2 . 2H_2O$ = 36 g H_2O
= 2 mole
$\therefore$ 488 $BaCl_2 . 2H_2O = \frac{2\times488}{244}$
= **4 mole H_2O**

3. Haemoglobin contains 0.25% iron by weight. The molecular weight of Haemoglobin in 89600. Calculate the number of iron atoms per molecule of Haemoglobin.

Sol. $\because$ 100 g Haemoglobin has = 0.25 g Fe
$\therefore$ 89600 g Haemoglobin has = $\frac{0.25\times89600}{100}$ g Fe
= 224 g Fe

i.e., 1 mole or N molecules of Haemoglobin has

$= \frac{224}{56}$ g atom Fe = 4 g atom Fe

4. Find the weight of NaOH in its 50 milli equivalents.

Sol. $\because$ Meq. $= \frac{W}{E} \times 1000$

$\therefore$ **50** $= \frac{w}{40} \times$ **1000**

$\therefore$ w = 2 g

5. The formula weight of an acid is 82.0 100 cm^3 of a solution of this acid containing 39.0 g of the acid per litre were completely neutralized by 95.0 cm^3 of aqueous NaOh containing 40.0 g of NaOH per litre. What is the basicity of the acid?

Sol. Normality of acid $= \frac{39}{82/n \times 1}$ (n is basicity of acid)

Normality of NaOH $= \frac{40}{40} \times \frac{1000}{1000} = 1$

Now, Meq. of acid = Meq. of NaOH

$\frac{39n}{82} \times 100 = 1 \times 95$ n = 2;

i.e., acid is dibasic.

6. 20% surface sites have absorbed N_2. On heating N_2 gas is evolved from sites and were collected at 0.001 atm and 298 K in a container of volume 2.46 cm^3. Density of surface sites is 6.023×10^{14} cm^{-2} and surface area is 1000 cm^2. Find out the number of surface sites occupied per molecule of N_2.

Sol. For absorbed N_2 on surface sites

F_{N_2} = 0.001 atm, V = 2.46 cm^3, = 2.46×10^{-3} L, T = 298 K

$\therefore \quad n_{N_2} = \frac{PV}{RT} = \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 298} = 1.0 \times 10^{-7}$

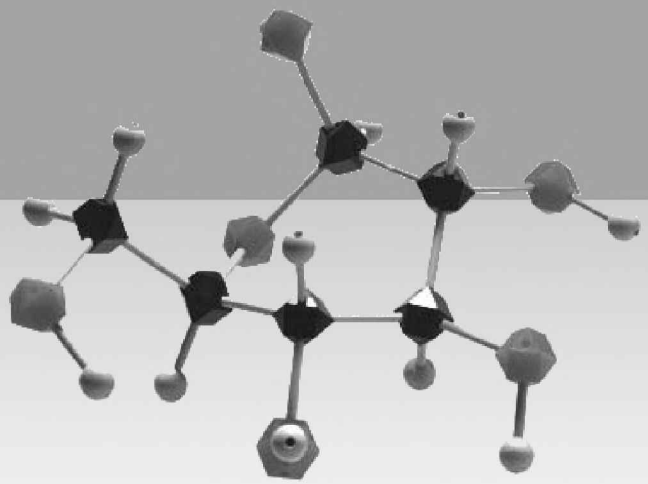
$\therefore$ Molecules of absorbed $N_2 = 1.0 \times 10^{-7} \times 6.023 \times 10^{23} = 6.023 \times 10^{16}$

Total surface sites available = Number of sites per cm^2 × Area = $6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$

Surface sites on which N_2 is absorbed = 20% × Available sites $= \frac{20}{100} \times 6.023 \times 10^{17} = 12.046 \times 10^{16}$

$\therefore$ Number of sites absorbed per molecule of N_2

$= \frac{12.046 \times 10^{16}}{6.023 \times 10^{16}} = 2$



CHAPTER 4

Chemical Kinetics

INTRODUCTION TO CHEMICAL KINETICS



Kinetics is the study of the rates of chemical processes in an effort to understand what it is that influences these rates and to develop theories which can be used to predict them. A knowledge of reaction rates has many practical applications, for example, in designing an industrial process, in understanding the complex dynamics of the atmosphere and in understanding the intricate interplay of the chemical reactions that are the basis of life. At a more fundamental level we want to understand what happens to the molecules in a chemical reaction—that is, what happens in a single reactive encounter between two reagent molecules. By understanding this we may be able to develop theories that can be used to predict the outcome and rate of reactions.

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions (for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others. In consecutive reactions, the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts. Chemical kinetics is the branch of chemistry which addresses the question: "how fast do reactions go?" Chemistry can be thought of, at the simplest level, as the science that concerns itself with making new substances from other substances. Or, one could say, chemistry is taking molecules apart and putting the atoms and fragments back together to form new molecules. (OK, so once in a while one uses atoms or gets atoms, but that doesn't change the argument.) All of this is to say that chemical reactions are the core of chemistry.

If Chemistry is making new substances out of old substances (i.e., chemical reactions), then there are two basic questions that must be answered:

1. Does the reaction want to go? This is the subject of chemical thermodynamics.
2. If the reaction wants to go, how fast will it go? This is the subject of chemical kinetics.

Here are some examples. Consider the reaction,

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l).$$

We can calculate $\Delta_r G^\circ$ for this reaction from tables of free energies of formation (actually this one is just twice the free energy of formation of liquid water). We find that $\Delta_r G^\circ$ for this reaction is very large and negative, which means that the reaction wants to go very strongly. A more scientific way to say this would be to say that the equilibrium constant for this reaction is very very large.

However, we can mix hydrogen gas and oxygen gas together in a bulb or other container, even in their correct stoichiometric proportions, and they will stay there for centuries, perhaps even forever, without reacting. (If we drop in a catalyst-say a tiny piece of platinum-or introduce a spark, or even illuminate the mixture with sufficiently high frequency uv light, or compress and heat the mixture, the mixture will explode.) The problem is not that the reactants do not want to form the products, they do, but they cannot find a "pathway" to get from reactants to products.

Another example: consider the reaction,

$$C(\text{diamond}) \rightarrow C(\text{graphite}).$$

If you calculate $\Delta_r G^\circ$ for this reaction from data in the tables of thermodynamic properties you will find once again that it is negative (not very large, but still negative). This result tells us that diamonds are thermodynamically unstable. Yet diamonds are highly regarded as gem stones ("diamonds are forever") and are considered by some financial advisors as a good long-term investment hedge against inflation. On the other hand, if you were to vaporize a diamond in a furnace, under an inert atmosphere, and then condense the vapor, the carbon would come back as graphite and not as diamond.

How can all these things be?

The answer is that thermodynamics is not the whole story in chemistry. Not only do we have to know whether a reaction is thermodynamically favoured, we also have to know whether the reaction can or will proceed at a finite rate. The study of the rate of reactions is called chemical kinetics.

The study of chemical kinetics requires new definitions, new types of experimental data, and new theories and equations to organize the data. We begin with the definition of reaction rate present in the reaction.

Reaction Rates

Consider the reaction,

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g).$$

We can specify the rate of this reaction by telling the rate of change of the partial pressures of one the gases. However, it is convenient to convert these pressures into concentrations, so we will write our rates and rate equations in terms of concentrations, where square brackets, [ ], mean concentration in mol/L.

We might try to write the rate variously as,

$$\frac{d[NO_2]}{dt},$$

or as

$$-\frac{d[O_2]}{dt}$$

But these are not the same because each molecule of O_2 gives two molecules of NO_2. To arrive at an unambiguous definition of reaction rate, we define the "reaction veloci ," v, as

$$v = \frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[NO]}{dt}. \qquad (1)$$

This is unambiguous. The negative sign tells us that that species is being consumed and the fractions take care of the stoichiometry. Any one of the three derivatives can be used to define the rate of the reaction.

For a general reaction,

$$aA + bB \rightarrow cC + dD, \tag{2}$$

the reaction velocity can be written in a number of different but equivalent ways,

$$v = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}. \tag{3}$$

As in our previous example, the negative signs account for material that is being consumed in the reaction and the positive signs account for material that is being formed in the reaction. The stoichiometry is preserved by dividing the rate of change of concentration of each substance by its stoichiometric coefficient.

Rate of reaction is not uniform. It goes on decreasing from moment to moment due to decrease in the concentration(s) of reactant(s) with the progress of reaction i.e., with time as shown below by rate vs time curve. Thus, the rate defined above is actually the average rate of reaction during the time interval considered.

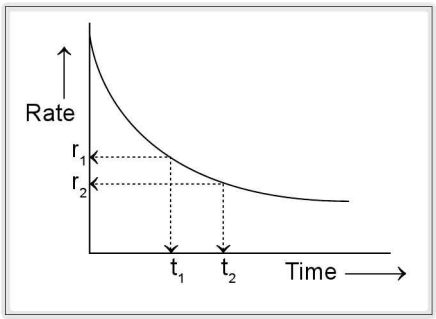


Fig. 4.1

The rate of reaction at any time t also called instantaneous rate is as defined belo .

$$r_{inst} = \mp\frac{dc}{dt}$$

Where dc is the infinitesimal change in the concentration of the reactant or product during the infin - tesimal small time interval dt after time t i.e., between t and t + dt.

dt being infinitesimal small, the rate of reaction may be assumed to be constant (uniform) during this time interval.

$$\text{Unit of rate of reaction} = \frac{\text{Unit of concentration}}{\text{Unit of time}}$$

$$= \text{mole litre}^{-1}\text{time}^{-1}$$

The rate of reaction at any time t may be determined by plotting concentration (of reactant or product) vs time and drawing a tangent at the point P of the curve corresponding to time t at which rate is to be determined. The slope of the tangent gives rate of reaction at the required time.

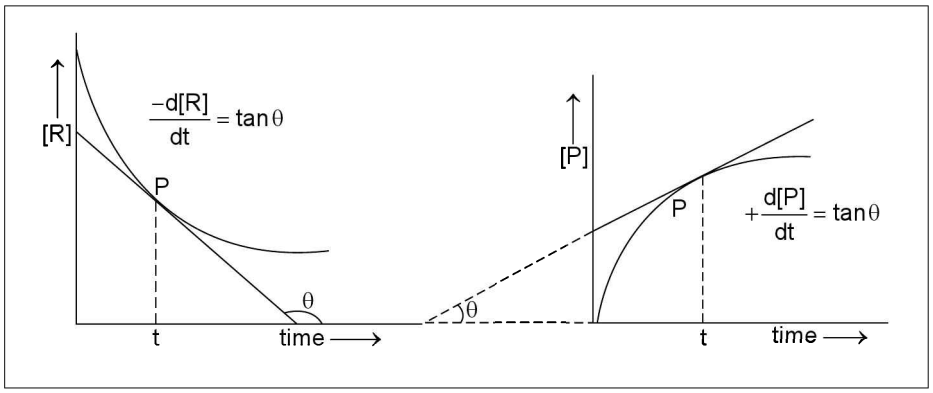


Fig. 4.2

([R] = concentration of reactant and [P] = concentration of product)

Rate at the time t = slope of tangent = tanθ

Worked-out Examples

1. Units of rate constant of first and zero order reactions in terms of molarity M are respectively: **[AIEEE-2002]**

(a) s^{-}, Ms^{-1} (b) s^{-}, M

(c) Ms^{-1}, s^{-1} (d) M, s^{-1}

Solution (a)

2. The differential rate law for the reaction: **[AIEEE-2002]**

$H_2 + I_2 \rightleftharpoons 2HI$ is:

(a) $\frac{-d[H_2]}{dt} = \frac{-d[I_2]}{dt} = \frac{-d[HI]}{dt}$ (b) $\frac{dH_2}{dt} = \frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

(c) $\frac{1}{2}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[I_2]}{dt} = \frac{-d[HI]}{dt}$ (d) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

Solution (d)

3. For a reaction $\frac{1}{2}A \rightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **[AIEEE-2008]**

(a) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$ (b) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$

(c) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$

Solution (b) The rates of reactions for the reaction,

$\frac{1}{2}A \rightarrow 2B$

can be written either as,

$$-2\frac{d}{dt}[A] \text{ with respect to 'A'}$$

or $\frac{1}{2}\frac{d}{dt}[B]$ with respect to 'B'

From the above, we have,

$$-2\frac{d}{dt}[A] = \frac{1}{2}\frac{d}{dt}[B]$$

or $$-\frac{d}{dt}[A] = \frac{1}{4}\frac{d}{dt}[B]$$

4. Consider the chemical reaction, $N_2(g) + 3H_2,(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions. **(2002S)**

(a) Rate $= -d[N_2]/dt = -1/3d[H_2]/dt = 1/2\ d[NH_3]/dt$

(b) Rate $= -d[N_2]/dt = -3d[H_2]/dt = 2d\ [NH_3]/dt$

(c) Rate $= -d[N_2]/dt = 1/3d[H_2]/dt = 1/2d\ [NH_3]/dt$

(d) Rate $= -d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

Solution (a) Individual rates become equal when each of these is divided by their respective stoichiometric coefficient. Further the rate of the consumption of the reactant goes on decreasing and the rate of formation of the product goes on increasing with time hence –ve and +ve sign, respectively.

5. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, **[1994-Marks]**
under certain conditions of temperature and partial pressure of the reactants, the rate of for of NH_3 is 0.001 kg h^{-1}. The rate of conversion of H_2 under the same condition is.....kg

Solution 1.765×10^{-3}kg/h;

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Here, Rate of reaction $= \frac{1}{3}$ [Rate of disappearance of H_2] $= \frac{1}{2}$ [Rate of appearance of NH_3]

or $$\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

$$\Rightarrow \frac{d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt}$$

$$\frac{d[NH_3]}{dt} = 0.01\,kg/h = \frac{0.001}{17} \times 1000 = \frac{1}{17}mole/h$$

$$\therefore \quad \frac{d[H_2]}{dt} = \frac{1}{17} \times \frac{3}{2} = \frac{3}{34}mole/h = \frac{3}{34} \times \frac{2}{2000}kg/h = 1.765 \times 10^{-3}kg/h.$$

Factors affecting the reaction rate

The rate of any particular reaction depends upon the following factors:

1. **Temperature**
   The most well known method of making reactions go faster is to heat the reactants. Heat increases the average speed of molecules. This has two results. First, the greater their energy, the more likely it is that bonds will brack, thereby allowing new ones to be made. We can put this in a different way by saying that:
   The higher the temperature, the greater is the chance of the reactants having an energy greater than the activation energy of the reaction.
   Secondly, the greater their speed, the more likely the particles are to collide, and so the greater the chance of reaction. However, it is possible for reactants to have too much energy.
2. **Concentration**
   If we do not wish to increase the temperature of a reaction mixture, there is another way of speeding things up. We can increase the chance of collision by increasing the number of particles in the mixture. That is, we can increase the concentration of the reactants. Again, the world of atoms and molecules has some surprises for us. Some reactions do not go faster if we increase concentrations.
3. **Surface area**
   There is a convenient way of speeding up reactions that involve solids. All that is necessary is to use a powder rather than large lumps of the solid. For example, marble chips react with hydrochloric acid giving off carbon dioxide. The hydrogen ions in the acid attack the carbonate ions at the surface of the chips. By grinding the chips to a powder, the surface area in contact with the acid is greatly increased. The more the surface area, the greater the chance of the hydrogen ions attacking the carbonate ions; hence, the rate of reaction increases.
4. **Catalysts**
   In industry, time means money, and the speed with which reactions take place is of great importance. For example, if one company can make a drug faster than another, that company has a greater chance of making a profit on its sales. If success could be achieved simply by heating or increasing concentrations, then every company would be equally successful. Clearly, life is not so simple, one reason being that too much heat can destroy the substance that is being made. A more subtle approach is to find a catalyst for a reaction
   An ideal catalyst will increase the speed of a reaction without itself being destroyed during the reaction.
   In fact the majority of catalysts are not ideal. Eventually they lose their ability to catalyse a reaction
5. Presence of light: Some reactions do not take place in the dark but take place in the presence of light. Example $H_2 + Cl_2 \longrightarrow 2HCl$. Such reactions are called "photochemical reactions".

Order and Molecularity of Reaction

Single step reaction is called elementary reaction while a reaction occurring in two or more steps is called complicated or consecutive reaction. Each step of a complicated reaction is an elementary reaction.

The minimum number of molecules, atoms or ions of reactants required for an elementary reaction to occur is indicated by the sum of the lowest integer values of stoichiometric coefficients of the every reactant(s) in the chemical equation, is known molecularity of the reaction. Thus, for an elementary reaction represented by the general chemical equation.

$$aA + bB \longrightarrow \text{products}$$

molecularity = a + b

Examples,	Reactions	Molecularity
	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ ……	1…… correct
	$H_2 + I_2 \rightleftharpoons 2HI$----------	2 …… correct

$2H_2 + 2I_2 \rightleftharpoons 4HI$---------- 4 ……. **incorrect**

$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$---------- 1---------- **incorrect**

According to kinetic theory, molecularity is the number of molecules colliding simultaneously in one step of a chemical reaction.Since it is very less probable that more than three molecules collide simultaneously in one step, molecularity rarely exceeds three.

A complicated reaction has no molecularity of its own but molecularity of each of the steps involved in its mechanism.

For example, the reaction: $2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$, takes place in the sequence of following three steps:

I. $NO + NO \rightleftharpoons N_2O_2$ (fast and reversible)
II. $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)
III. $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The molecularity of each step involved in mechanism is 2 i.e., each step is bimolecular. So as regards the molecularity of the reaction under consideration we simply say that the reaction has mechanism and each step involved in it is bimolecular.

However, there is another view also-according to which molecularity of a complicated reaction is taken to be equal to the number of molecules, atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step i.e., the rate-determining step of the reaction.

For example, the reaction $ROH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$, which actually is a nucleophilic substitution reaction.

I. $R\ddot{O}H + H^+ \rightleftharpoons R\overset{\oplus}{\ddot{O}}H_2$ (fast)

II. $R - \overset{\ddot{}}{O}H_2 \rightleftharpoons R^+ + H_2\ddot{O}$ (slow)

III. $R^+ + :\ddot{C}l:^- \longrightarrow R - \ddot{C}l:$ (fast)

Here the step II is the slowest step and hence the r.d.s. the molecularity of which is one.

The **order of reaction** , in chemical kinetics, with respect to a certain reactant, is defined as the power to which its concentration term in the rate equation is raised

For example, given a chemical reaction $2A + B \rightarrow C$ with a rate equation

$$r = k[A]^2[B]^1$$

The reaction **order with respect to** A would be 2 and with respect to B would be 1, the **total reaction order** would be 2+1=3. It is not necessary that the order of a reaction be a whole number-zero and fractional values of order are possible-but they tend to be integers. Reaction orders can be determined only by experiment. Their knowledge allows conclusions about the reaction mechanism.

The reaction order is *not necessarily* related to the stoichiometry of the reaction, unless the reaction is elementary. Complex reactions may or may not have reaction orders equal to their stoichiometric coefficients.

For example:

- The alkaline hydrolysis of ethyl acetate is a complex reaction:
- $CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$.
- It has the following rate equation: $r = k[CH_3COOC_2H_5][OH]$
- The rate equation for imidazole catalysed hydrolysis is:
  $r = k$ [imidazole][$CH_3COOC_2H_5$] although no imidazole is present in the stoichiometric chemical equation.

- In the reaction of aryldiazonium ions with nucleophiles in aqueous solution $ArN_2^+ + X^- \rightarrow ArX + N_2$ the rate equation is,

$$r = k[ArN_2^+]$$

Reactions can also have an undefined reaction order with respect to a reactant, for example one can not talk about reaction order in the rate equation found when dealing with a bimolecular reaction between adsorbed molecules:

$$r = k\frac{K_1K_2C_AC_B}{(1+K_1C_A+K_2C_B)^2}.$$

If the concentration of one of the reactants remains constant (because it is a catalyst or it is in great excess with respect to the other reactants) its concentration can be included in the rate constant, obtaining a **pseudo constant**: if B is the reactant whose concentration is constant then $r = k[A][B] = k'[A]$. The second order rate equation has been reduced to a **pseudo first order** rate equation. This makes the treatment to obtain an integrated rate equation much easier.

Zero-order reactions are often seen for thermal chemical decompositions where the reaction rate is independent of the concentration of the reactant (changing the concentration has no effect on the speed of the reaction):

In **broken-order reactions,** the order is a non-integer typical of reactions with a complex reaction mechanism. For example the chemical decomposition of ethanal into methane and carbon monoxide proceeds with an order of 1.5 with respect to ethanal. The decomposition of phosgene to carbon monoxide and chlorine has order 1 with respect to phosgene itself and order 0.5 with respect to chlorine.

In a **mixed-order reaction,** the order of a reaction changes in the course of a reaction as a result of changing variables such as pH. An example is the oxidation of an alcohol to a ketone by a ruthenate (RuO_4^{2-}) and a hexacyanoferrate, the latter serving as the sacrificial catalyst converting Ru(IV) back to Ru(VI) [3]: the disappearing-rate of the ferrate is zero-order with respect to the ferrate at the onset of the reaction (when its concentration is high and the ruthenium catalyst is quickly regenerated) but changes to first-order when its concentration decreases

Negative order reactions are rare, for example, the conversion of ozone (order 2) to oxygen (order 1).

The mathematical equation showing the relation of rate of reaction with concentration of reactant(s) is called rate-law of the reaction. For example, the kinetic experiment carried on the reaction.

$$2NO + 2H_2(g) \longrightarrow N_2(g) + 2H_2O\ (g)$$

has shown that (i) rate increases 4-fold when concentration of NO is doubled keeping the conc. of H_2 constant (ii) rate gets just doubled when conc. of H_2 is doubled keeping that of NO constant, and (iii) rate increases 8-fold when concentrations of both NO and H_2 are doubled simultaneously. These experimental rate data fit into following equation.

$$\text{Rate } \alpha\ [NO]^2[H_2]$$

This equation is called experimentally observed "Rate law" of the reaction.

Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law. Thus for the reaction (reduction of nitric oxide by hydrogen) considered above.

Order w.r.t. NO = 2

Order w.r.t. H_2 = 1

Overall order = 2+ 1 = 3

In general, let a reaction represented by the chemical equation:

$$aA + bB \longrightarrow \text{Products}$$

Obeys the following rate law.

$$\text{Rate } \alpha\ [A]^m\ [B]^n, \text{ or Rate } = k[A]^m\ [B]^n$$

Where k = rate constant of reaction, a constant at constant temp and is actually the rate of reaction when concentration of each reactant is equal to unity k is also called velocity coefficient or specific reaction rate.

Note that m and n are experimental quantities which may or may not be equal to the respective stoichiometric coefficients

Also note that if either of A or B is taken in large excess as compared to another, the order w.r.t this reactant will be zero so order = m (when B is in large excess), and order = n (when A is large excess), i.e.,

Rate = $k'[A]^m$, $k' = k[B]^n$ another constant, when B is in large excess.

Order w.r.t. A = m

Order w.r.t. B = 0

Rate = $k''[B]^n$, $k'' = k[A]^m$ = another constant, when A is in large excess.

Order w.r.t. A = 0

Order w.r.t. B = n

k′ or k″ is actually known as pseudo rate constant.

Thus, a bimolecular reaction conforms to the first-order when one of the reactants is taken in large excess and the reaction is said to be pseudo unimolecular or pseudo first order. An example of this is the hydrolysis of ester by acid i.e.,

$$CH_3COOC_2H_5 + H_3O^+ \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

The reaction is originally of second-order obeying the kinetics.

$$\text{Rate} = k\ [CH_3COOC_2H_5]\ [H_2O]$$

But the reaction is usually carried out taking dilute aqueous solution of ester and acid (HCl) such that in the reaction mixture water exists in large excess as compared to ester or better to say, water has almost its maximum concentration of 55.5 mole L^{-1}. So there is no appreciable change in the concentration of water and the same remains practically constant. $k[H_2O]$ becomes another constant (k′) called pseudo rate constant and reactions obeys the following 1st order kinetics.

$$\text{Rate} = k'\ [CH_3COOC_2H_5]$$

Thus, the molecularity of the above reaction is ‘two’ but its order is ‘one;.

In the light of the above concept, one may define order of reaction as “ the number of molecules of the reactant(s) whose concentration alters during the chemical change is the order of reaction”.

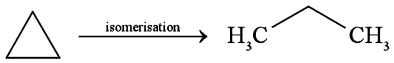
Distinction between molecularity and order

(i) Molecularity is a theoretical property while order is an experimental property.

(ii) Molecularity concerns to mechanism, order concerns to kinetics.

(iii) Molecularity is always a whole number and never zero while order may be any number zero, fractional and integral.

(iv) Molecularity is invariant but order may vary with change in experimental condition. As for example, the isomerisation of cyclo-propane represented by the chemical equation given below is a first order reaction at high cyclo-propane pressure and is a second order reaction at low cyclo-propane pressure.



(v) Reactions of higher molecularity is rare since the chance of coming into contact and colliding simultaneously decreases as the number of molecules involved in collision increases.

Unit of rate constant,

$nA \longrightarrow$ Product

$$\frac{dx}{dt} = k[\text{conc.}]^n$$

$$\frac{[\text{conc.}]}{\text{sec}} = k[\text{conc.}]^n$$

$$\mathbf{k = [conc.]^{1-n} sec^{-1}}$$

$$= [\text{mole/litre}]\text{sec}^{-1}$$



Worked-out Examples

6. For a reaction $A + 2B \longrightarrow C$, rate is given by $R = K[A][B]^2$. The order of reaction is: **[AIEEE-2002]**

(a) 3 (b) 6

(c) 5 (d) 7

Solution (a)

7. The rate law of a reaction, $A + B \longrightarrow$ Product is rate $= K[A]^n[B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of new rate to the earlier rate of reaction will be: **[AIEEE-2003]**

(a) $n - m$ (b) 2^{n-m}

(c) $\frac{1}{2^{m+n}}$ (d) $m + n$

Solution (b) $r_0 = K[A]^n[B]^m$

$r_1 = K[2A]^n[B/2]^m$

$r_1 = K2^{n-m}[A]^n[B]^m$ or $r_1 = r \times 2^{n-m}$

8. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr;

Step I $NO_{(g)} + Br_{2(g)} \overset{\text{fast}}{\rightleftharpoons} NOBr_{2(g)}$

Step II $NOBr_{2(g)} + NO_{(g)} \xrightarrow{\text{slow}} 2NOBr_{(g)}$

If the second step is the rate determining step, the order of the reaction with respect to $NO_{(g)}$ is: **[AIEEE-2006]**

(a) 1 (b) 0

(c) 3 (d) 2

Solution (d) $r = K'[NOBr_2][NO]$ ... (i)

$$K_c = \frac{[NOBr_2]}{[NO][Br_2]}$$

By eq. (i) and (ii)

$$r = K'K_c.[NO][Br_2][NO] = K'[NO]^2[Br_2]$$

Thus, order with respect to NO is 2.

9. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]$; $k_1 = 6.8 \times 10^{-3}$

$[Ag(NH)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.6 \times 10^{-3}$

then the formation constant of $[Ag(NH_3)_2]^+$ is **[IIT-2006]**

(a) 6.8×10^{-6} (b) 1.08×10^{-5}

(c) 1.08×10^{-6} (d) 6.8×10^{-5}

Solution (b) The required reaction is

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ ; K = ?$$

$$K_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]}; K_2 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]}$$

$\Rightarrow K = K_1 \times K_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 1.08 \times 10^{-5}$.

10. Consider a reaction aG + bH $\rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is **[IIT-2007]**

(a) 0 (b) 1

(c) 2 (d) 3

Solution (d)

Exp. Number	*[G] mole litre^{-1}*	*[H] mole litre^{-1}*	*Rate (mole litre$^-$ time^{-1})*
1	a	b	r
2	2a	2b	8r
3	2a	b	2r

Applying $r = k [G]^x[H]^y$

$x = 1, y = 2$

$\therefore$ overall order is 3.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

A **rate law** is a mathematical equation that describes the progress of the reaction. In general, rate laws must be determined experimentally. Unless a reaction is an elementary reaction, it is not possible to predict the rate law from the overall chemical equation. There are two forms of a rate law for chemical kinetics: the **differential rate law** and the **integrated rate law**.

The differential rate law relates the rate of reaction to the concentrations of the various species in the system.

Differential rate laws can take on many different forms, especially for complicated chemical reactions. However, most chemical reactions obey one of three differential rate laws. Each rate law contains a constant, k, called the **rate constant**. The units for the rate constant depend upon the rate law, because the rate always has units of mole L^{-1} sec^{-1} and the concentration always has units of mole L^{-1}.

As already mentioned in the reaction:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

Obeys the following third order kinetics

$$\text{Rate } \alpha\ [NO]^2\ [H_2]$$

The kinetics is not in tune with chemical equation. As the law of mass action suggests each concentration term should be raised to power 2. Neither experimental facts nor those coming from Law of mass action can be unacceptable to us. Under this condition, we are led to believe that the reaction does not occur according to the chemical equation as written. That is the reaction is not elementary but is complicated. In order to explain the observed rate law following mechanism has been proposed.

I $NO + NO \rightleftharpoons N_2O_2$ (fast and reversible)

II $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)

III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The step II being the slowest i.e., the rate-determining step (r.d.s.). Note that the rate of formation of N_2 cannot be faster than the rate of formation of N_2O. So, the rate of overall reaction or rate of formation of N_2 will be equal to the rate of step II which according to law of mass action may be given as.

Rate of overall reaction = Rate of step II = $k[N_2O_2]\,[H_2]$

Where k = rate constant of step II

The concentration of the intermediate (N_2O_2) may be evaluated by applying law of mass action upon the equilibrium existing in step I as mentioned below.

$$K_c = \frac{[N_2O_2]}{[NO]^2} \text{ or } [N_2O_2] = K_c\,[NO]^2$$

Putting this in the rate expression, we get

$$\text{Rate} = k.k_c[NO]^2[H_2] = k_{obs}\,[NO]^2[H_2]$$

Where $k_{obs} = k.k_c$ = observed rate constant of the reaction

$$\text{Rate } \alpha\ [NO]^2\,[H_2]$$

This is the same rate-law as observed experimentally.



Worked-out Examples

11. The possible mechanism for the reaction

$$2\,NO + Br_2 \longrightarrow 2\,NOBr$$

is $NO + Br_2 \longrightarrow NOBr_2$ (fast);

$NOBr_2 + NO \longrightarrow 2\,NOBr$ (slow).

Establish the rate law.

Solution As the slowest step is the rate determining step, therefore the rate law is

$$R = k[NOBr_2]\,[NO]$$

Now, since $NOBr_2$ is an intermediate its concentration can be calculated from step 1 as follows:

$$K = \frac{[NOBr_2]}{[NO][Br_2]}\ [K = \text{eq. constant}]$$

or $[NOBr_2] = K\,[NO]\,[Br_2]$

Substituting this value in above equation,

$$r = k.\,K[NO]^2[Br_2]$$

or rate = k' $[NO]^2 [Br_2]$ [$\because$ k · K = constant k']

$\therefore$ Rate = k' $[NO]^2 [Br_2]$

Note that the rate of the slowest step can be taken as the rate of the over all reaction but rate constant of the slowest step imay not be the rate constant of the over all reaction.

12. The rate equation for the reaction; $2A + B \longrightarrow C$ is rate = K[A] [B]. The correct statement about this is: **[AIEEE-2004]**

(a) K is independent of [A] and [B]

(b) $t_{1/2}$ is constant

(c) Unit of a: is sec^{-1}

(d) Rate of formation of C is twice the rate of disappearance of A

Solution (a) Rate constant 'K' is characteristic constant for a given reaction.

13. A reaction involving two different reactants can never be: **[AIEEE-2005]**

(a) Unimolecular reaction (b) I order reaction

(c) II order reaction (d) Bi-molecular reaction

Solution (a)

14. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept as same, the rate of reaction will: **[AIEEE-2006]**

(a) Remain unchanged (b) Be tripled

(c) Increase by a factor four (d) Be doubled

Solution (c) $r_1 = K[CO]^2$ $r_2 = K[2CO]^2$ $\therefore \frac{r_2}{r_1} = 4$

15. The rate law for the reaction:

RCl + NaOH (aq.) → ROH + NaCl is given by, Rate = k, [RCl]. The rate of the reaction will be

(a) doubled on doubling the concentration of sodium hydroxide.

(b) halved on reducing the concentration of alkyl halide to one half.

(c) increased on increasing the temperature of the reaction.

(d) unaffected by increasing the temperature of the reaction.

Solution (b, c) As rate = k [RCl], on decreasing the concentration of RCl to half, the rate will also be halved. Rate will also increase with temperature.

A. Zero order reaction:

A reaction is said to be of zero order if the rate of reaction is independent of concentration of the reactant.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

Rate Expression:

Let $A \longrightarrow$ Product

[K is a constant called Rate Constant]

$dx = Kdt$

On integration,

$x = Kt + C$ [where C is the integration constant]

when, $t = 0,\ x = 0$

$\Rightarrow \quad C = 0$

$\therefore \quad x = Kt$

Characteristics:

(a) Unit of K = mol L^{-1} $time^{-1}$

(b) Half life period: Time required for the completion of half of the reaction.
Half life for zero order reaction is directly proportional to initial concentration of the reactant

(c) The concentration of reactant decreases linearly with time.

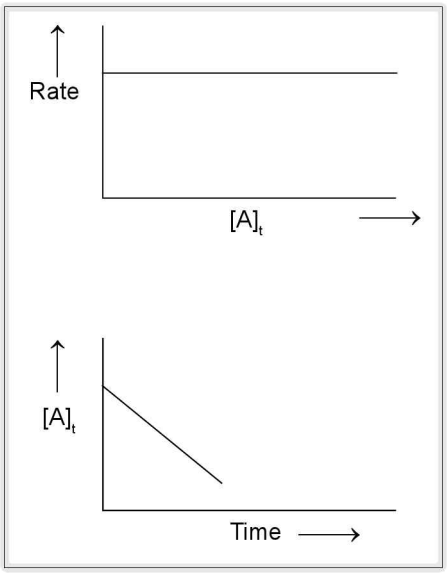


Fig. 4.3

B. First Order Reaction:

A first order reaction is one whose rate is determined by the variation of one concentration term onl .
All radioactive disintegration reactions are of the first orde .

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

Rate Expression

Let	A	⟶	Product
initially	a		0
after time t,	a–x		x

On integration,

$$-\ln (a-x) = Kt + C \text{ [where, C is the integration constant]}$$

When, $t = 0,\ \times = 0$

$\Rightarrow \quad C = -\ln a$

$\therefore \quad -\ln (a - x) + \ln a = Kt$

$$\ln \frac{a}{a-x} = kt$$

$$k = \frac{1}{t}\ln\frac{a}{a-x}$$

$$\boxed{K = \frac{1}{t}2.303\log\frac{a}{a-x}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

Where, $\frac{x}{a}$ = f=extent of reaction

$$t_f = \frac{2.303}{k_1}\log\frac{1}{(1-f)} = -\frac{2.303}{k_1}\log(1-f) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The above equation is very useful to find a direct relation between extent of completion of reaction and time. For example , when a reaction is 75% completed ;we write f = 0.75

Further, putting $a = [A]_0$ and $(a - x) = [A]$ in eqn. (1), we get,

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$kt = \ln\frac{[A]_0}{[A]}$$

Which can be written in the exponential form as,

$$\frac{[A]_0}{[A]} = e^{kt} \text{ or } \frac{[A]}{[A]_0} = e^{-kt}$$

or $[A] = [A]_0 e^{-kt}$



Worked-out Examples

16. It was found that a cane sugar solution in water was hydrolysed to the extent of 25 per cent in one hour. Calculate the time that will be taken for the sugar to be hydrolyzed to the extent of 50%, assuming that the reaction is of the first order.

Solution

$$t_f = \frac{2.303}{k_1}\log\frac{1}{(1-f)} = -\frac{2.303}{k_1}\log(1-f) \qquad \ldots (1)$$

Putting, f = 0.25 at $t_{0.25}$ = 1 hour from the data

$$t_{0.25} = 1\text{ hr} = \frac{2.303}{k_1}\log(1-0.25) = \frac{2.303}{k_1}\log\frac{4}{3} \qquad \ldots (2)$$

Similarly, $t_{0.5} = -\frac{2.303}{k_1}\log(1-0.5) = \frac{2.303}{k}\log 2$ ... (3)

Dividing (iii) by (ii) $\frac{t_{0.5}}{1\text{hr}} = \frac{\log 2}{\log 4} = \frac{\log 2}{2\log 2} = \frac{1}{2}$

Hence, time required for 50% hydrolysis = $\frac{1}{2}$ hr or 30 minutes

17. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2(s) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate

(a) time taken for NH_2NO_2 to decompose 99% and

(b) volume of dry N_2O produced at this point measured at STP.

Solution For a first-order reaction, rate constant expression is $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$

Initial moles of nitramide $= \frac{6.2}{62} = 0.1$

$$\therefore \quad t = \frac{2.303 \times 2.1}{0.693}\log\frac{0.1}{0.001} = 13.95 \text{ hours}$$

Since, the decomposition is 99%, so 99% of the initial moles of NH_2NO_2 would be converted to N_2O.

$$\text{Moles of } N_2O = \frac{0.1 \times 99}{100}$$

$$\therefore \quad \text{Volume of } N_2O \text{ at STP} = \frac{0.1 \times 99 \times 22.4}{100} = 2.217 \text{ litre}.$$

Some important characteristics of first order reactions

(a) **Substitution method:** Starting with a known concentration 'a' or $[A]_0$, the concentration of the reactant (a – x) or [A] at different intervals of time may be noted. For every value of t, the corresponding value of (a – x) i.e., [A] may be substituted in equation,

$$\boxed{K = \frac{1}{t}2.303\log\frac{a}{a-x}}$$

If the values of k thus obtained are nearly constant (within the experimental error), the reaction is of the first orde .

(b) **Graphical method:** Equation $[A] = [A]_0 e^{-kt}$ may be written as,

$$\frac{k}{2.303}t = \log\frac{[A]_0}{[A]} = \log[A]_0 - \log[A]$$

$$\text{or} \quad \log[A] = -\frac{k}{2.303}t + \log[A]_0$$

This is the equation of a straight line (y = mx + c). Thus if log [A] or log (a – x) values are plotted against time `t', the graph obtained should be a straight line if the reaction is of the first order.

The intercept made on the y-axis would be `log $[A]_0$' and the slope of the line would be equal to $\left(-\frac{k}{2.303}\right)$

$$\text{i.e., slope} = -\frac{k}{2.303}$$

From this, the value of k can be calculated.

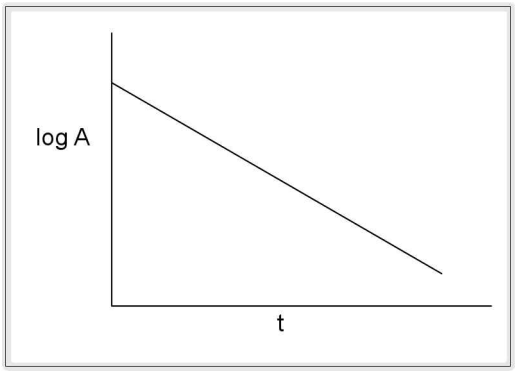


Fig. 4.4

(ii) **Half-life Period:** The time taken for any fraction of the reaction to be completed is independent of the initial concentration. For example, let us test the truth of this statement for half of the reaction to be completed. From equation,

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

When half of the reaction is completed, × = a/2. Representing the time taken for half of the reaction to be completed by $t_{1/2}$ equation becomes,

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{k} \log 2 = \frac{0.693}{k}$$

i.e., $t_{1/2} = \frac{0.693}{k}$

Thus, 'a' does not appear in this equation so that $t_{1/2}$ is independent of a. Similarly, it can be seen that $t_{1/2}$, $t_{2/3}$ etc., will also be independent of the initial concentration.

The time taken for half of the reaction to be completed i.e., the time in which the concentration of a reactant is reduced to half of its original value is called Half-life period of the reaction.

The above result can also be used to test a reaction of the first order. The method is called fractional life method.

(iii) The units of k are independent of the units in which the concentrations are expressed. This is obvious from equation,

$$\boxed{K = \frac{1}{t} 2.303 \log \frac{a}{a - x}}$$

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 units of k, therefore, depend only upon the units of time 't'. Depending upon whether t is expressed in second, minutes or hours, k would be in sec^{-1}, min^{-1} or hr^{-1} respectively.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry



Worked-out Examples

18. In a first order reaction, the concentration of the reactant decreases from 0.8 M to 0.4 M in 15 minute. The time taken for the concentration to change from 0.1 M to 0.025 M is: **[AIEEE-2004]**

(a) 60 minute (b) 15 minute

(c) 7.5 minute (d) 30 minute

Solution (d) $t_{1/2} = 15$ minute

$$\therefore \quad t = \frac{2.303 \times 15}{0.693} \log \frac{0.1}{0.025} = 30 \text{ minute}$$

19. $t_{1/4}$ can be taken as the time taken for concentration of reactant to drop to 3/4 of its initial value. If the rate constant for a first order reaction is K, then $t_{1/4}$ can be written as: **[AIEEE-2005]**

(a) 0.10/K (b) 0.29/K

(c) 0.69/K (d) 0.75/K

Solution (b) $K = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t_{1/4}} \log \frac{a}{\frac{3a}{4}} = \frac{2.303}{t_{1/4}} \log \frac{4}{3}$

$$K = \frac{2.303 \times 0.125}{t_{1/4}} = \frac{0.29}{t_{1/4}}$$

20. Consider the reaction, $2A + B \longrightarrow$ Products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is: **[AIEEE-2007]**

(a) L mol^{-1} s^{-1} (b) No unit

(c) mol L^{-1} s^{-1} (d) s^{-1}

Solution (a) For a first order reaction $t_{\frac{1}{2}} = \frac{0.693}{K}$ i.e., for a first reaction $t_{\frac{1}{2}}$ does not depend up on the concentration. From the given data, we can say that order of reaction with respect to B = 1 because change in concentration of B does not change half life. Order of reaction with respect to A =1 because rate of reaction doubles when concentration of B is doubled keeping concentration of A constant.

$\therefore$ Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol^{-1} sec^{-1}.

21. The hydrolysis of ethyl acetate in ..... medium is a..... order reaction. **[IITJEE-1986]**

Solution acidic, first (or basic, second).

22. For a first order reaction, the rate of the reaction doubles as the concentration of the reaction doubles. **[IITJEE-1986]**

Solution True: The rate of reaction of first order is directly proportional to the concentration of reacting substance.

23. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 2×10^4 sec. The rate constant of reaction in sec^{-1} is **[IITJEE-2003]**

(a) 2×10^4 (b) 3.45×10^5 (c) 1.386×10^{-4} (d) 2×10^{-4}

Solution (c) $K = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{2 \times 10^4} \log \frac{800}{50} = 1.386 \times 10^{-4} s^{-1}$

24. The reaction, × → Product, follows first order kinetics. In 40 minutes the concentration of changes from 0.1 to 0.025 M. The rate of reaction, when concentration of × is 0.01 M is

[IITJEE-2004]

(a) 1.73×10^{-4} M min^{-1}
(b) 3.47×10^{-5} M min^{-1}
(c) 3.47×10^{-4} M min^{-1}
(d) 1.73×10^{-5} M min^{-1}

Solution

(c) Since 0.1 M of × changes to 0.025 M in 40 minutes, $t_{1/2}$ of reaction = 40/2 = 20 minutes

Rate of reaction of x = $k[X] = 0.693/t_{1/2} \times [X] = 0.693/20 \times 0.01 = 3.47 \times 10^{-4}$ M min^{-1}

25. Which one of the following statement for order of reaction is not correct?

[IITJEE-2005]

(a) Order can be determined experimentally
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
(c) It is not affected with the stoichiometric coefficient of the reactants.
(d) Order cannot be fractional.

Solution

(d) Order of a reaction can be fractional. All other statements are true.

26. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is

(a) 0.5 mol^{-1} dm^3 (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1} dm^{-3}

Solution **[IIT-2008]**

(a) $[A]_i = 1.38$ L mol/L $\xrightarrow{\text{first order}} \frac{1.38}{2}$ in 40 sec.

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}$$

for zero order

$$t_{1/2} = 20 \text{ sec} = \frac{[A]_o}{2k_o}$$

$$k_0 = \frac{a}{2t_{1/2}} = \frac{1.38}{2 \times 20}$$

$$\Rightarrow \quad \frac{k_1}{k_0} = \frac{\frac{0.693}{40}}{\frac{1.386}{40}} = \frac{0.693}{1.38} = 0.502_{\text{mol}^{-1}\text{ dm}^3}$$

27. The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301): **[AIEEE-2009]**

(a) 230.3 minutes (b) 23.03 minutes

(c) 46.06 minutes (d) 460.6 minutes

Solution (c)

$$\because \lambda = \frac{0.6932}{t_{1/2}} = \frac{0.6932}{6.93}\text{min}^{-1}$$

$$\text{Also } t = \frac{2.303}{\lambda}\log\frac{[A_o]}{[A]}$$

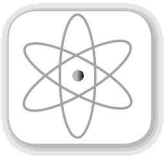
$[A_o]$ = initial concentration (amount)

$[A]$ = final concentration (amount

$$\because t = \frac{2.303 \times 6.93}{0.6932}\log\frac{100}{1}$$

$$= 46.06 \text{ minutes}$$

SOME SIMPLE FIRST ORDER REACTIONS



As we have to generally deal with only first order reactions, we examine some of these reactions from the point of calculating the rate constant based on different experimental data. Now we present several problems in which we shall learn how to calculate the rate constant of reactions based on the variety of data given.



Worked-out Examples

28. We are given a first order reaction,

$A \rightarrow B+C$ where we assume that A, B and C are gases.The data given to us is

Time	0	t
Partial pressure of A	P_1	P_2

And we have to find the rate constant of the reaction.

Solution Since A is a gas and assuming it to be ideal, we can state that $P_A = [A]RT$ [From PV = nRT].

$\therefore$ At t = 0, $P_1 = [A]_o RT$ and at t = t, $P_2 = [A]_t RT$. Thus the ratio of the concentration of A at two different time intervals is equal to the ratio of its partial pressure at those same time intervals.

$$\therefore \frac{[A]_o}{[A]_t} = \frac{P_1}{P_2}$$

$$\therefore \quad k = \frac{1}{t}\ln\frac{P_1}{P_2}$$

29. Now we consider the same reaction with different set of data

$A \longrightarrow B + C$

Time	0	t
Total pressure of A +B+C	P_1	P_2

Find k.

Solution In this we are given total pressure of the system at these time intervals. The total pressure obviously includes the pressure of A, B and C. At t = 0, the system would only have A. Therefore the total pressure at t = 0 would be the initial pressure of A $\therefore$ P_1 is the initial pressure of A. At time t let us assume that same moles of A decomposed to give B and C because of which its pressure is reduced by an amount × while that of B and C is increased by × each. That is

Initial,	P_1	0	0
At time t,	$P_1 - x$	x	x

$\therefore$ Total pressure at time $t = P_1 + x = P_2 \quad \Rightarrow x = P_2 - P_1$

Now the pressure of A at time t would be $P_1 - x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

$$\therefore \quad \mathbf{k} = \frac{1}{t} \mathbf{ln} \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{P_1}{(2P_1 - P_2)}$$

30. In this case, we have

$A \longrightarrow B + C$

Time	t	∞
Total pressure of A+B+C	P_2	P_3

Find k.

Solution Here ∞ means that the reaction is complete. Now we have,

	A	$\longrightarrow$	B	+	C
At t = 0	P_1		0		0
At t = t	$(P_1 - x)$		x		x
At t = ∞	0		P_1		P_1

$\therefore \quad 2P_1 = P_3$

$$\Rightarrow \quad P_1 = \frac{P_3}{2}$$

At time t,

$$P_1 + x = P_2$$

$$\Rightarrow \quad \frac{P_3}{2} + x = P_2$$

$$\Rightarrow \quad x = P_2 - \frac{P_3}{2}$$

$$\Rightarrow \quad P_1 - x = \frac{P_3}{2} - \left(P_2 - \frac{P_3}{2}\right) = P_3 - P_2$$

$$\therefore \quad k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{P_3/2}{(P_3 - P_2)} = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$$

31. $A \longrightarrow B + C$

Time	T	∞
Total pressure of (B+C)	P_2	P_3

Find k.

Solution

	A	$\longrightarrow$	B	+	C
At	$t = 0$	P_1	0		0
At	$t = t$	$P_1 - x$	x		x
At	$t = \infty$	0	P_1		P_1

$\therefore \quad 2P_1 = P_3$

$\Rightarrow \quad P_1 = \dfrac{P_3}{2}$

$2x = P_2$

$\Rightarrow \quad x = \dfrac{P_2}{2}$

$\therefore \quad P_1 - x = \dfrac{P_3}{2} - \dfrac{P_2}{2} = \dfrac{P_3 - P_2}{2}$

$\therefore \quad k = \dfrac{1}{t}\ln\dfrac{[A]_0}{[A]_t} = \dfrac{1}{t}\ln\dfrac{P_3}{(P_3 - P_2)}$

32. Now let us assume that A, B and C are substances present in a solution. From a solution of A, a certain amount of the solution (small amount) is taken and titrated with a suitable reagent that reacts with A. The volume of the reagent used is V_1 at $t = 0$ and V_2 at $t = t$

Time	0	T
Volume of reagent	V_1	V_2

The reagent reacts only with A. Find k.

Solution It can be understood that the volume of the reagent consumed is directly proportional to the concentration of A. Therefore, the ratio of volume of the reagent consumed against A at $t = 0$ and $t = t$ is equal to $[A]_0/[A]_t$

$\therefore \quad k = k = \dfrac{1}{t}\ln\dfrac{[A]_0}{[A]_t} = \dfrac{1}{t}\ln\dfrac{V_1}{V_2}$

33. $A \longrightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

The reagent reacts with A,B and C. Find k.

Solution As we had seen in the previous case that the result of illustration 5 matches that of illustration of 1, we can use a similar logic for solving this one. That is,

	$A \longrightarrow$	B	+	C	
At $t = 0$	V_1	0		0	
At $t = t$		$V_1 - x$		x	x
At $t = \infty$	0	V_1		V_1	

where x is the volume of the reagent for those moles of A which have been converted into B and C

$$\therefore \quad V_1 + x = V_2 \qquad \Rightarrow x = V_2 - V_1 \qquad \Rightarrow V_1 - x = 2V_1 - V_2$$

$$\therefore \quad k\frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{V_1}{(2V_1 - V_2)}$$

This result looks perfectly ok. The problem is that this is true only if we make an assumption in the beginning of this problem (which you may have thought about). The assumption is that the 'n' factor of A,B and C with the reagent is same.

This can be made clear as follows. Let y moles of A be converted to B and C. If y moles of A require x ml of reagent and if the 'n' factor of A is n_1 with the reagent then the equivalents of A converted are n_1y and in x ml of reagent n_1y equivalents of the reagent are present. Now, since the same y moles of B and C are formed and we find the same volume of reagent used for B and C, it can be calculated that y moles of B and C also contain n_1y equivalents, each, which implies that 'n' factor of B and C are also 'n_1'.

34. $A \longrightarrow B+C$

Time	T	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A,B and C and have 'n' factors in the ratio of 1:2:3 with the reagent. Find k.

Solution

	$A \longrightarrow$	B	+	C
At $t = 0$	V_1	0		0
At $t = t$	$V_1 - x$	2 x		3x
At $t = \infty$	0	$2V_1$		$3V_1$

$$\therefore \quad 5V_1 = V_3$$

$$V_1 = V_3/5$$

$$V_1 + 4x = V_2$$

$$x = \frac{V_2 - V_1}{4}$$

$$\therefore \quad V_1 - x = \frac{V_3}{5} - \frac{V_2}{4} + \frac{V_3}{20} = \frac{5V_3 - 5V_2}{20}$$

$$\therefore \quad k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{V_3/5}{5V_3 - 5V_2/20}$$

$$\mathbf{k} = \frac{1}{t}\ln\frac{4V_3}{5(V_3 - V_2)}$$

35. $A \xrightarrow{D} B+C$

Time	0	t	∞
Volume of reagent	V_1	V_2	V_3

The reagent reacts with only B,C and D. Find k.

Solution $V_1 = V_D$

$V_2 = 2x + V_D$

$V_3 = 2V_A + V_D$

$$\therefore \quad \frac{V_3 - V_1}{2} = V_A$$

$$\frac{V_3 - V_2}{2} = V_A - x$$

$$\therefore \quad k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{(V_3 - V_1)}{(v_3 - V_2)}$$

36. $A \xrightarrow{D} B + C$

Time	0	t	∞
Volume of reagent	V_1	V_2	V_3

The reagent reacts with only C and D. Find k.

Solution $V_1 = V_D$

$V_2 = \times + V_D$

$V_3 = V_A + V_D$

$V_3 - V_1 = V_A$

$V_3 - V_2 = V_A - x$

$$\therefore \quad k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{(V_3 - V_1)}{(V_3 - V_2)}$$

37. Now we shall see how to find the rate constant of a reaction using a very different set of data. There are some organic compounds which have a property of rotating a plane polarized light in a particular direction by a particular value. The compounds are called optically active compounds. One reaction in which an optically active substance converts to some other optically active substance is, Sucrose $\xrightarrow{H^+}$ Glucose + Fructose

Sucrose, Glucose and Fructose are all optically active and while the first two compounds are dextro rotatory (rotating the plane polarised light in the right hand direction and the last is laevo rotatory (rotating the plane polarized light in the left hand direction). All the three compounds rotate the plane polarized light by different angles and their rotation is directly proportional to concentration.

Now the problem is S⟶ G + F and the data is,

Time	0	t
Rotation of sucrose	r_0	r_t

Find k.

Solution Let the rotation of Sucrose be $r_1°$ per mole and the initial moles of Sucrose be a.

$\therefore \quad r_0 = ar_1^o$

Let the moles of Sucrose that is converted to Glucose and Fructose be x.

$\therefore \quad r_t = (a-x)\ r_1^o \qquad \therefore \quad \dfrac{a}{a-x} = \dfrac{r_0}{r_t}$

$\therefore \quad \mathbf{k} = \dfrac{1}{t}\ln\dfrac{a}{a-x}\ln\dfrac{r_0}{r_t}$

38. $S \longrightarrow G + F$

Time	t	∞
Rotation of Glucose and Fructose	r_t	r_∞

Find k.

Solution Let the rotation of Glucose be r_2^0 and that of fructose be $-r_3^0$ (since it is laevo–rotatory) per mole.

$\therefore$

$S \longrightarrow$	G	+	F
At t = 0	a	0	0
At t = t	a– x	x	x
At t = ∞	0	a	a

$\therefore \quad r_t = \times\ (r_2^o - r_3^o)$

$r_\infty = a\ (r_2^o - r_3^o)$

$a = \dfrac{r_\infty}{r_2^o - r_3^o}, \times = \dfrac{r_t}{r_2^o - r_3^o} \quad \therefore a-x = \dfrac{r_\infty - r_t}{r_2^o - r_3^o}$

$\therefore \quad k = \dfrac{1}{t}\ln\dfrac{a}{a-x} - = \dfrac{1}{t}\ln\dfrac{r_\infty}{(r_\infty - r_t)}$

39. Now, let us assume that the first order reaction is $A \longrightarrow B+C$ and this solution is taken in a tube. We radiate this solution with a monochromatic light of wavelength λ and we will assume that this radiation is absorbed only by A. Let the intensity of incident light be I_0 and that of the transmitted light be I_t. $\log \dfrac{I_t}{I_o}$ is called transmittance and it is inversely proportional to the concentration of A.

That is $\log \dfrac{I_t}{I_o}$ = transmittance $\propto \dfrac{1}{[A]}$

The data given is,

Time	0	t
$\log I_t/I_0$	x	y

Find k.

Solution $x \propto \dfrac{1}{[A]_0}$ and $y \propto \dfrac{1}{[A]_t}$

$\therefore \quad k = \dfrac{1}{t}\ln\dfrac{[A]_0}{[A]_t} = \dfrac{1}{t}\ln\dfrac{y}{x}$

Examples of the reactions of first order

1. Decomposition of Nitrogen Pentoxide: The compound, 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, chloroform etc., according to the equation.

$$N_2O_5 \longrightarrow N_2O_4 \equiv 2NO_2 + \frac{1}{2}O_2$$
$$\Downarrow\Uparrow$$
$$2NO_2$$

When the reaction is carried out in the 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. It is obvious that,

Volume of oxygen gas collected at any time (V_t) left

$\propto$ Amount of N_2O_5 decomposed (x)

i.e.,

Volume of oxygen gas collected at infinite time (V_∞) (which is done by heating the reaction vessel) $\left.\begin{matrix} x \propto V_t \\ a \propto V_\infty \end{matrix}\right\} \propto$ Amount of N_2O_5 initially taken (a)

i.e., Substituting these values in the first order equation viz

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

We get $k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$

The constancy in the value of k proves the reaction to be of the first orde .



Worked-out Example

40. For decomposition of N_2O_5 in CCl_4 solution at 320 K

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

show that the reaction is of first order and also calculate the rate constant:

Time in minutes	10	15	20	25	∞
Volume of O_2 evolved (in ml)	6.30	8.95	11.40	13.50	34.75

Solution If the reaction is of first order, it must obey the equation

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

In the above reaction, NO_2 remains in solution and oxygen is liberated and collected at different intervals of time.

Therefore, $V_t \propto x$

$V_\infty \propto a$

Substituting these values in the first order equation

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

Time	V_t	$V_\infty - V_t$	$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$
10	6.30	34.75 – 6.30 = 28.45	$k = \frac{2.303}{10}\log\frac{34.75}{28.45} = 0.0198$
15	8.95	34.75 – 8.95 = 25.80	$k = \frac{2.303}{15}\log\frac{34.75}{25.80} = 0.0198$
20	11.40	34.75 – 11.40 = 23.35	$k = \frac{2.303}{200}\log\frac{34.75}{23.35} = 0.0198$
25	13.50	34.75 – 13.50 = 21.25	$k = \frac{2.303}{25}\log\frac{34.75}{21.25} = 0.0198$

The value of k comes of to be constant, therefore, the reaction is of first order. The average value of rate constant is 0.0198 min^{-1}.

Decomposition of Hydrogen Peroxide: The decomposition of hydrogen peroxide in aqueous solution (catalysed by the presence of finely divided platinum) takes place according to the equation

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

The kinetics of this reaction may be studied either by the same method as done earlier (i.e., collecting the oxygen gas produced and noting its volume at different intervals of time) or 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 cc) at regular intervals of time and titrating against the same $KMnO_4$ solution, the amount of H_2O_2 present can be found every time. It is obvious that for the same volume of the reaction solution withdrawn,

$$\left.\begin{matrix}\text{Volume of } KMnO_4 \text{ solution used}\\ \text{before the commencement of the}\\ \text{reaction i.e., at zero time } (V_0)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Initial concentartion}\\ \text{of } H_2O_2 \text{ (a)}\end{matrix}\right.$$

i.e., $a \propto V_0$

$$\left.\begin{matrix}\text{Volume of } KMnO_4 \text{ solution used}\\ \text{at any instant of time t } (V_t)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of } H_2O_2\\ \text{present at that}\\ \text{instant i.e., } (a-x)\end{matrix}\right.$$

$(a-x) \propto V_t$

Substituting these values in the first order equation, we get

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

or $$k = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

The decomposition of hydrogen peroxide, as tested by this equation, is found to be of the first orde .



Worked-out Example

41. From the following data, show that the decomposition of an aqueous solution of hydrogen peroxide is of first order:

Time (minutes)	**0**	**10**	**20**	**30**
V (ml)	**46.1**	**29.8**	**19.6**	**12.3**

Where, V is the volume of potassium permanganate solution in ml required to decompose a definite volume of the peroxide solution.

Solution It is evident from the given data that the zero – time titre – value is proportional to the original concentration of hydrogen peroxide, i.e., a. The titre value at any time t corresponds to undecomposed hydrogen peroxide, i.e., (a – x).
Substituting the value in the equation,

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x}, \text{ we get}$$

(i) $k_1 = \frac{2.303}{10}\log\frac{46.1}{29.8} = 4.364\times10^{-2}$

(ii) $k_1 = \frac{2.303}{20}\log\frac{46.1}{19.6} = 4.276\times10^{-2}$

(iii) $k_1 = \frac{2.303}{30}\log\frac{46.1}{12.3} = 4.404\times10^{-2}$

Since, k_1 comes out to be constant in the two cases, the reaction is a first order one with the average value of three.

Pseudo first order reactions

There are circumstances where a second order reaction might appear, in an experiment, to be first order. That is when one of the reactants in the rate equation is present in great excess over the other in the reaction mixture.

As an example, let's look again at the mixed second order rate law that we treated in the last section.

In the last section we had the rate law, $\frac{d[B]}{dt} = -k[B][A]$, with a reaction whose stoichiometry is,

$$2A + B \rightarrow P + \text{etc (P = product).}$$

Sometimes, $[A]_o >> [B]_o$.

For example, say we prepare the system such that,

$[A]_o = 2.0$ M, and

$[B]_o = 0.001$ M.

Then, when the reaction has run to completion, (at time = infinity),

$$[A]_{inf} = [A]_o - 2\,[B]_o = 2.0 - 0.001 = 1.998 \approx 2.0.$$

So [A] is approximately constant throughout the entire reaction.

Then the rate law becomes,

$$\frac{d[B]}{dt} = -k[B][A] \approx -k[B][A]_o, \quad (1)$$

which is effectively a first order rate equation. This rate equation has the solution,

$$[B] = [B]_o e^{-k[A]_o t}, \quad (2)$$

where, the "effective" first order rate constant is $k[A]_o$.

We can also prove it as follows,

A reaction will be of the second order when the reaction rate would depend upon the product of two concentrations. This may arise in two ways:

(i) $\underset{(a-x)}{2A} \rightarrow$ Products;

(ii) $\underset{(a-x)(b-x)}{A+B} \rightarrow$ Products

If the two substances have the same initial concentration (a) and if x denotes the concentration of the reactants which disappears in time t, then the rate will be,

$$\frac{dx}{dt} = k(a\text{-}x)^2$$

Rearranging, $$\frac{dx}{(a-x)^2} = kdt$$

Integrating, $$\frac{1}{a-x} = kt + z \text{ (constant)}$$

When $t = 0, \times = 0,$ $\therefore \frac{1}{a} = z$

Hence, $$\frac{1}{a-x} - \frac{1}{a} = kt$$

The velocity constant, $$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

Hence, at time t, the fractional extent of the reaction would be,

$$\frac{x}{b} = 1 - \frac{1}{1+kta}$$

When the initial concentrations of the two substances participating are different, say a and b, then the rate is given by,

$$\frac{dx}{dt} = k\,(a\text{–}x)\,(b\text{–}x)$$

Where x is the amount of any reactant transformed in time t.

Rewriting, $$\frac{dx}{(a-x)(b-x)} = kdt$$

Or $$\frac{1}{a-b}\left[\frac{1}{b-x} - \frac{1}{a-x}\right] dx = kdt$$

Integrating, $$\frac{1}{a-b}[-\ln (b\text{–}x) + \ln(a\text{–}x)] = kt + z \text{ (constant)}$$

Or $$\frac{1}{a-b}\ln\frac{a-x}{b-x} = kt + z$$

When, $t = 0, \times = 0$, therefore, $\frac{1}{a-b}\ln\frac{a}{b} = z$

Substituting, $\frac{1}{a-b}\ln\frac{a-x}{b-x} - \frac{1}{a-n}\ln\frac{a}{b} = kt$

or $k = \frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}$

It may also be written as, $t = \frac{2.303}{k(a-b)}\log\frac{b(a-x)}{a(b-x)}$, ……(4)

There are a number of reactions which follow the first order kinetics though more than one kind of reactants are involved in the reaction. Common examples are the inversion of cane sugar or the hydrolysis of an ester in an acid medium.

(i) $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$

(ii) $CH_3COOEt + H_2O = CH_3COOH + EtOH$

These are truly second-order reactions. Two substances water and conesugar, or water and estr participate, but the rate of reaction is experimentally observed to depend only on the conc. Of cane sugar or of ester.

A second-order reaction is governed by the eqn4. If the conc. Of one of the participants is very large compared to that of the other, say b >>a, then $b - \times \approx b$, and a–b, which is practically constant. Hence, eqn. '4' reduces to

$$kb = \frac{1}{t}\ln\frac{a}{a-x}, \text{ or } k' = \frac{1}{t}\ln\frac{a}{a-x}$$

Pseudo first order reactions are sometimes used to find the rate constant of a second order reaction when one of your two components is very expensive and the other one is relatively cheap. You can use an excess of the inexpensive reagent and use a small amount of the expensive one. Notice that you can still obtain the second order rate constant by dividing the effective first order rate constant by the concentration of the excess component.

The kinetics of the above reactions have been studied as follows:

1. **Hydrolysis of Ethyl acetate**

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

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 catalyst, also reacts with NaOH solution. Hence, a little careful though, reveals that for the same volume of reaction mixture withdrawn at different times.

Volume of NaOH solution used in the beginning i.e., at zero time (V_0) $\propto$ Amount of acid present only as catalyst (as no CH_3COOH is produced at t = 0) … (i)

Volume of NaOH solution used at any instant of time t (V_t) $\propto$ Amount of acid present as catalyst + amount of CH_3COOH produced … (ii)

Combining results (i) and (ii), we find that

Amount of CH_3COOH produced at any instant of time $\propto (V_t - V_0)$ … (iii)

$$\left.\begin{matrix}\text{But amount of } CH_3COOH \text{ produced} \\ \text{at any instant of time}\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of } CH_3COOC_2H_5 \\ \text{that has reacted (x)}\end{matrix}\right.$$

Hence, $x \propto (V_t - V_0)$ ... (iv)

Further,

$$\left.\begin{matrix}\text{Volume of NaOH solution used after the reaction} \\ \text{has taken place for a long time, say 24 hours or so,} \\ \text{called infinite time } (V_\infty)\end{matrix}\right\} \propto \left\{\begin{matrix}\text{Amount of acid present as} \\ \text{catalyst + Max. amount} \\ \text{of } CH_3COOH \text{produced}\end{matrix}\right. \quad \ldots (v)$$

Combining results (i) and (v), we find that

Maximum amount of CH_3COOH produced $\propto (V_\infty - V_0)$

But Maximum amount of CH_3COOH produced $\propto$

Initial concentration of $CH_3COOC_2H_5$ ... (vi)

Hence, $a \propto (V_\infty - V_0)$

From equations (iv) and vi), we have,

$$(a - x) \propto (V_\infty - V_0) - (V_t - V_0)$$

or $(a - x) \propto (V_\infty - V_t)$ ... (vii)

Substituting the values of a and (a – x) from equations (vi) and (vii) in the first order equation, we get,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

or $$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$



Worked-out Example

42. In an experiment to study hydrolysis of an ester, 0.5 M HCl at 300 K was used. 5 cm^3 of the reaction mixture was withdrawn after definite intervals and titrated against 0.2 M NaOH solution. Calculate the rate constant at 300K from the following data.

t (sec)	**0**	**600**	**1200**	**1800**	**∞**
v (cm^3 of NaOH used)	**11.5**	**12.0**	**12.5**	**13.0**	**25.5**

Solution From the given data, V0 = 11.5 cm3; V∞ = 25.5 cm3

$\therefore$ $a \alpha V_\infty - V_0 = 25.5 - 11.5 = 14.0$ and $(a - x) \alpha V_\infty - V_t$

Putting the values of V_t = 12.0 at 600 sec.; 12.5 at 1200 sec. and 13.0 at 1800 seconds in the equation

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}, \text{ we get,}$$

(i) $k_1 = \frac{2.303}{600}\log\frac{14.0}{(25.5-12.0)} = \frac{2.303}{600}\log\frac{14.0}{13.5} = 6.061\times10^{-5}\,s^{-1}$

(ii) $k_1 = \frac{2.303}{1200}\log\frac{14.0}{(25.5-12.0)} = \frac{2.303}{1200}\log\frac{14.0}{13.0} = 6.176\times10^{-5}\,s^{-1}$

(iii) $k_1 = \frac{2.303}{1800}\log\frac{14.0}{(25.5-12.0)} = \frac{2.303}{1800}\log\frac{14.0}{12.5} = 6.296\times10^{-5}\,s^{-1}$

The average value of rate constant $k_1 = 6.177 \times 10^{-5}\ s^{-1}$.

Optical Rotation Method

Inversion of cane sugar (sucrose)

$$\underset{\text{((+); 66.5°)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose ((+); 52.5°)}}{C_6H_{12}O_6} + \underset{\text{fructose ((–); –92°)}}{C_6H_{12}O_6}$$

dextro-rotatory → laevo-rotatory

In this reaction, the hydrolysis of dextro-rotatory sucrose produces a mixture of glucose (dextro-rotatory) and fructose (laevo rotatory). As laevo rotation of fructose is more therefore the resulting mixture is laevo rotatory.

The kinetics of above reaction is studied by noting the angle of rotation at different intervals of time using polarimeter.

Say angle of rotation at the start of experiment = r_0

Angle of rotation at any time t = r_t

Angle of rotation at ∞ time = r_∞

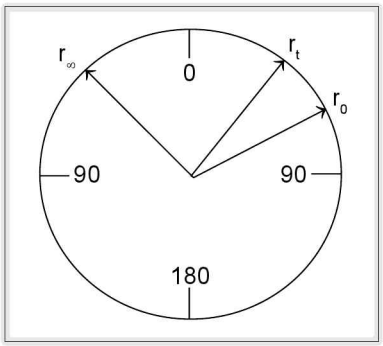


Fig. 4.5

Now,

Angle of rotation at any instant of time

= $(r_0 - r_t) \propto$ amount of sucrose hydrolyzed

or $x \propto (r_0 - r_t)$

Similarly, angle of rotation at ∝ time

= $(r_0 - r_\infty) \propto$ initial concentration of sucrose (a)

or $a \propto (r_0 - r_t)$

Thus, $(a - x) \propto (r_0 - r_\infty) - (r_0 - r_t)$

$\propto (r_t - r_\infty)$

Hence, $k = 2.303\log\frac{r_0 - r_\infty}{r_t - r_\infty}$

Worked-out Example

43. The optical rotation of sucrose in 0.5 N-hydrochloric acid at 308 K and at various time intervals are given below. Find out the rate constant for the first order hydrolysis of sucrose.

Time (minutes)	0	10	20	30	60	∞
Rotation (degrees)	+32	25.5	20.0	15.5	5.0	-10.50

Solution Here a, the initial concentration $\propto (r_0 - r_\infty)$

x, the change in time t α $(r_0 - r_t)$

$\therefore$ $(a - x) \propto (r_t - r_\infty)$

Substituting these values for different (a – x) values corresponding to time t from the data in the equation for first order reactio

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{r_0 - r_\infty}{r_t - r_\infty}, \text{ we get}$$

(i) $k_1 = \frac{2.303}{10}\log\frac{32-(-10.5)}{25.5-(-10.5)} = \frac{2.303}{10}\log\frac{42.5}{36.0} = 0.0166 \text{ min}^{-1}$

(ii) $k_1 = \frac{2.303}{20}\log\frac{32-(-10.5)}{20.0-(-10.5)} = \frac{2.303}{20}\log\frac{42.5}{30.0} = 0.0166 \text{ min}^{-1}$

(iii) $k_1 = \frac{2.303}{30}\log\frac{32-(-10.5)}{15.5-(-10.5)} = \frac{2.303}{30}\log\frac{42.5}{26.0} = 0.0164 \text{ min}^{-1}$

(iv) $k_1 = \frac{2.303}{60}\log\frac{32-(-10.5)}{5.0-(-10.5)} = \frac{2.303}{60}\log\frac{42.5}{15.5} = 0.0168 \text{ min}^{-1}$

Average value of $k_1 = 0.0166 \text{ min}^{-1}$

n^{th} Order Reaction($n \neq 1$)

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

	A ⟶	Product
t = 0	a	0
t = t	a – ×	x

$$\frac{dx}{dt} \propto (a-x)^n$$

$$\frac{dx}{dt} = K(a-x)^n$$

$$\int_0^x \frac{dx}{(a-x)^n} = \int_0^t K\,dt$$

$$\frac{1}{(n-1)}\left[\frac{1}{(a-x)^{(n-1)}} - \frac{1}{a^{(n-1)}}\right] = Kt \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Now we can get the integrated rate law for first, second,third order reactions by putting n=1, n=2, n=3. respectively.(there is a limitation that initial concentrations of all the reactants should be same or there should one reactant)

We can also get the half life as follows:

$$\int_0^{a/2} \frac{dx}{(a-x)^n} = \int_0^{t_{1/2}} Kdt$$

Let, $a - \times = z$

$-dx = dz$, when $\times = 0$, $z = a$

When, $x = a/2$, $z = a/2$

$$\int_a^{a/2} \frac{-dz}{z^n} = \int_0^{t_{1/2}} Kdt \quad -\left[\frac{Z^{-n+1}}{-n+1}\right]_a^{a/2} = kt_{1/2}$$

$$\frac{a^{1-n}}{n-1}\left[\left(\frac{a}{2}\right)^{1-n} - a^{1-n}\right] = kt_{1/2}$$

$$\frac{1}{a^{n-1}(n-1)}[2^{n-1}-1] = kt_{1/2}, \; (a^{n-1}).t_{1/2} = \left(\frac{1}{K(n-1)}(2^{n-1}-1)\right) = k$$

Therefore, for a nth order reaction, half life period in inversely related to initial amount.

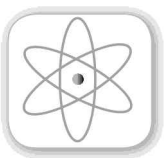
$$t_{1/2}a^{n-1} = \text{constant}$$

The following table is a summary of important information related to 0, 1st and 2nd order reactions:

Order	*rate expression*	*conc-time relationship*	*half-life*	*linear plot*
0	rate = k	$X_0 - \times = k$	$X_0/2k$	X vs t
1	rate = kX	$\log X_0/X = kt/2.30$	0.693/k	log × vs t
2	rate = kX^2	$1/x - 1/X_0 = kt$	$1/X_0k$	1/X vs t

To decide if a reaction is 0, 1st or 2nd order, list X, $\log_{10}X$, and 1/X in a table, then plot each against time. The one with the linear plot is the order of the reaction.

COLLISION THEORY OF KINETICS



Collisions

Two chemicals will only react if they come into contact. Put in a slightly different way we can say that:

The reactants must collide together.
We can also be sure that:

The more particles there are in a given volume, the more likely they are to collide and react together.
This gives us a clue as to why the rates of reactions often change when the concentrations of the reactants change.

Unfortunately, it is not easy to say just what counts as a collision. When two atoms come close together, the electric fields of the electron clouds interact with one another. It is the disturbance caused by the electron clouds that starts the reaction between them. The problem is to discover how close the atoms have to be for the disturbance to be significant. One rule of thumb is to say that the atoms have to be no further apart than the sum of their van der Waals radii.

We can give each reaction a collision frequency, which will be given the symbol Z. If the average speed of the molecules is known, it is possible to estimate the value of Z. A typical value for 1 mol of particles is 10^{13} collisions every second in a volume of 1 cm^3, i.e., $Z=10^{13} cm^3\ mol^{-1}\ s^{-1}$. However, we have said that not all collisions are effective because the particles often have to meet at a particular angle. We can allow for this by multiplying Z by a steric factor, P. We shall write the effective number of collisions as N where, N = PZ.

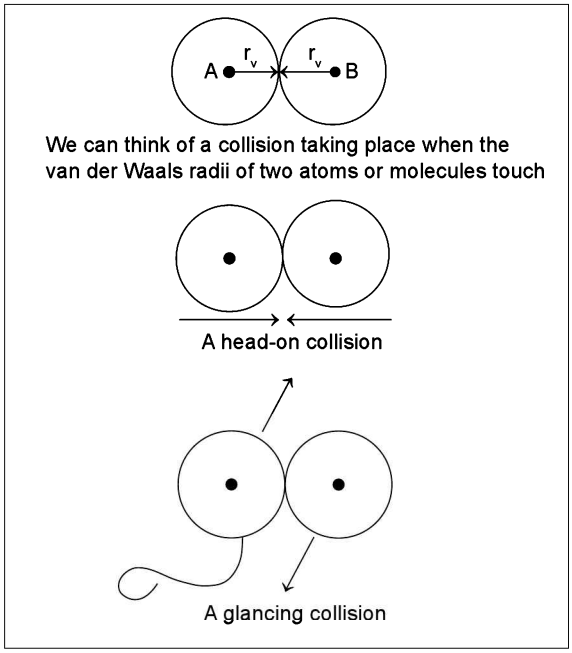


Fig. 4.6

Because the rate depends on the number of collisions, we have rate is proportional to N, i.e., to PZ

Energy

The reactants must have the right energy.

This is especially true for reactions between covalent substances. If a new substance is to be made, new bonds must be formed. Also, one or more of the original bonds has to break. Breaking bonds needs energy. If the molecules collide only weakly, they may not have enough energy to break the necessary bonds. (Alternatively, bonds that we do not want to break may be disrupted instead!).

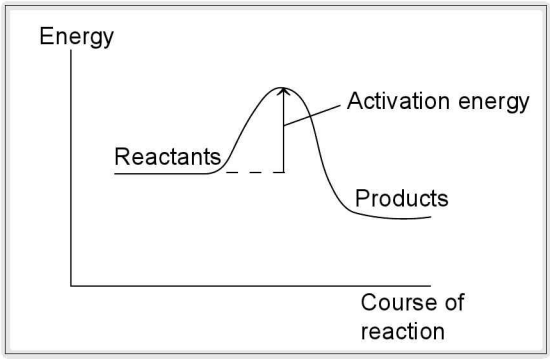


Fig. 4.7

We can use a diagram, figure 7, to show the minimum energy that chemicals must have if they are to react. The minimum energy needed to make a reaction take place is called the activation energy. Reactions that take place easily at room temperature have fairly low activation energies; reactions that require higher temperatures have higher activation energies.

Rates of reactions increase as temperature increases. However, the way the rate increases is not simple. The increase is given by an exponential factor, called the Arrhenius factor:

rate is proportional to $\exp(-E_a/RT)$

Here, E_a is the activation energy of the reaction, R is the gas constant and T the Kelvin temperature. The activation energy is the minimum energy the particles need in order to react.

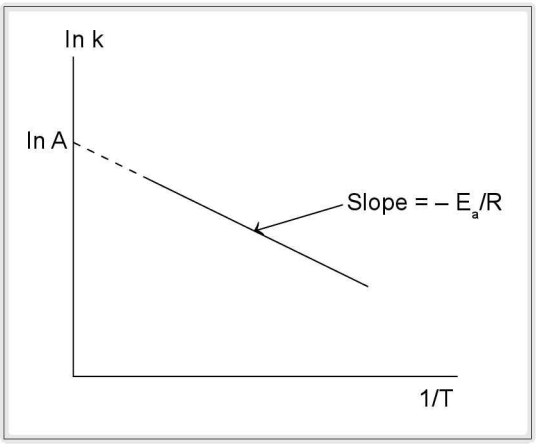


Fig. 4.8

We can put our two requirements about collisions and energy together in one equation. Any individual reaction will have its own particular values for P, Z and E_a. This means that, at a given temperature, the two factors N and $\exp(-E_a/RT)$ will be constant. This allows us to define the rate constant, k, for a reaction as $k = PZ \exp(-E_a/RT)$.

An equation just like this was established from experiment by Arrhenius. He wrote the rate constant as,

$K = A \exp(-Ea/RT)$ Arrhenius equation

The difference is that we have used collision theory to give an explanation of what his constant, A, might mean.

We can use the Arrhenius equation to help us measure the activation energy of a reaction. If we take the natural logarithm of both sides, we have,

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

or

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$

A graph of In A: against 1/T should be a straight line (Figure 8.). The slope will be $-E_a/R$, and the intercept on the In k axis will give the value of In A, from which we can find the value of A.

Note that $e^{E_a/RT}$ is a fraction .It is the fraction of the total number of reactant molecules in the activated state(activated molecules with proper energy, i.e., the activation energy.)

More about the activation energy

We can illustrate the importance of the activation energy on a diagram like that in Figure 4.9. The reactants start with an energy that can be greater or less than that of the products. If the reactants have more energy than the products, then we have an exothermic reaction; otherwise the reaction is endothermic. The diagram shows that there is an energy barrier between the reactants and products. If the reactants are to change into products, they have to get over the energy barrier. That is, they must gain at least the activation energy.

The diagram we drew in Figure 4.9, which shows

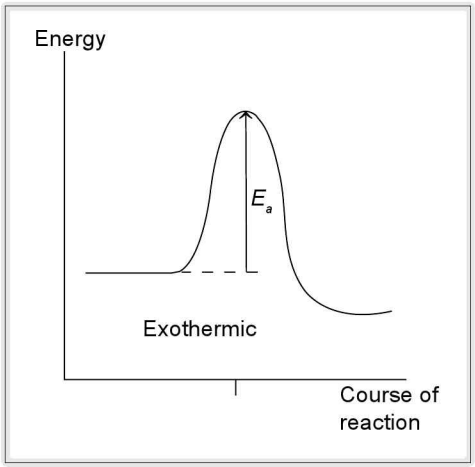


Fig. 4.9

the spread of energies among gas molecules, allows us to understand why rates increase with temperature. Figure 4.9 tells us that, at a higher temperature the energy distribution curve stretches out. The shaded areas give the proportion of molecules that have an energy equal to or greater than the activation energy. The area increases at the higher temperature. That is, more molecules can get over the energy barrier at a higher temperature than at a lower temperature.

Catalysts and activation energy

Catalysts increase the rate of a reaction without the necessity of increasing the temperature. They do this by providing a different route for the reaction to take place. We say that the mechanism of the reaction is different in the presence of the catalyst. The key thing is that the new mechanism has a lower activation energy than the uncatalysed reaction (Figure 4.10). With the decrease in the activation energy, many more reactant particles are able to surmount the new energy barrier and turn into products.

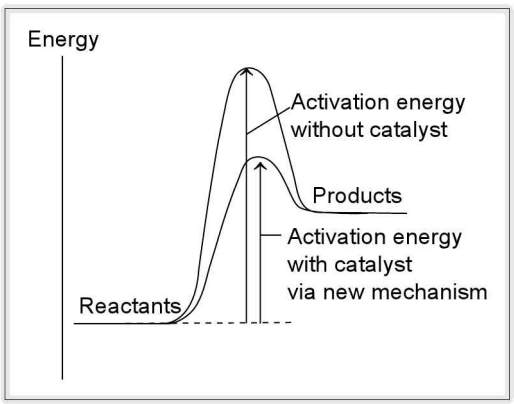


Fig. 4.10

3. Orientation

A reaction will not take place (i) if the particles do not collide, or (ii) if their energy is less than the activation energy. We have said that it is not always obvious what counts as a collision, but there is evidence that the way some molecules approach each other is extremely important. If they approach in one way, they react; if they approach in a different way, they do not react. Such a thing happens in the reaction between hydroxide ions and iodomethane (Figure 11). We will discover later that the two types of particle normally have to collide in the very particular way shown in Figure 11.

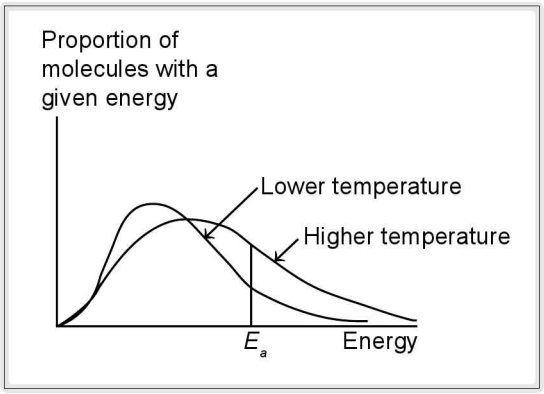
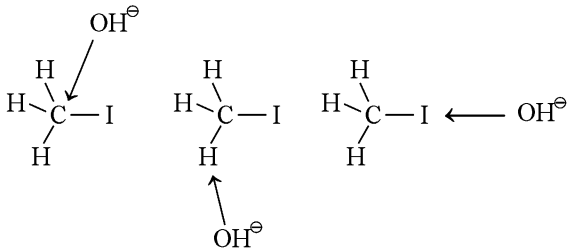
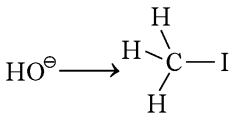


Fig. 4.11

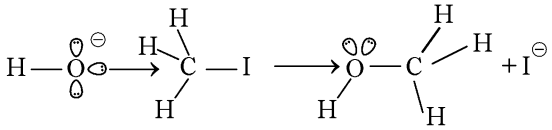
(a) Unsuccessful collisions



(b) Possibly successful collision



(c) Successful reaction



$$OH^- + CH_3I \longrightarrow CH_3OH + I$$

If the hydroxide ion meets the Iodomethane at a different angle, for example, if it bumps into one of the hydrogen atoms, the reaction fails. When reactions are influenced by the shapes of the molecules, we say that there is a steric factor in the reaction. In some cases the atoms, or groups of atoms, in a molecule can hinder the course of a reaction. If a group is particularly large, then it can get in the way of an attacking molecule or ion. If this happens, we say that the reaction suffers from steric hindrance.

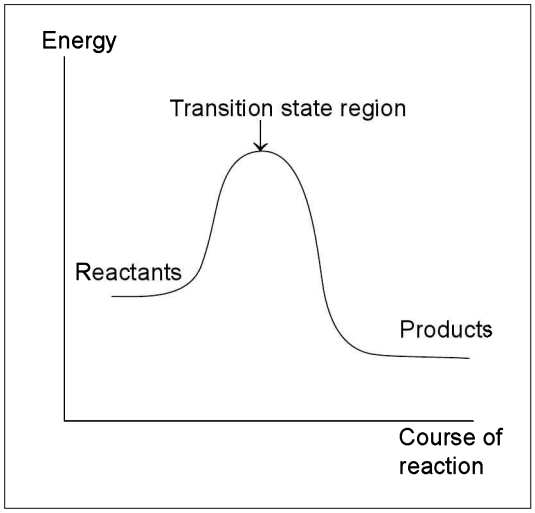
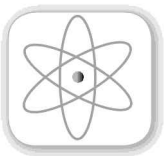


Fig. 4.12

The progress of a reaction that takes place in a solution can also be influenced by the solvent. For example, if two molecules or ions in water are to react, they have to find a way through the surrounding layers of water molecules. The speed with which the molecules react might be limited by the ease with which they can travel through the water. A measure of their movement through the water is their rate of diffusion. If the solvent is changed, for example, by using ethanol rather than water, then the rate of diffusion changes and the rate of the reaction changes.

TRANSITION STATE THEORY



Transition state theory explains rates of reactions in a rather different way to collision theory. In transition state theory we concentrate on what happens to the reactants when they are about to change into products. This change takes place at the top of the energy barrier, so this is called the transition state region (Fig 4.13).

When a reactant molecule, or combination of molecules, is changing into products, some of its old bonds are breaking, and new bonds are being made. When the reactants are in this state of change they make up the activated complex. The activated complex does not always change into products, it can equally well change back into the reactants.

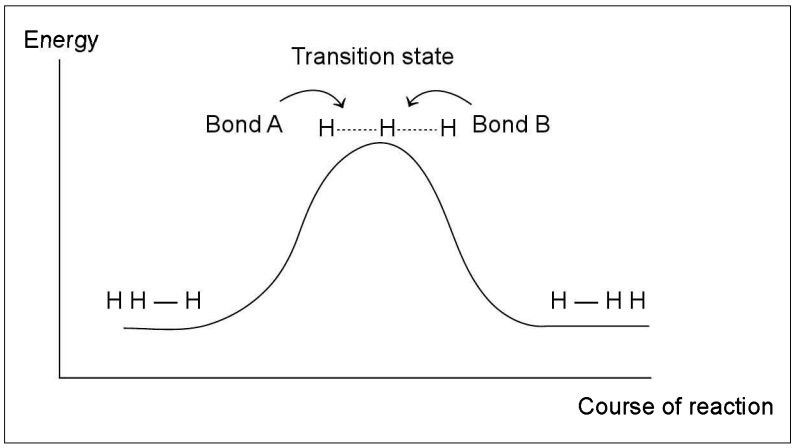


Fig. 4.13

One example is the reaction between a hydrogen atom and a hydrogen molecule. The transition state is linear, with the two bonds somewhere between being made and being broken (Figure 14). If the energy possessed by the transition state is concentrated in bond A, then it changes back into reactants; if it concentrates in bond B, then it makes products.

It can happen that the activated complex changes into an intermediate that is more energetically stable than the activated complex. The intermediate may last for sufficiently long time to allow it to be isolated, but this is rare. More often, it is possible to spot an intermediate by virtue of its spectrum. The intermediate may change into another activated complex before finally being converted into products.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Arrhenius Theory-Temperature Dependence of the Rate Constant

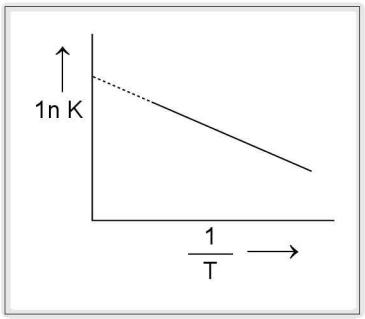


Fig. 4.14

(Named after its discoverer, Gustav Arrhenius)

It was known very early in the study of chemical kinetics that reaction rate constants were functions of temperature. That is,

$$k = k(T).$$

It was found that an experimental plot of lnK vs 1/T appeared to be approximately linear with a negative slope. This implies that,

$$\ln k = -b\frac{1}{T} + c.$$

Call c = lnA for simplicity, then,

$$\ln k - \ln A = -b\frac{1}{T} = \ln\frac{k}{A}.$$

We can solve the above equation for k by taking the antilog of this equation,

$$\frac{k}{A} = e^{-\frac{b}{T}},$$

or

$$k = Ae^{-\frac{b}{T}}.$$

It is usual to set $b = E_a/R$ to get,

$$k = Ae^{-\frac{E_a}{RT}}.$$

E_a is called the Arrhenius activation energy. The interpretation of this equation is that there is some intermediate configuration of the molecules involved in the reaction which is "half-way" between the reactants and products. This configuration of molecules, in the process of reacting, is called the "activated complex." The idea is that it takes energy to form this complex and the probability of the system attaining that energy at a temperature, T, is proportional to the exponential of (the negative of) the activation energy divided by RT.

This makes sense. Recall that kT and RT are thermal energies and we have seen exponentials of a mechanical energy divided by a thermal energy before. For example, the probability distribution function for molecular velocities in one dimension was given as,

$$f(v_x) \propto e^{-\frac{mv_x^2}{2kT}} = e^{-\frac{\text{molecular energy}}{kT}} = e^{-\frac{\text{molar energy}}{RT}}.$$

Actually, the preexponential factor, A = A(T), is also a function of temperature, but the temperature dependence is much weaker. Sometimes, for example,

$A \propto T^{1/2}$, or $T^{-1/2}$, or $T^{3/2}$, or etc.

But the major portion of the rate constant's temperature dependence is in the exponential term,

$$e^{-\frac{E_a}{RT}}$$

$$k = Ae^{-E_a/RT} \quad \ldots (1)$$

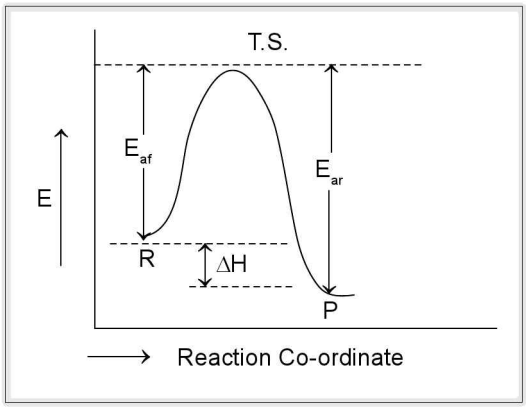


Fig. 4.15

k is the rate constant (of any order other than zero order), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. Activation energy (E_a) is the minimum energy required by a reactant at a certain temperature to undergo transformation into product. Arrhenius clearly assumed that reactions occur because of collisions between atoms and molecules of the reactant. He assumed the activation energy to be the least value of energy which the colliding molecules must possess for the collision to yield a product. If we plot graph between activation energy and progress of a reaction (expressed as reaction co-ordinate),we get a graph as shown in figure

The difference between the energies of the reactant and the transition state (TS) is called E_{a_f}.

$$\Delta H = E_{a_f} - E_{a_r}$$

A, the pre-exponential factor or the frequency factor or the Arrhenius constant is the number of effective collisions occurring per unit time. Effective collision is the number of collisions occurring per unit time in which orientation of the colliding molecules is proper. $e^{-E_a/RT}$ gives the fraction of the effective collision that have the sufficient activation energy. Therefore, the product of A and $e^{-E_a/RT}$ gives the number of collisions per unit time that forms the product and is called its number of productive collisions which is the rate constant, k.

For all practical calculations, we shall assume that E_a and A are temperature independent. Both A and E_a are characteristics of the reaction.

Determination of A and E_a

First Method: Taking log of both sides of equation (1)

$$\ln k = \ln A - \frac{E_a}{RT}$$

Converting natural log to common log, $\log k = \log A - \frac{E_a}{2.303\ RT}$

If log k is plotted against 1/T, a straight line is obtained which is shown as:
The slope of this line is given by,

$$\text{slope} = \frac{-E_a}{2.303\ R}$$

Thus, knowing the slope, the E_a can be easily calculated. The intercept of the line will give the value of log A.

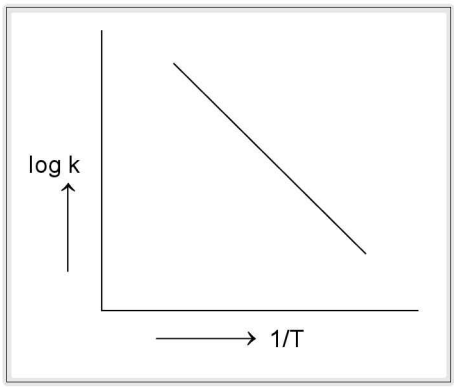


Fig. 4.16

Second Method: The logarithmic form of Arrhenius equation is rearranged as,

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Differentiating with respect to temperature, we get,

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

Integrating with in the limits of temperature T_1 and T_2, we get,

$$\int_{k_1}^{k_2} d \ln k = \int_{T_1}^{T_2} \frac{E_a}{RT^2} dT$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{or } \log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots (2)$$

Where, k_1 and k_2 are rate constants at temperatures T_1 and T_2 respectively. Thus, knowing these values E_a can be calculated. When the value of E_a is known, the value of A can be calculated by substituting its

value in equation $k = Ae^{-E_a/RT}$. In equation (2), the value of R has to be inserted in the same unit in which E_a is desired.

Temperature Coefficient: "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by 10°C".

$$\therefore \text{ Temperature coefficient} = \frac{k_{T+10}}{k_T} \approx 2 \text{ to } 3$$

Where, k_T is the rate constant at temperature T K and k_{T+10} is the rate constant at temperature (T+10) K. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every 10°C rise in temperature.



Worked-out Examples

44. Two reactions (I) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (I) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (i) is half that of reaction (ii), calculate the rate constant of the reaction (ii) at 300 K.

Solution Let $T_1 = 300$ K and $T_2 = 310$ k
we know that,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

For (i) reaction,

$$\log \frac{2k_1}{k_1} = \frac{E_A}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\text{or} \quad \log 2 = \frac{E_A}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad \text{---- (i)}$$

For (ii) reaction,

$$\log \frac{k_2}{k_1} = \frac{E_B}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\text{Since,} \quad = \frac{0.893}{t_{1/2}}$$

$$\text{Here, } k_2 = 2\left(\frac{0.693}{30 \text{ Min}}\right)$$

$$k_2 = 0.0462 \text{ min}^{-1}$$

$$\text{and } E_B = \frac{1}{2}E_A$$

$$\text{Therefore, } \log \frac{0.0462}{k_1} = \frac{E_A}{2 \times 2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

From equation (i)

$$\log \frac{0.0462}{k_1} = \frac{1}{2}\log 2 = \log \sqrt{2}$$

or $$\frac{0.462}{k_1} = \sqrt{2}$$

or $$k_1 = \frac{0.462 \text{ min}^{-1}}{\sqrt{2}} = \mathbf{0.327 \text{ min}^{-1}}$$

45. Which one is correct for $K = A\, e^{-Ea/RT}$: **[AIEEE-2003]**

(a) E_a is energy of activation
(b) R is Rydberg constant
(c) K is equilibrium constant
(d) A is adsorption factor

Solution (a)

46. The energy of activation for forward and backward change for an endothermic reaction; $x \longrightarrow Y$ are E_f and E_b respectively. Which of is these correct? **[AIEEE-2005]**

(a) $E_b < E_f$
(b) $E_b > E_f$
(c) $E_b = E_f$
(d) No relation between them

Solution (a) $\Delta H = E_f - E_b$

$\Delta H = +ve$

$\therefore \quad E_f > E_b$

47. Rate of reaction can be expressed by Arrhenius equation as:

$K = Ae^{-Ea/RT}$

In this equation Ea represents: **[AIEEE-2006]**

(a) The energy above which all the colliding molecules will react
(b) The energy below which colliding molecules will not react
(c) The total energy of the reactant molecules at a temperature T
(d) The fraction of molecules with energy greater than the activation energy of the reaction

Solution (b) E is activation energy. Thus, order with respect to NO is 2.

If $E_a + E_R = E_{\text{Threshold energy}}$ then only molecule may react.

48. The energies of activation for forward and reverse reaction for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \longrightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1}) **[AIEEE-2007]**

(a) 300
(b) 120
(c) 280
(d) –20

Solution (d) $\Delta H_R = E_f - E_b = 180–200 = –20$ kJ/mol

The nearest correct answer given in choices may be obtained by neglecting sign.

49. In the Arrhenius equation, k=A exp(-E/RT), A may be termed as the rate constant at ..... **(1997-1Marks)**

Solution Very high temperature or zero activation energy.

50. Catalyst makes a reaction more exothermic. (True or False) **(1987-1 Marks)**

Solution **False**: Catalyst does not makes a reaction more exothermic, but decrease the activation energy and hence increase the rate of reaction.

51. Catalyst does not affect the energy of activation in a chemical reaction. **(1989-1 Marks)**

Solution **False**: Catalysts lowers the energy of activation and therefore, influences the rate as well as rate constant of the reaction.

52. The rate of an exothermic reaction decreases with increasing temperature. **(1990-1 Mark)**

Solution **False**: The rate of a reaction increases with increase in temperature because at higher temperature more number of molecules attain the activation energy.

53. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0 × 10-4s-1,104.4 kJ mol-1 and 6.0 × 1014 s-1 respectively. The value of the rate constant as T → ∞ is

(a) $2.0 \times 10^{18}\ s^{-1}$ (b) $6.0 \times 10^{14}\ s^{-1}$ (c) infinit (d) $3.6 \times 10^{30} s^{-1}$

Solution (b) The Arrhenius equation is: $k = A \exp(-E_a/RT)$

As $T \to \infty$, $\exp(-Ea/RT) \to 1$. Hence, $k = A$

where A, the Arrhenius parameter, is $6.0 \times 1014\ s^{-1}$

54. A catalyst: **(1984-1 Marks)**

(a) increases the average kinetic energy of reacting molecules.
(b) decreases the activation energy.
(c) alters the reaction mechanism.
(d) increases the frequency of collisions of reacting species.

Solution (b, c) A catalyst provides the path of lower activation energy. The catalyst reacts with the reactants to form an intermediate of low activation energy. The intermediate then decomposes to form the product along with regeneration of catalyst. Thus the reaction mechanism changes completely.

55. For a first order reaction, (1998-2 Marks)

(a) the degree of dissociation is equal to $(1 - e^{-ktl})$.
(b) a plot of reciprocal concentration of the reactant vs time gives a straight line.
(c) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction
(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}.

Solution (a, d) In first order reaction, if *a* is the degree of dissociation therefore,

$$kt = \log \frac{1}{(1-\alpha)} = -\log_e(1-\alpha) \quad \text{or } e^{-kt} = 1-\alpha$$

$$\therefore \quad \alpha = 1 - e^{-kt}$$

The Arrhenius equation is, $k = Ae^{-Ea/RT}$

Plot of reciprocal concentration of the reactant vs time is linear. Dimensions of pre-exponential factor 'A' are equivalent to dimensions of K, which is T^{-1} for a first order reaction.

56. For a first order reaction A → P, the temperature (T) dependent rate constant (k) was found to follow the equation $\log\ k = -(2000)\frac{1}{T} + 6.0$. The pre – exponential factor A and the activation energy E_a, respectively, are

(a) $1.0 \times 10^6\ s^{-1}$ and 9.2 kJ mol^{-1} (b) $6.0\ s^{-1}$ and 16.6 kJ mol^{-1}
(c) $1.0 \times 10^6\ s^{-1}$ and 16.6 kJ mol^{-1} (d) $1.0 \times 10^6\ s^{-1}$ and 38.3 kJ mol^{-1} **[IIT-2000]**

Solution (d) $\mathbf{k = Ae^{-Ea/RT}}$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$\text{Log } A = 6,\ A = 10^6 s^{-1}$

$$-\frac{E_a}{2.303 \times 8.3 \times T} = -\frac{2000}{T}$$

$E_a = 2000 \times 2.303 \times 8.3\ J = 38.3\ kJ$

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

REACTIONS INVOLVING TWO FIRST ORDER PARALLEL REACTIONS OR CONCURRENT REACTIONS

Competing or Parallel Reactions

Sometimes a given substance reacts or decomposes in more than one way. Then the alternative or parallel reaction must also be taken into consideration while analyzing the kinetic data. Consider the simplest case of a first order irreversible reaction, leading to the formation of two products through two different pathways of first orde .

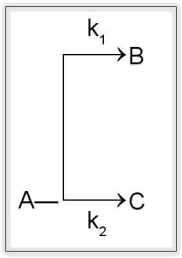


Fig. 4.17

The overall rate of reaction can be written as,

$$\frac{dx}{dt} = k_1(a-x)+k_2(a-x)$$

where, (a–x) is the concentration of A at any instant during the course of reaction. The above equation may be expressed as,

$$\frac{dx}{dt} = (k_1 + k_2)(a-x)$$

Integration under the condition that at $t = 0$ $x = 0$, gives

$$k = (k_1 + k_2) = \frac{1}{t}\ln\left(\frac{a}{a-x}\right)$$

From the above equation,

$$[A]_t = (a-x) = a \exp\,[-k_1+k_2)t]$$

Then,

$$\frac{d[B]}{dt} = k_1[A]_t = k_1 a \exp\,[-(k_1 + k_2)t]$$

Which on integration gives,

$$[B]_t = -\frac{k_1}{(k_1 + k_2)}\ a \exp\,[-(k_1+k_2)t] + \text{constant}$$

At, $t = 0, [B]_t = 0$, the

$$\text{Constant} = \frac{k_1 a}{(k_1 + k_2)}$$

Therefore,

$$[B]_t = \frac{k_1 a}{(k_1 + k_2)} \{1 - \exp[-(k_1 + k_2)t]\} \ldots\ldots\ldots\ldots$$

and similarly,

$$[C]_t = \frac{k_2 a}{(k_1 + k_2)} [1 - \exp[-(k_1 + k_2)t]] \ldots\ldots\ldots\ldots$$

The variation in the concentrations of A, B, and C with time is shown in Figure.

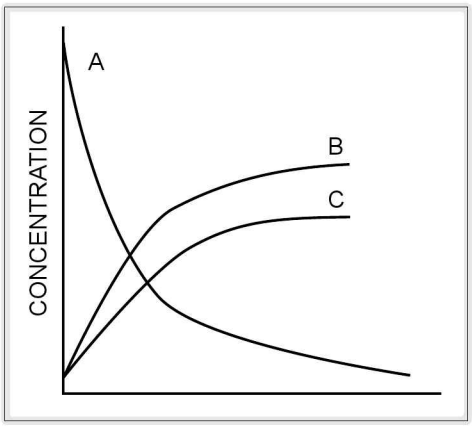


Fig. 4.18 Variation with time of the concentration of reactant A, and products B and C for two first order parallel reactions (for $k_1/k_2 = 2$).

From the above two equations,

$$\frac{[B]_t}{[C]_t} = \frac{k_1}{k_2}$$

i.e., the ratio of the product concentrations at any instant is equal to the ratio of the corresponding rate constants.

Thus, if the concentration ratio is determined at any stage and k is found from the kinetic equation, the individual rate constants can be determined.

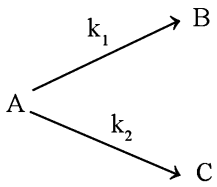
This type of reactions are very common in organic chemistry (substitution reaction). For example, the chlorination of methane may give mono, di, tri/or tetra halogen derivative. Some examples of side reactions are:

(i) $C_6H_5N = NCl + CH_3CH_2OH \longrightarrow \begin{cases} C_6H_6 + N_2 + HCl + CH_3CHO \\ C_6H_6\,OC_2H_5 + N_2HCl \end{cases}$

(ii) $CH_3CH_2Br + KOH \longrightarrow \begin{cases} CH_3CH_3OH + KBr \\ CH_2 = CH_2 + KBr + H_2O \end{cases}$

Worked-out Examples

57.



Let $k_1:k_2 = 1:10$. Calculate the ratio, $\frac{[C]}{[A]}$ at the end of one hour assuming that $k_1 = \times\ hr^{-1}$

Solution $\frac{-d[A]}{dt} = (k_1 + k_2)[A]$

$\therefore \quad \frac{-d[A]}{[A]} = (k_1 + k_2)dt$

Integrating with in the required limits, we get,

$$\ln \frac{[A]_0}{[A]_t} = (k_1 + k_2)t$$

$$\therefore \ \ln \frac{[A]_t + [B] + [C]}{[A]_t} = (k_1 + k_2)t$$

Since, $\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{1}{10}$

$$\therefore \ \ln \frac{[A]_t + \frac{[C]}{10} + [C]}{[A]_t} = 11x$$

$$\frac{[C]}{[A]_t} = \frac{10}{11}(e^{11x} - 1)$$

58. Show that if A undergoes two simultaneous reactions to produce B and C according to $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$, then E_a, the observed activation energy for the disappearance of A is given by–

$$E_{av} = \frac{k_1E_1 + k_1E_2}{k_1 + k_2}$$

Solution We know that,

$$k_1 = A_{1.e}^{\frac{-E_1}{RT}}$$

$$k_2 = A_{2.e}^{\frac{-E_2}{RT}},$$

Where k_1 and k_2 are specific rate constants for the 1st and 2nd steps of the reaction and A_1 and A_2 are Arrhenius factors for steps 1 and 2. E_1 and E_2 are activation energies for steps 1 and 2. The specific rate for overall change for A to B and C is $k_1 + k_2$.

$$\therefore \quad \frac{d\ln k}{dT} = \frac{d\ln(k_1 + k_2)}{dT} = \frac{E_a}{RT^2},$$

Where E_a is the overall activation energy for the decomposition of A.

$$\text{But,} \quad \frac{d\ln(k_1 + k_2)}{dT} = \frac{1}{k_1 + k_2}\frac{d}{dT}(k_1 + k_2) = \frac{1}{k_1 + k_2}\left(\frac{dk_1}{dT} + \frac{dk_2}{dT}\right)$$

$$= \frac{1}{k_1 + k_2}\left[\frac{d}{dT}.(A_1 e^{-E_1/RT}) + \frac{d}{dT}.\left(A_2 e^{-E_2/RT}\right)\right]$$

$$= \frac{1}{k_1 + k_2}\left[A_1.\frac{E_1}{RT^2}.e^{-E_1/RT} + A_2.\frac{E_2}{RT^2}.e^{-E_2/RT}\right]$$

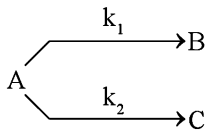
$$= \frac{1}{k_1 + k_2}\frac{1}{RT^2}\left[E_1.A_1.e^{-E_1/RT} + E_2.A_2 e^{-E_2/RT}\right]$$

$$= \frac{1}{k_1 + k_2}\frac{1}{RT^2}[E_1 k_1 + E_2 k_2]$$

$$\therefore \quad \frac{1}{k_1 + k_2}\frac{1}{RT^2}[E_1 k_1 + E_2 k_2] = \frac{E_a}{RT^2}$$

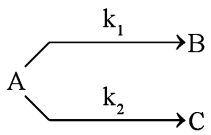
$$\therefore \quad E_a = \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2}.$$

59. Consider the parallel reaction.



In an experiment, it was observed that 60% decomposition of A takes place in 20 min and analysis of product showed that 75% of B and 25% of C are present. Calculate k_1 and k_2.

Solution



By the problem; $\frac{k_1}{k_2} = 3$.

$\therefore \quad k_1 = 3k_2$.

We know that for parallel reaction.

$$\frac{1}{t}\ln\frac{a}{a-x} = (k_1 + k_2).$$

By the problem.

$$\frac{1}{20}\ln\frac{a}{a-0.6a} = 3k_2 + k_2$$

or, $\frac{1}{20}\ln\frac{1}{0.4} = 4k_2$

$\therefore\ k_2 = 0.0114\ \text{min}^{-1}$

$\therefore\ k_1 = 3\,k_2 = 3 \times 0.0114 = 0.0342\ \text{min}^{-1}$

Sequential (consecutive) reactions

A Typical Example: In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

$$A \xrightarrow{k_1} B \xrightarrow{k'_1} C$$

Let the initial concentration of A be $[A]_0$ and let after time t, the concentrations of A, B and C be [A], [B] and [C], respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C] \qquad \ldots(1)$$

Differential Rate Law: The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \qquad \ldots(2)$$

$$\frac{d[B]}{dt} = k_1[A] - k'_1[B] \qquad \ldots(3)$$

$$\frac{d[C]}{dt} = k'_1[B] \qquad \ldots(4)$$

On integrating equation (2), we get

$$[A] = [A]_0 e^{-k_1 t} \qquad \ldots(5)$$

Substituting [A] from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k'_1[B]$$

$$\frac{d[B]}{dt} + k'_1[B] = k_1[A]_0 e^{-k_1 t}$$

Integrated Rate Law: Multiplying the above expression throughout by exp ($k'_1 t$), we get,

$$\frac{d[B]}{dt} + k'_1[B]e^{k'_1 t} = k_1[A]_0 e^{-(k_1 - k'_1)t}$$

The left side of the above expression is equal to $d([B]e^{k'_1 t})/dt$. Hence, the above expression can written as,

$$d\{[B]e^{k'_1 t}\} = k_1[A]_0 e^{-(k_1 - k'_1)t} dt$$

Integrating the above expression with [B] = 0 at t = 0, we get,

$$[B]e^{k't} = k_1[A]_0 \left[\frac{e^{-(k_1 - k'_1)t}}{-(k_1 - k'_1)} + \frac{1}{k_1 - k'_1} \right]$$

$$[B] = k_1[A]_0 \left[\frac{e^{-k_1 t}}{-(k'_1 - k_1)} + \frac{e^{-k'_1 t}}{k_1 - k'_1} \right]$$

$$[B] = k_1[A]_0 \left(\frac{k_1}{k'_1 - k_1} \right) \{e^{-k_1 t} - e^{-k'_1 t}\} \quad \ldots (6)$$

Substituting equations (5) and (6) in equation (1), we get,

$$[A]_0 = [A]_0 e^{-k_1 t} + [A]_0 \left(\frac{k_1}{k'_1 - k_1} \right) (e^{-k_1 t} - e^{-k'_1 t}) + [C]$$

$$\text{or } [C] = [A]_0 \left[1 - \frac{1}{k'_1 - k_1} (k'_1 e^{-k_1 t} - k_1 e^{-k'_1 t} \right] \quad \ldots (7)$$

Figure (4.19) Illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

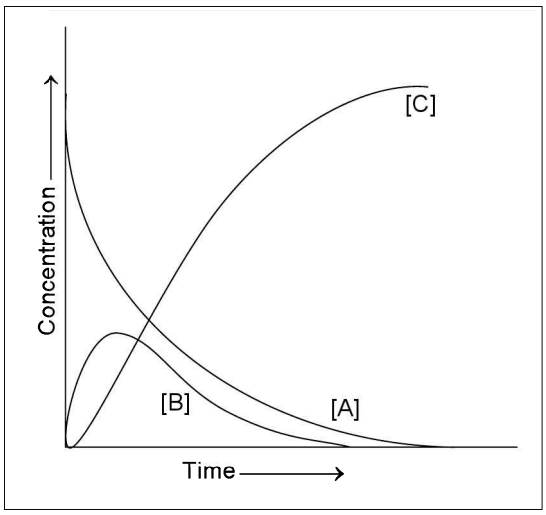


Fig 4.19 Typical variations of concentration of A, B and C during the progress of the reaction A → B → C. The actual variations on the values of k_1 and k'.

In general, concentration of A decreases exponentially, the concentration of B initially increases upto a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[A]_0$, when all A has changed into C.

Maximum Concentration of B: Equation (6) is

$$[B] = [A]_0 \left(\frac{k_1}{k_1' - k_1} \right) \{ e^{-k_1 t} - e^{-k_1' t} \} \quad \ldots (6)$$

At the maximum concentration of B, we have,

$$\frac{d[B]}{dt} = 0$$

Hence, differentiating equation (6) with respect to t, we get,

$$\frac{d[B]}{dt} = [A]_0 \left(\frac{k_1}{k_1' - k_1} \right) \{ -k_1 e^{-k_1 t} + k_1' e^{-k_1' t} \} \quad \ldots (8)$$

Equating equation (8) to zero, we get,

$$-k_1 e^{-k_1 t_{max}} + k_1' e^{-k_1' t_{max}} = 0$$

$$\text{or} \quad \frac{k_1}{k_1'} = e^{(k_1 - k_1')t_{max}}$$

$$\text{or} \quad \ln \left(\frac{k_1}{k_1'} \right) = (k_1 - k_1')t_{max}$$

$$\text{or} \quad t_{max} = \frac{1}{k_1 - k_1'} \ln \left(\frac{k_1}{k_1'} \right) \quad \ldots (9)$$

Substituting equation (9) in equation (6), we get,

Different cases

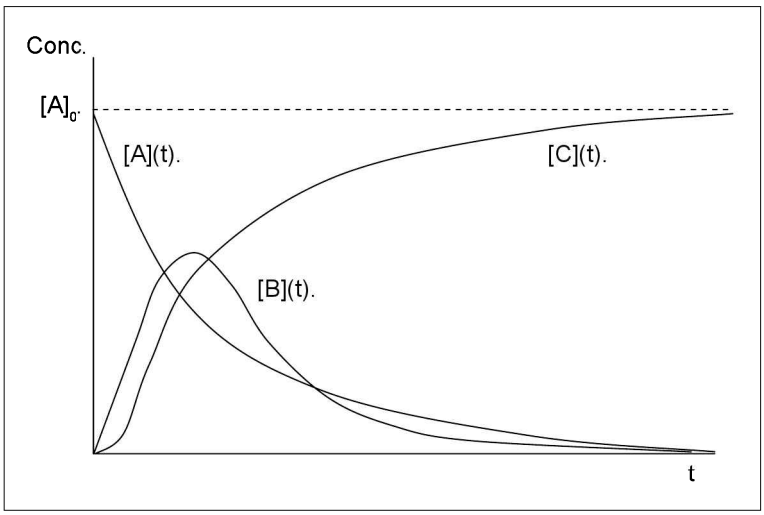


Fig. 4.20

The plots of [A], [B], and [C] appear as follows (when k_1 and k_2 are similar in magnitude)

Observe the following:

(1) [A](t) follows first-order kinetic
(2) [B](t) and [C](t) each consist of two exponentials: one with a positive coefficient and one with a negative coefficien
(3) Thus, [B](t) exhibits a maximum
(4) [C](t) is sigmoidal in shape and exhibits a short "lag" or "induction period" before rising like a product of a 1st order reaction

Limiting behaviour of consecutive reactions

The solutions to the consecutive reactions scheme can be used to illustrate two very useful approximations that may be applied to more complicated reaction schemes.:

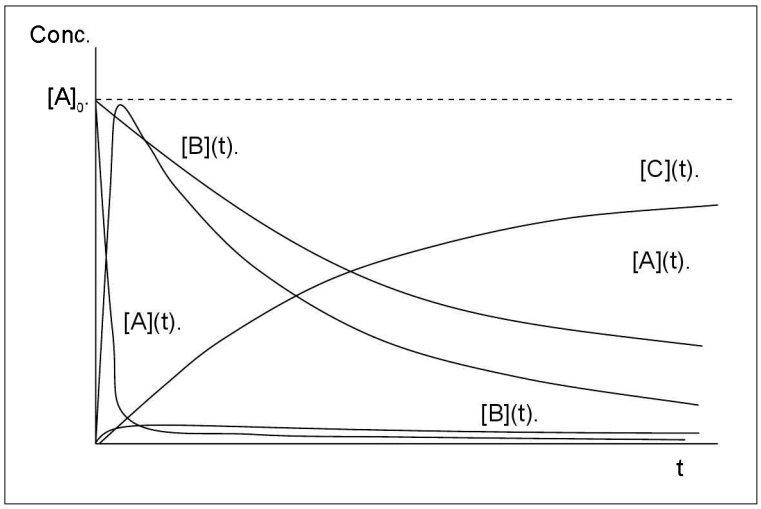


Fig. 4.21

(1) $k_2 >> k_1$. B is consumed as quickly as it is formed. It is only present at a low, nearly constant concentration during the reaction. In this case, B is said to be present in the steady state. A disappears and C appears with an effective 1st order rate constant $k \approx k_1$.
(2) $k_2 >> k_1$. Almost immediately, A disappears and [B] approachs $[A]_0$., then $B \rightarrow C$ proceeds as a 1st order reaction with rate constant k_2.

Note that when one rate constant is significantly slower than the other, the product is formed with that effective rate constant. The slow step is rate determining (or rate limiting).

The steady-state approximation

The steady-state approximation applies to reaction intermediates that are present at low and near constant concentrations. (example, [B] in the consecutive reaction example when $k_2 >> k_1$)

In the SS-approximation, set the overall rate of appearance and disappearance of the intermediate to 0. In above example,

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \approx 0$$

$$[B] = \frac{k_1}{k_2}[A]$$

At t = 0, $[B] = k_1[A]_0/k_2$, which is the result obtained by neglecting k_1 with respect to k_2 in the expression for [B](t).

Reactions involving opposing or reversible reactions: Such reactions results in equilibrium. In other words, the reactant changes to product and vice versa.

Say we have an opposing reaction in which both forward and backward reactions are first orde , viz.,

(k_1 and k_2 are rate constant of forward and backward reaction)

Say initial concentration of A and B are a and b mol L^{-1} respectively.

If after time t, × moles/L of A change into B, then concentration of A and B will be (a – x) and (b + x) respectively.

The net rate of the reaction would be given as:

$$\text{Rate} = k_1 (a - x) - k_2 (b + x) \quad \ldots \text{(i)} \; [\because \text{both processes occur simultaneously}]$$

When equilibrium is reached, the net rate is zero

Thus, $k_1 (a - x_e) = k_2 (b + x_e)$ (e = equilibrium)

$$\text{Hence, } (b + x_e) = \frac{k_1}{k_2} (a - x_e)$$

$$\text{or} \qquad b = \frac{k_1}{k_2} (a - x_e) - x_e$$

Substituting value of b in euqation (i)

$$\text{Rate of reaction, } \frac{dx}{dt} = k_1(a - x) - k_2\left[\frac{k_1}{k_2}(a - x_e) - x_e + x\right]$$

on solving, we get,

$$\text{Rate} = (k_1 + k_2)(x_e - x)$$

After rearranging and integrating the equation, we get an equation similar to first order reaction as shown below.

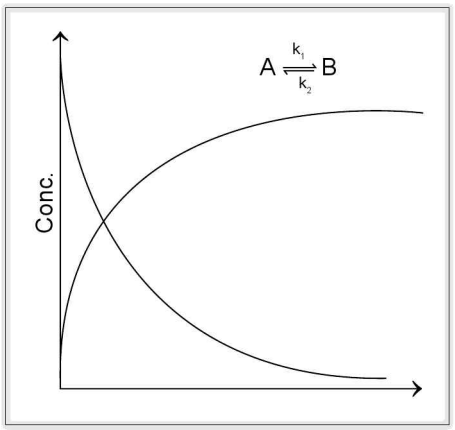


Fig. 4.22

$$\text{or} \qquad \frac{dx}{x_e - x} = (k_1 + k_2)dt$$

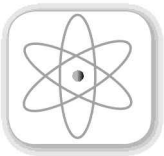
$$\int_{x_0}^{x} \frac{dx}{x_e - x} = \int_0^t (k_1 + k_2)dt$$

$$\text{or} \quad \log \frac{x_e - x_0}{x_e - x} = (k_1 + k_2)t$$

$$\text{or} \quad (k_1 + k_2) = \frac{1}{t} \log \frac{x_e - x_0}{x_e - x}$$

The equation is similar to first order reaction except that the measured rate constant is now the sum of the forward and the reverse rate constants.

CATALYST



Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually, two terms are used for catalysis:

Positive Catalysis: The phenomenon in which presence of catalyst accelerates the rate of reaction.

Negative catalysis: The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

Characteristics of catalyst

(i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. For example, MnO_2 used as catalyst in granular form for the decomposition of $KClO_3$, is left in powder form at the end of reaction.

(ii) A catalyst never initiates a chemical reaction. It simply influences the rate of reaction. Exception: combination of H_2 and Cl_2 takes place only when moisture (catalyst) is present.

(iii) A small quantity of catalyst is sufficient to influence the rate of reaction example 1 g atom of Platinum is sufficient to catalyse 108 litre of H_2O_2 decomposition.

(iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward and backward reactions equally.

(v) A catalyst normally does not alter the nature of products in a reaction. However, some exceptions are found to this characteristic.

(a) $HCOOH \xrightarrow{AlCl_3} H_2O + CO$, $\quad HCOOH \xrightarrow{Cu} H_2 + CO_2$

(b) $CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$, $\quad CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$

$CO + H_2 \xrightarrow{Cu} HCHO$

It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

(vi) A catalyst does not make reaction more exothermic.

(vii) Catalyst's activity is more or less specific: A catalyst for one reaction is not necessary to catalyse the another reaction.

Types of catalysis

1. **Homogeneous catalysis:** The reaction in which catalyst and the reactants have same phase. It includes two types.
   (a) **Gaseous phase catalysis:** When reactants and catalyst are in gaseous phase example chamber process for H_2SO_4.

$$2SO_2(g) + O_2(g) \xrightarrow[\text{catalyst}]{NO} 2SO_3(g)$$

   (b) **Solution phase catalysis:** The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

$$\underset{\text{ester}}{RCOOR'_{(l)}} + H_2O_{(l)} \xrightarrow{H^+} RCOOH + R'OH$$

2. **Heterogeneous catalysis:** The reactions in which catalyst and reactants form phase ≥ 2.

   (a) **Solid-liquid catalysis:** $\left.\begin{matrix}\text{Reactant : Liquid}\\ \text{Catalyst : Solid}\end{matrix}\right\}$ Immiscible

$$2H_2O_{2(l)} \xrightarrow[\text{Catalyst}]{MnO_{2(s)}} 2H_2O + O_2$$

   (b) **Liquid-Liquid catalysis**: $\left.\begin{matrix}\text{Reactant : Liquid}\\ \text{Catalyst : Solid}\end{matrix}\right\}$ Immiscible

$$2H_2O_{2(l)} \xrightarrow[\text{catalyst}]{Hg(l)} 2H_2O + O_2$$

   (c) **Solid-gas catalysis:** $\left.\begin{matrix}\text{Reactant : gases}\\ \text{Catalyst : solid}\end{matrix}\right\}$ Immiscible

   Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as 10^{10} times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example, n-heptane selectivity gives toluene in presence of Pt catalyst. Similarly, $CH_3—CH = CH_2 + O_2$ give $CH_2 = CHCHO$ selectivity over Bismuth molybdate catalyst.

Photochemical reactions

Chemical reactions resulting from exposure of a system to radiation lying in the visible and ultraviolet regions, that is, in the wave length range from 8000 A to 2000 A are known as photochemical reactions.

Reactions of many types, polymerization, isomeric change, oxidation and reduction, can be brought about by exposure to such radiation. Strictly speaking the term "radiation" includes X-rays and gamma rays, and it has also been applied to beams of particles, such as α-rays, electrons, neutrons and protons.

Einstein

The energy corresponds to one Einstein of photon is–

$$E = N_A h\nu = \frac{N_A hc}{\lambda}$$

Where, N_A is the Avogadro number, c is the velocity of light and λ is the wavelength of the radiation.

Quantum yield

The quantum yield or efficien y: The results of a photochemical process are frequently expressed by means of the quantum efficienc or quantum yield of the reaction; this is defined as the number of moles

of the light-absorbing substance that react for each Einstein of absorbed radiation . By the law of the photochemical equivalent, one mole of the substance should be involved in the reaction which is a direct result of the absorption of light, for each Einstein absorbed. It is to be expected, therefore, that if the only reaction which occurred in a given process was the one associated with the light absorption, the quantum yield should be unity.

$$\text{Quantum yield } (\phi) = \frac{\text{Number of moles reacting}}{\text{Number of einsteins absorbed}}$$

If the reaction takes place by a chain mechanism, then the primary process is the chain initiating step and the secondary processes are chain propagating (the last step being chain terminating). For a large number of chain reaction, ϕ is greater than 1. A classic example is the photochemical combination of H_2 and $Cl_2(\phi \approx 10^6)$. However, if a chain propagation step is slow (and endothermic) and requires high activation energy, ϕ may be less than 1. A classic example is H_2 and Br_2 reaction for which $Br + H_2 \rightarrow HBr + H$ is a step requiring 75kJ/mole as $E_{act.}$ There is also a chain inhibiting step and ϕ is about 0.01. Therefore, for high quantum yield, the secondary processes should be fast.



Worked-out Examples

60. In an experiment to measure the quantum efficiency for a photochemical reaction, the absorbing substance was exposed to 480 nm light from a 150 W source for a period to 30 minutes. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of this, 0.35 mole of the substance decomposed. Calculate ϕ.

Solution Energy of 1 Einstein

$$= \frac{6.022 \times 10^{23} \times 6.625 \times 10^{-34}\,\text{J.sec} \times 2.9979 \times 10^{8}\,\text{m/sec}}{480 \times 10^{-9}\,\text{m}} = 249173.89\ \text{J}$$

Energy coming out from 150 W source in 30 minutes

$$= 150\ \frac{\text{J}}{\text{sec}} \times 30 \times 60\ \text{sec} = 27000\ \text{J}.$$

$\therefore$ Number of Einstein of the incident light $= \frac{270000}{249173.89} = 1.08358 = 1.08.$

$\therefore$ Number of Einstein absorbed $= 0.6 \times 1.08 = 0.65$

$\therefore\ \phi = \frac{0.35\,\text{mole}}{0.65\,\text{einstein}} = 0.5384615 = 0.54\ \text{mole. einstein}^{-1}.$

61. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process, AB + hv $\rightarrow$ AB, the rate of formation of AB is directly proportional to

(a) C (b) I (c) I^2 (d) C.I

Solution (b) The rate of photochemical process varies with the intensity of absorption since greater the intensity of absorbed light more photons will fall at a point, and further each photon causes one molecule to undergo reaction.

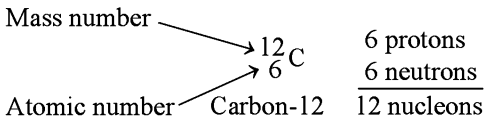
Nuclear chemistry

Nature of radiations from radioactive substances. Nuclear reactions; Radioactive disintegration series; Artificial transmutation of elements; Nuclear fission and Nuclear fusion: Isotopes and their applications: Radio carbon-dating.

Purely chemical reactions involve the rearrangement of the outermost electrons, i.e., atoms combine by sharing electrons (covalency) and by transferring electrons from one atom to another (electrovalency); in these processes atomic nuclei remain unchanged. Nuclear chemistry, however, investigates changes that occur in the atomic nucleus itself.

Nuclear reactions and their characteristics

An atom is characterized by its atomic number, Z, and its mass number, A. The atomic number, written as a subscript to the left of the element symbol, gives the number of protons in the nucleus. The mass number, written as a superscript to the left of the element symbol, gives the total number of nucleons, a general term for both protons (p) and neutrons (n). The most common isotope of carbon, for example, has 12 nucleons: 6 protons and 6 neutrons.



Atoms with identical atomic numbers but different mass numbers are called isotopes, and the nucleus of a specific isotope is called a nuclide. There are 13 known isotopes of carbon, 2 of which occur commonly (^{12}C and ^{13}C) and 1 of which (^{14}C) is produced in small amounts in the upper atmosphere by the action of neutrons from cosmic rays on ^{14}N. The remaining 10 carbon isotopes have been produced artificiall . Only the 2 commonly occurring ones are indefinitely stable; the other 11 undergo spontaneous nuclear reactions, which change their nuclei. Carbon-14, for example, slowly decomposes to give nitrogen-14 plus an electron, a process we can write as:

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{e}_{-1}e$$

The electron is often written as $^{0}_{-1}e$, where the superscript 0 indicates that the mass of an electron is essentially zero when compared with that of a proton or neutron, and the subscript –1 indicates that the charge is –1. (The subscript in this instance is not a true atomic number.)

Nuclear reactions, such as the spontaneous decay of ^{14}C, are distinguished from chemical reactions in several ways:

1. A nuclear reaction involves a change in an atom's nucleus, usually producing a different element. A chemical reaction, by contrast, involves only a change in distribution of the outer-shell electrons around the atom and never changes the nucleus itself or produces a different element.
2. Different isotopes of an element have essentially the same behaviour in chemical reactions but often have completely different behavior in nuclear reactions.
3. The rate of a nuclear reaction is unaffected by a change in temperature or pressure or by the addition of a catalyst.
4. The nuclear reaction of an atom is essentially the same, regardless of whether the atom is in a chemical compound or in uncombined elemental form.
5. The energy change accompanying a nuclear reaction is far greater than that accompanying a chemical reaction. The nuclear transformation of 1.0 g of uranium-235 releases 8.2×10^7kJ, for example, whereas, the chemical combustion of 1.0 g of methane (natural gas) releases only 56 kJ.

A nuclear power plant for generating electricity. The characteristically shaped stacks are cooling towers for the steam produced by heat from the nuclear reaction.

Nuclear reactions and radioactivity

Scientists have known since 1896 that many nuclides are radioactive—that is, they spontaneously emit radiation. Early studies of radioactive nuclei (radionuclides) by the British physicist Ernest Rutherford in

1897 showed that there are three common types of radiation with markedly different properties: alpha (α), beta (β), and gamma (γ) radiation, named after the first three letters of the Greek alphabet

Alpha (α) radiation

Using the simple experiment shown in figure, Rutherford found that a radiation consists of a stream of particles that are repelled by a positively charged electrode, are attracted by a negatively charged electrode, and have a mass-to-charge ratio identifying them as helium nuclei, ${}^{4}_{-1}He^{2+}$. Alpha particles thus consist of two protons and two neutrons.

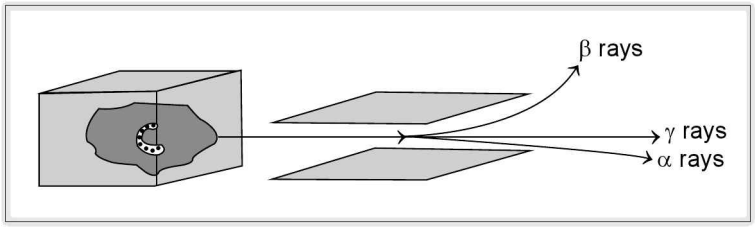
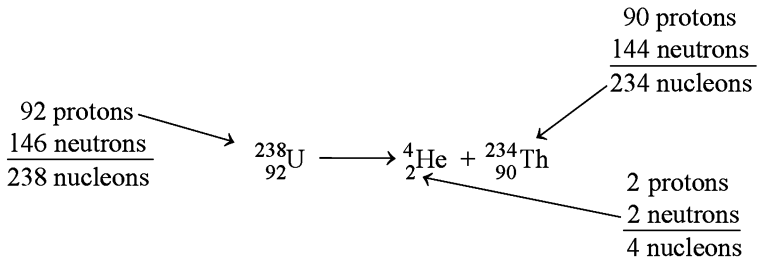


Fig. 4.23

Fig. 4.23 The effect of an electric field on α, β, γ radiation. The radioactive source in the shielded box emits radiation, which passes between two electrodes. Alpha radiation is deflected toward the negative electrode, β radiation is strongly deflected toward the positive electrode, and γ radiation is undeflected.

Because the emission of an alpha particle from a nucleus results in a loss of two protons and two neutrons, it reduces the mass number of the nucleus by 4 and reduces the atomic number by 2. Alpha emission is particularly common for heavy radioactive isotopes, or radioisotopes: Uranium-238, for example, spontaneously emits an alpha particle and forms thorium-234.



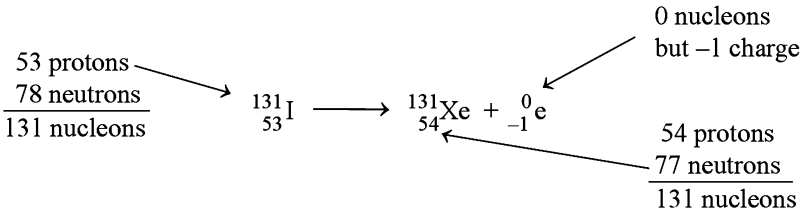
Note how the nuclear equation for the radioactive decay of uranium-238 into lighter elements is written. The equation is not balanced in the usual chemical sense because the kinds of nuclei are not the same on both sides of the arrow. Instead, we say that a nuclear equation is balanced when the sums of the nucleons are the same on both sides of the equation and when the sums of the charges on the nuclei and any elementary particles (protons, neutrons, and electrons) are the same on both sides. In the decay of ${}^{238}_{92}U$ to give ${}^{4}_{2}He$ and ${}^{234}_{90}Th$, for example, there are 238 nucleons and 92 nuclear charges on both sides of the nuclear equation.

Note also that we are concerned only with charges on elementary particles and on nuclei when we write nuclear equations, not with ionic charges on atoms. The alpha particle is thus written as ${}^{4}_{2}He$ rather than as ${}^{234}_{90}Th^{2-}$, and the thorium resulting from radioactive decay of ${}^{238}_{92}U$ is written as ${}^{234}_{90}Th$ Th rather than as ${}^{234}_{90}Th^{2-}$. We ignore the ionic charges both because they are irrelevant to nuclear disintegration and because they soon disappear. The ${}^{4}_{2}He^{2+}$ ion immediately picks up two electrons from whatever it strikes,

yielding a neutral helium atom, and the $^{234}_{90}Th^{2-}$ ion immediately gives two electrons to whatever it is in electrical contact with, yielding a neutral thorium atom.

Beta (β) radiation

Further work by Rutherford in the late 1800s showed that β radiation consists of a stream of particles that are attracted to a positive electrode, are repelled by a negative electrode, and have a mass-to-charge ratio identifying them as electrons, $^{0}_{-1}e$ or β. Beta emission occurs when a neutron in the nucleus spontaneously decays into a proton plus an electron, which is then ejected. The product nucleus has the same mass number as the starting nucleus because a neutron has turned into a proton, but it has a higher atomic number because of the newly created proton. The reaction of ^{131}I to give ^{131}Xe is an example:



Writing the emitted β particle as $^{0}_{-1}e$ in the nuclear equation makes clear the charge balance of the nuclear reaction: The subscript in the $^{131}_{53}I$ nucleus on the left (53) is balanced by the sum of the two subscripts on the right (54–1 = 53).

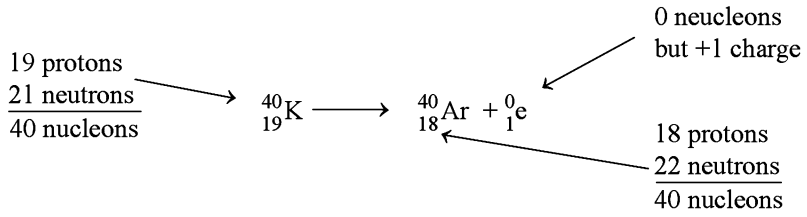
Gamma (γ) radiation

Gamma radiation is unaffected by electric fields, has no mass, and is simply electromagnetic radiation of very high energy and thus of very short wavelength. In modern terms, we would say that γ rays are a stream of high-energy photons. Gamma radiation almost always accompanies α and β emission as a mechanism for the release of energy, but it is often not shown when writing nuclear equations because it changes neither the mass number nor the atomic number of the product nucleus.

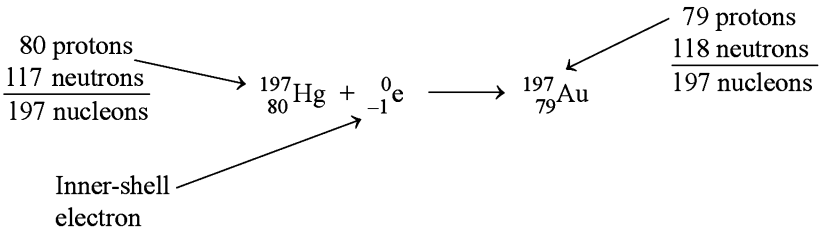
	Property	*α-rays*	*β-rays*	*γ-rays*
1.	Mass	6.64×10^{-24} g or 4 a.m.u.	9.11×10^{-28} g	Negligible
2.	Charge	+2 units	–1 units	0
3.	Identity	Helium nuclei (He^{2+})	Electrons	High energy radiations
4.	Energy	about $(6–16) \times 10^{-13}$ J	$(0.03–5.0) \times 10^{-13}$J	Same range as of β-particles
5.	Velocity	Nearly $\frac{1}{10}$th of light	Same as that of light (3.0×10^{8} m s^{-1})	Same as that of light
6.	Effect of electric and magnetic fields	Deflected towards negative pole	Defected towards positive pole	Not deflecte
7.	Penetrating power	Small	Large, 100 times that of α-rays	Very large, 10,000 times that of α-ray
8.	Power to ionize gases	Very large	Small	Very small
9.	Effect on photographic sulphide	Both are affected strongly more than β and γ-rays	Effect less than α-rays	Least effect on both

Positron Emission and Electron Capture

In addition to α, β, and γ radiation, two other common types of radioactive decay processes also occur. Positron emission involves the conversion of a proton in the nucleus into a neutron plus an ejected positron, ${}_{+1}^{0}e$ or β^+, a particle that can be thought of as a "positive electron." A positron has the same mass as an electron but an opposite charge. The result of positron emission is a decrease in the atomic number of the product nucleus but no change in the mass number. Potassium-40, for example, undergoes positron emission to yield argon-40, a nuclear reaction is important in geology for dating rocks. Note once again that the sum of the two subscripts on the right of the nuclear equation (18 + 1 = 19) is equal to the subscript in the ${}_{19}^{240}K$ nucleus on the left.



Electron capture is a process in which the nucleus captures an inner-shell electron and a proton is thereby converted into a neutron. The mass number of the product nucleus is unchanged, but the atomic number decreases by 1, just as in positron emission. The conversion of mercury-197 into gold-197 is an example:



Characteristics of the different kinds of radioactive decay processes are summarized in

Radioactive decay

The decay of a radioactive element is a random process and is not influenced by external factors such as temperature changes. The rate of decay is directly proportional to the number of atoms present, following an exponential law, the rate of decay decreasing with time. Kinetically, the process is a first order reaction and can be expressed by the equation:

$$-\frac{dN}{dt} = kN$$

Where N is the number of radioactive atoms present, t is the time, and k is the velocity constant Rearrangement of equation (1) followed by integration gives:

$$-\int \frac{dN}{N} = k\,dt$$

or $\quad -\log_e N = kt + \text{const.}$

If the number of radioactive atoms present at time t = 0 is N_0, then,

$$-\log_e N_o = \text{constant}$$

and $\quad -\log_e N = kt - \log_e N_o \qquad$ or $\qquad \log_e (N_o/N) = kt$

Conversion of Napierian logarithms to ordinary logarithms gives,

$$2{\cdot}303\log_{10}(N_o/N) = kt$$

Let $t_{\frac{1}{2}}$ represent the time needed for the original activity to decrease to a half, i.e., $N_0 = 2N$, then,

$$2{\cdot}303\log_{10}(N_o/\frac{1}{2}N_o) = 2{\cdot}303\log_{10}2 = kt_{\frac{1}{2}}$$

or $0{\cdot}6932 = kt_{\frac{1}{2}}$

or $t_{\frac{1}{2}} = \frac{0{\cdot}6932}{k}$

As equation shows, the time taken for half the activity to disappear ($t_{\frac{1}{2}}$), or the half-life as it is often called, is independent of the number of radioactive atoms. The half-life of a particular radioactive element is a characteristic constant of that element, and so too is the value of k which is termed the radioactive decay constant; it is often represented by the symbol 1 instead of k.

If radioactive decay proceeds by a number of individual steps, i.e., if the first radioactive decay product is itself radioactive and thus decays further, then each stage in the process is represented by its own characteristic rate equation and thus, by its own half-life and radioactive decay constant.

Half-Life

Just like a 1st order reaction the half life of radioactive decay is given by $t_{1/2} = \frac{0.693}{\lambda}$

Note: Let us start with 10 nuclei. If the half life is 5 minutes, then at the end of first 5 minutes, number of nuclei would be 5. Now, what would be the number of nuclei after next 5 minutes? Will it be 2.5 or 2 or 3? We can clearly see that it cannot be 2.5 and if it is 2 or 3 then it cannot be called as half life. This dilemma can be overcome by understanding that all formula relating to kinetics are only valid when the sample size is very large and in such a large sample size ,a small difference of 0.5 will be insignificant.

The fact that radioactive decay follows the exponential law implies that this phenomenon is statistical in nature. Every nucleus in a sample of a radionuclide has a certain probability of decaying, but there is no way to know in advance which nuclei will actually decay in a particular time span. If the sample is large enough – that is, if many nuclei are present – the actual fraction of it that decays in a certain time span will be very close to the probability for any individual nucleus to decay. To say that, a certain radioisotope has a half –life of 5 hour, then, signifies that every nucleus of this isotope has a 50 per cent chance of decaying in every 5 hour period. This does not mean a 100 per cent probability of decaying in 10 hour. A nucleus does not have a memory, and its decay probability per unit time is constant until it actually does decay. A half life of 5 hour implies a 75% probability of decay in 10 hour, which increases to 87.5% in 15 hour to 93.75% in 20 hour and so on, because in every 5 hour interval the probability of decay is 50 per cent.

Average–life time

Average life time is defined as the life time of a single isolated nucleus. Let us imagine a single nucleus which decays in 1 second. Assuming 1 second time interval to be very small the rate of change of nuclei would be 1/1 (because –dN = 1 and dt =1). We can also see that since $\frac{-dN}{dt} = \lambda N$, for a single isolated nucleus N = 1, $\frac{-dN}{dt} = \lambda$. Therefore, in this present case λ=1.

Now, let us assume the same nucleus decays in 2 seconds, we can see that $\frac{-dN}{dt}$ i.e., λ is equal to ½. You will also notice that in the 1st case the nucleus survived for 1 second and in the second case it survived for 2 second. Therefore, the life time of a single isolated nucleus is $\frac{1}{\lambda}$.

$$\therefore \quad t_{av} = \frac{1}{\lambda}$$

Activity

Activity by definition is the rate of decay of a radioactive element. It is represented as 'A' and is equal to λN. By no means should activity be confused with rate of change of radioactive nuclei represented by $\frac{-dN}{dt}$. This is because $\frac{-dN}{dt}$ talks about the overall change in the number of nuclei in a given instant of time while activity only talks about that change which is decay. For example, if you go out to a market with Rs 50 in your pocket and you spend Rs20 in 5 minutes then your rate of change of money in the wallet is Rs 4/min and in fact the rate of spending the money is also Rs 4/min. Here, you can see both are same. But if while spending Rs 20 in 5 minutes, somebody keeps Rs 10 in your wallet, then the rate of change of money in your wallet would became Rs 2.5/min, while the rate of spending the money is Rs 4/min. This implies that as long as the radioactive substance is only decaying the rate of change of nuclei and activity are same and equation (1) in terms of activity of a radioactive substance can be written as $A_t = A_o e^{-\lambda t}$. But if the radioactive substance is also being produced this $\frac{dN}{dt}$ = rate of production – activity,

Specific activity

This is activity per unit mass of the sample. Let radioactive sample weighing w gms have a decay constant λ. The number of nuclei in the w gms would be $\frac{w}{M} \times Av$, where M = molecular weight of the radioactive substance and Av= Avogadro's number.

$$\therefore \quad \text{Specific activity} = \frac{\left(\lambda \times \frac{w}{M} \times Av\right)}{w} = \frac{\lambda \times Av}{M}$$

It should be remembered that if a radioactive sample is pure and the product does not remain with reactant then specific activity is a constant

Units of activity

The unit of radioactivity of a substance is measured as the rate at which it changes into daughter nucleus. It has been derived on the scale of disintegration of Radium.

Let us consider 1g of radium (atomic mass = 226 and $t_{½}$=1600 yrs) undergoes decay, then

Rate of decay of radium = $\lambda \times$ Number of nuclei of Ra in 1 g

$$= \frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60} \times \frac{1 \times 6.023 \times 10^{23}}{226}$$

$= 3.7 \times 10^{10}$ dps $= 3.7 \times 10^{10}$ Becquerrel.

$=$ 1 curie ($\because$ 1 Ci $= 3.7 \times 10^{10}$ dps) $= 3.7 \times 10^{4}$ Rutherford ($\because$ 1 rd $= 10^{6}$ dps)

The SI unit of activity is dps or Becquerrel.

Carbon-14 dating

The ratio of $^{12}_{6}C$ and $^{14}_{6}C$(produced by neutron bombardment of $^{14}_{7}N$ due to cosmic ray interaction) is 10^{12}. 1 in nature. Carbon, in the form of CO_2, containing the above ratio of $^{12}_{6}C$: $^{14}_{6}C$, is taken up by plants during photosynthesis. Thus, in living plants, the ^{12}C:^{14}C ratio is 10^{12} : 1. Animals which feed on the plants and those which consume the animals also have the same ^{12}C: ^{14}C ratio in their life time. When the plant or animal dies, it cannot take up carbon any more, and henceforth, the $^{14}_{6}C$ goes on decaying without being replenished and so its amount gradually decreases depending on is life period. Thus, the determination of the ^{12}C: ^{14}C ratio can tell us when the plant or the animal had died.

Let us consider an example: In an Egyptian mummy, the ^{12}C:^{14}C ratio was found to be half of that in living human being. Calculate the approximate ime when the man had died. Given, $T_{\frac{1}{2}}$ of ^{14}C = 5760 years.

We know that, $\lambda = \frac{0.693}{T_{\frac{1}{2}}} = \frac{0.693}{5760}$ year. Let be the required time period.

According to the conditions of the problem, $\frac{N_0}{N} = \frac{1}{0.5}$

We know that, $2.303 \log \frac{N_0}{N} = \lambda_t$;

or, $\log \frac{N_0}{N} = \frac{\lambda_t}{2.303}$; or $\frac{2.303}{\lambda} \times \log \frac{N_0}{N} = t$.

$$\therefore \quad t = \frac{2.303 \times 0.3010 \times 5760}{0.693} = 5750 \text{ years.}$$

So, the man had died 5750 years ago.

Age of rock (by uranium dating)

Suppose × g of $^{206}_{82}Pb$ is found with y g of $^{238}_{92}U$.

$\lambda \rightarrow$ decay constant of uranium

$$^{238}_{92}U \rightarrow {}^{206}_{82}Pb$$

Amount of $^{238}_{92}U$ disintegrated = $\frac{x}{206} \times 238$ in time t

Hence, initial amount of $^{238}_{92}U = y + \frac{x}{206} \times 238$

$\lambda t = 2.303 \log (N_0/N)$

$t = ? \ \lambda =$ known, $N_0 = y + \frac{x}{206} \times 238$, $N = y$

$$\Rightarrow \quad t = \frac{2.303}{\lambda} \log \left(\frac{y + \frac{x}{206} \times 238}{y} \right)$$

(t = age of the rock)

Note: Age of mineral is determined by helium dating.



Worked-out Examples

62. A sample of pitchblende contains 0.05 g of Pb-206 for every gram of U-238 present in it. Calculate the age of rock ($t_{1/2}$ of U-238 = 4.5×10^9 years).

Solution Now amount of U-238 present N = 1 g
Amount of U-238 originally present, N_0

N_0 = Amount of U-238 now present + Amount of U-238 changed to Pb-206

$$= 1 + \frac{0.05 \times 238}{206} = 1.0578\text{g}$$

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}, \text{ where, } \lambda = \frac{0.693}{4.5 \times 10^9} \text{ year}^{-1}$$

$$\therefore \quad t = \frac{2.303}{0.693} \times 4.5 \times 10^9 \log \frac{1.0578}{1} = 3.65 \times 10^8 \text{ years}$$

63. An analysis of the rock shows that the relative number of ^{87}Sr and ^{87}Rb atom is $^{87}Sr/^{87}Rb$ = 0.052. Determine age of the rock. Given that the half-life period of β-decay of Rb to Sr is 4.7×10^{10} yer.

Solution $$\frac{\text{Atoms of Sr}}{\text{Atoms of Pb}} = 0.052 \text{ or } \frac{\text{Atoms of (Sr + Pb)}}{\text{Atoms of Pb}} = 1.052$$

or $$\frac{\text{Initial atoms of Pb}}{\text{Present atoms of Pb}} = 1.052$$

Now, $$t = \frac{2.303}{\lambda} \log \frac{[Pb]_0}{[Pb]} = \frac{2.303}{(0.693 / t_{1.2})} \log \frac{[Pb]_0}{[Pb]}$$

We get, $$t = \frac{2.303 \times 4.7 \times 10^{10}}{0.693} \log 1.052 = 3.44 \times 10^9 \text{y}$$

64. In nature, a decay chain series starts with $_{90}Th^{232}$ and finally terminates at $_{82}Pb^{208}$. A thorium ore sample was found to contain 8×10^{-5} mL of helium at STP and 5×10^{-7} g of Th^{232}. Find the age of the ore sample assuming the source of helium to be only due to the decay of Th^{232}. Also assume complete retention of helium with the ore. (Half life of $_{90}Th^{232} = 1.39 \times 10^{10}$y).

Solution $^{232}_{92}\text{Th} \longrightarrow {}^{208}_{82}\text{Pb}$

Number of α-particles emitted = 232 – 208/4 = 6

$\because$ 22400 mL He at STP contains = 6.023×10^{23} He atoms

$\therefore$ 8×10^{-5} mL He at STP contains = $\frac{6.023 \times 10^{23} \times 8 \times 10^{-5}}{22400} = 2.151 \times 10^{15}$ He atoms

$\because$ 6 α-particles are emitted by $^{232}_{92}\text{Th}$ atom

$\therefore$ 2.151×10^{15} α-particle are emitted by = $\frac{2.15 \times 10^{15}}{6}$ Th atoms = 3.585×10^{14} atoms

or Number of $^{232}_{90}\text{Th}$ used up = 3.585×10^{14} atoms

$\because$ 232 g $^{232}_{90}$ Th contains = 6.032×10^{23} atoms

$\therefore\ 5\times10^{-7}$ g $^{232}_{90}Th$ contains $= \dfrac{6.032\times10^{23}\times5\times10^{-7}}{232} = 1.298\times10^{15}$ atoms

Number of $^{232}_{90}Th$ atoms left, $N = 1.298\times10^{15}$ atoms

Total number of $^{232}_{90}Th$ atoms, $N_0 = 3.585\times10^{14} + 1.298\times10^{15} = 16.565\times10^{14}$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.39\times10^{10}} = 4.98\times10^{-11}$$

Now, $$t = \frac{2.303}{\lambda}\log\frac{N_0}{N} = \frac{2.303}{4.98\times10^{-11}}\log\frac{16.565\times10^{14}}{1.298\times10^{15}}$$

$$= \frac{2.303}{4.986\times10^{-11}}\left[\log16.565\times10^{14} - \log1.298\times10^{15}\right]$$

$$= \frac{2.303}{4.986\times10^{-11}}[15.2191-15.1133] = \frac{2.303\times0.1058}{4.986\times10^{-11}} = 4.89\times10^{9}\text{ years}$$

Nuclear stability and binding energy

The origin of the forces that accounts for nuclear stability is still much of a mystery, although it is clear that proton-neutron interaction is of great importance since no atom, other than that of hydrogen, contains only protons. Nuclear forces, whatever their nature, act over incredibly short distances, example it has been estimated that nuclear radii are of the order of magnitude 10^{-13} cm compared with 10^{-8} cm for atomic radii. The protons and neutrons (collectively known as nucleons) which constitute atomic nuclei are extremely tightly packed together, and estimates have shown that the densities of all atomic nuclei are in the region of 10^{14} g cm^{-3}. Despite the fact that little is known about the origin of nuclear forces, it is possible to calculate the energy needed to separate atomic nuclei into their isolated protons and neutrons; this quantity is called the binding energy of the nucleus. Consider the helium nucleus which contains 2 protons and 2 neutrons; the mass of the helium nucleus (on the $^{12}C = 12$ scale) is 4.0017 a.m.u. (atomic mass units) whereas, the individual masses of the isolated proton and neutron are 1-0073 and 1-0087 a.m.u. respectively. The total mass of 2 protons and 2 neutrons is (2 × 1-0073) + (2 × 1-0087) = 4-0320 a.m.u., i.e., there is a loss in mass of 4-0320–4-0017 = 0303 a.m.u. when 2 protons and 2 neutrons form the helium nucleus, and this difference is called the **mass defect.** This annihilation of mass corresponds to the release of energy according to Einstein's equation:

$$E = mc^2$$

Where, E is the energy released (in joules), m is the loss in mass (in kg), and c is the velocity of light (approximately 3×10^8 m/sec). It is instructive to calculate the energy released when 1 mole of helium atoms is formed from isolated protons and neutrons as follows:

The loss in mass in grammes for the formation of 1 mole of helium atoms from isolated protons and neutrons is:

0-0303N = 0-0303 × 6 × 10^{23} (where N is Avogadro's Number)

But, 1 atonomic mass unit = l/N g, = l/(6 × 10^{23}) g. Therefore, the loss in mass is:

0-0303 g or 0-0303 × 10^{-3}kg

The energy released is calculated from Einstein's equation:

$E = mc^2 = 0{\cdot}0303\times10^{-3}\times(3\times10^8)^2$ J

$= 0{\cdot}2727\times10^{13}$ J

Thus, the energy released is 2-7 × 10^{12} J. (approx.)

Binding energies are generally quoted as energy (in million electron volts (mev) per nucleon. The binding energy of the helium nucleus is calculated below.

The electron volt is the energy gained or lost by a particle of unit charge when it passes through a potential difference of 1 volt; 1 million electron volts (mev) are approximately equivalent to 9.6×10^{10} J/mol. The formation of one helium nucleus from its isolated protons and neutrons results in the release of

$$\frac{2{\cdot}7 \times 10^{12}}{9{\cdot}6 \times 10^{10}} \text{mev} = 28 \text{ mev (approx.)}$$

But the helium nucleus contains 4 particles (2 protons and 2 neutrons),
thus the binding energy per nucleon is,

$$\frac{28}{4} \text{mev} = 7 \text{ mev (approx.)}$$

Binding energies of the nuclei of other atoms can be calculated in a similar manner shows the binding energies of the nuclei of atoms plotted against their respective mass numbers.

Binding energy per nucleon plotted against mass number

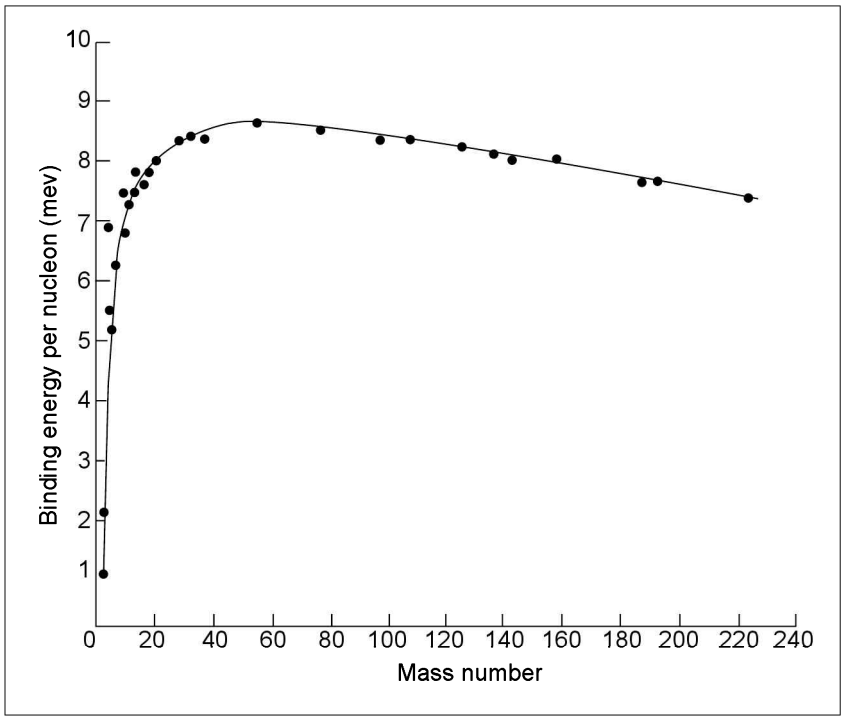


Fig. 4.24

Inspection of the graph shows that elements whose mass numbers lie in the region of 60 have the most stable nuclei, example iron, cobalt, nickel and copper. Elements with light nuclei, if they can be made to coalesce, should produce more stable and heavier nuclei with the release of energy, as in the hydrogen bomb explosion and in stellar reactions; similarly, elements whose nuclei are very heavy should be capable of fission into lighter and more stable nuclei with the release of energy, as in the atomic bomb explosion and in nuclear reactions. The nuclei of helium, beryllium, carbon and oxygen are exceptionally stable for their size, and they do not fit at all on the smooth binding energy curve. Since beryllium, carbon and oxygen have mass numbers which are integral multiples of the mass number of the helium nucleus, it is tempting to suggest that the nuclei of these elements contain respectively two, three and four closely associated

helium nuclei, i.e., 2 protons and 2 neutrons constitute a stable single entity. If the nuclei of all atoms can be considered to contain 'packets' of helium nuclei (not all the protons and neutrons can be considered to be arranged in this way since most elements have atoms which contain more neutrons than protons) then it is not difficult to see why radioactive decay results in the emission of β-particles (helium nuclei)



Worked-out Examples

65. The observed mass of $^{56}_{26}Fe$ is 55.9375 amu. Calculate the binding energy per nucleon of Fe atom. Take 1 amu = 931 MeV. [Mass of proton = 1.00737 amu, Mass of neutron = 1.00866 amu]

Solution The nucleus of $^{56}_{26}Fe$ contains 26 protons and 30 neutrons. Hence,

Mass of 26 protons = 26 × 1.00737 amu = 26.19162 amu

Mass of 30 neutrons = 30 × 1.00866 amu = 30.2598 amu

Total mass of 26 protons and 30 neutrons

= (26.19162 + 30.25980) amu = 56.45142 amu

Mass defect = (56.45142 – 55.9375) amu = 0.51392 amu

Binding energy = 0.51392 × 931 MeV = 478.45952 MeV

$$\text{Binding energy per nucleon} = \frac{478.45952\,\text{MeV}}{56} = 8.544\ \text{MeV}$$

66. Calculate the binding energy per nucleon (in MeV) in He atom, $^{4}_{2}He$, which has a mass of 4.00260 amu. (Mass of one neutron = 1.008665 amu and mass of 1 hydrogen atom = 1.007825 amu.)

Solution He atom contains 2 protons, 2 neutrons and 2 electrons

Mass of (2 protons + 2 electrons) = 2 × mass of 1 H atom

= 2 × 1.007825 amu = 2.01565 amu

Mass of 2 neutrons = 2 × 1.008665 amu = 2.017330 amu

∴ Mass of He atom = 2.01565 + 2.01733 = 4.03298 amu

Actual mass of He atom = 4.00260 amu

∴ Mass defect = 4.03298 – 4.00260 = 0.03038 amu

∴ Binding energy = 0.03038 × 931.5 MeV

= 28.298 MeV

(1 amu = 931.5 MeV)

$$\therefore\ \text{Binding energy per nucleon} = \frac{28.298}{4} = 7.0745\ \text{MeV}$$

Artificial breakdown of the atomic nucleus. The production of stable elements

The first artifici l breakdown of the atomic nucleus was achieved by Rutherford in 1919. He bombarded nitrogen gas with α-particles and obtained oxygen and a proton:

$$^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$$

Other nuclear transformations rapidly followed helium nuclei, protons and neutrons being used as the bombarding particles. For instance, the bombardment of beryllium with helium nuclei (α-particles) produces carbon and a neutron, thus:

$$^{9}_{4}Be + {}^{4}_{2}He \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n$$

Neutrons produced from the above nuclear reaction can be used in other transformations and they are convenient particles to use since, being uncharged themselves, they are not repelled by atomic nuclei. A typical neutron induced transformation is:

$$^{16}_{8}O + ^{1}_{0}n \longrightarrow ^{13}_{6}C + ^{4}_{2}He$$

An example of a proton induced transformation is:

$$^{27}_{13}Al + ^{1}_{1}H \longrightarrow ^{24}_{12}Mg + ^{4}_{2}He$$

Further research in this field led to the development of machines capable of accelerating the positively charged particles, example α-particles and protons, to very high speeds. One of the first machines, called the cyclotron, was designed by E. O. Lawrence in America; more powerful machines such as the synchrotron have since been developed.

The production of radioactive elements

The first nuclear transformation to give a radioactive element, which decayed to give a stable nucleus, was achieved by M. and Madme. Curie-Joliot in 1933. For instance, when magnesium was bombarded with α-articles, neutrons and positrons (positively charged electrons) were released. When the magnesium was removed from the source of the α-particles the formation of neutrons ceased but the production of positrons continued and aluminium was formed in the reaction. These results were explained by postulating the formation of an unstable isotope of silicon which then decayed to give aluminium by positron emission:

$$^{24}_{12}Mg + ^{4}_{2}He \longrightarrow \underset{\text{(radioactive)}}{^{27}_{14}Si} + ^{1}_{0}n$$

$$^{27}_{14}Si \longrightarrow ^{27}_{13}Al + ^{0}_{+1}e$$

The above reactions are conveniently written in a shorthand fashion thus:

$$^{24}_{12}Mg(\alpha,n)^{27}_{14}Si \longrightarrow ^{27}_{13}Al + ^{0}_{+1}e$$

Where α represents the projectile used in the reaction and n represents the particle emitted.

Other typical reactions which produce radioactive elements include the following:

α-particle induced reaction, Proton-induced reaction, Neutron-induced reaction

$$^{14}_{7}N(\alpha,n)^{17}_{9}F \longrightarrow ^{17}_{8}O + ^{0}_{+1}e$$

$$^{11}_{5}B(p,n)^{11}_{6}C \longrightarrow ^{11}_{5}B + ^{0}_{+1}e$$

$$^{23}_{11}Na(n,\gamma)^{24}_{11}Na \longrightarrow ^{24}_{12}Mg + ^{0}_{-1}e$$

Nuclear Fission

In 1939, Hahn and Stassmann discovered that a heavy atomic nucleus as of uranium-235 on bombardment by a neutron splits apart into two or more nuclei.

As illustrated in Figure 4.25, an incoming neutron causes the nucleus to split into two smaller pieces of roughly similar size. **The splitting of a heavy nucleus into two or more smaller nuclei is termed nuclear fission.** The smaller nuclei formed as a result of fission are called **fission products.** The process fission is always accompanied by the ejection of two or more neutrons and liberation of vast energy.

The fission of a nucleus does not occur in exactly the same way each time: More than 100 different fission pathways have been identified for uranium-235, yielding more than 200 different fission products. One of the more frequently occurring pathways generates barium-142 and krypton-91, along with two additional neutrons plus the one neutron that initiated the fission

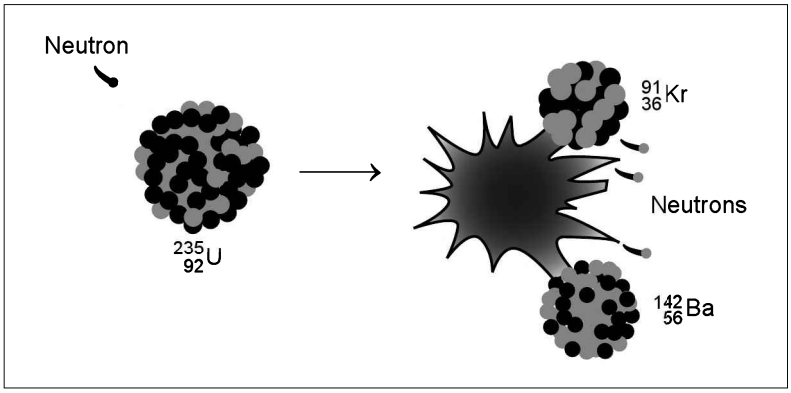


Fig. 4.25 A representation of nuclear fission. A uranium-235 nucleus fragments when struck by a neutron, yielding two smaller nuclei and releasing a large amount of energy.

$$^{1}_{0}n + {}^{235}_{92}U \longrightarrow {}^{142}_{56}Ba + {}^{91}_{36}Kr + 3\,{}^{1}_{0}n$$

The three neutrons released by fission of a ^{235}U nucleus can induce three more fissions yielding nine neutrons, which can induce nine more fissions yielding 27 neutrons, and so on indefinitel . The result is a chain reaction that continues to occur even if the supply of neutrons from outside is cut off (Figure 4.26). A chain reaction continues till most of the original nuclei in the given sample are fissioned, however, it may be noted that not all the neutrons released in the reaction are used up in propagating the chain reaction. Some of these are lost to the surroundings. Thus, for a chain reaction to occur, the sample of the fissionable material should be large enough to capture the neutron internally. If the sample is too small, most neutrons will escape from its surface, thereby breaking the chain. The **minimum mass of fissionable material required to sustain a chain reaction is called critical mass.**

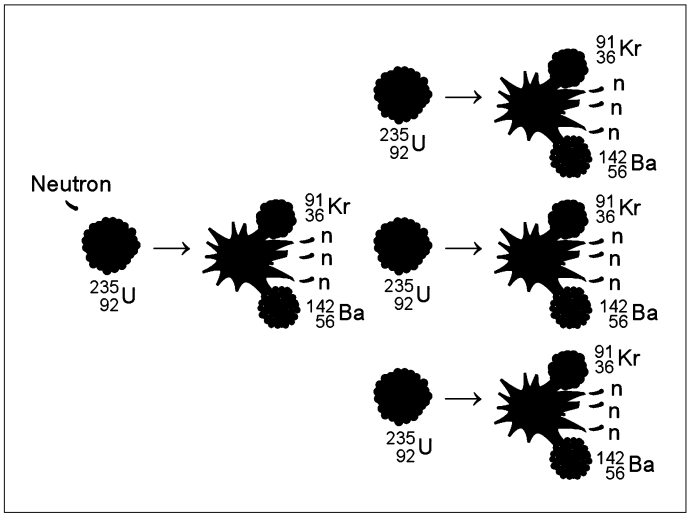


Fig. 4.26 A nuclear chain reaction, in which each fission event produces additional neutrons that induce more fissions. The rate of the process increaes at each stage.

At some point, the chain reaction may even occur so rapidly that a nuclear explosion results. For ^{235}U, the critical mass is about 56 kg, although the amount can be reduced to 15 kg by placing a coating of ^{238}U around the ^{235}U to reflect back some of the escaping neutrons. In these fission reactions, the mass of the products is less than the mass of the reactant. A decrease in mass of about 0.2 amu per uranium atom occurs. This mass is converted into an energy which is 2.5 million times of that produced by equivalent amount of coal.

Types of fission eaction : Two types

1. Uncontrolled or explosive fission reaction and (ii) controlled or critical fission reactio

(i) **Uncontrolled or explosive fission reaction**:

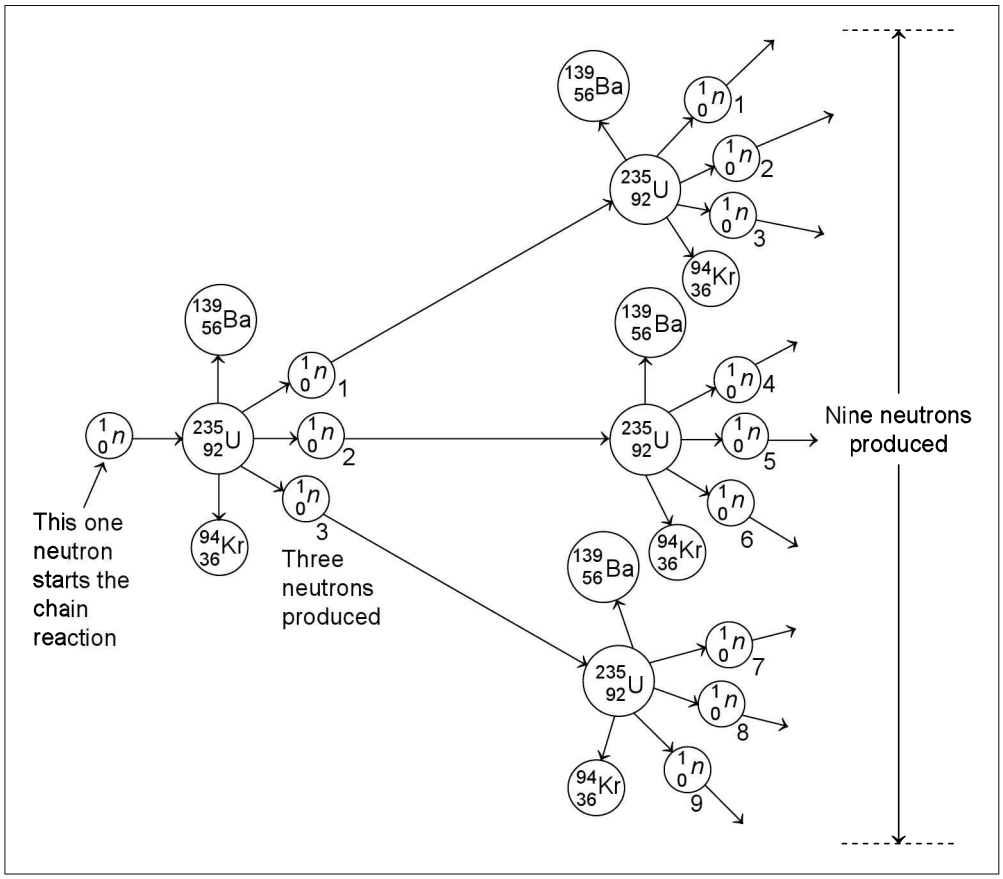


Fig. 4.27

This process of fission of U-235 goes on like an unending chain of fission reaction and ultimately an uncontrolled amount of heat energy (not useful for peaceful purpose) is produced in a very short time.

This explosive fission reaction takes place in atom bomb

Note: Why the chain reaction is not setup when we take natural uranium

Natural Uranium → $^{235}_{92}U$ (0.7%) (fissionable)

Natural Uranium → $^{238}_{92}U$ (99.3%) (nonfissionable)

When natural uranium without removing ^{238}U from it, is put to fission process, ^{235}U nuclei alone undergo fission but the chain reaction is not set up because the secondary neutrons produced in the fission of ^{235}U nuclei are absorbed by ^{238}U nuclei without causing any further fission reaction

$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U$$

Three different ways in which the fission chain eaction can take place (depending on value of K)

$$\text{Neutron-multilplication factor (K)} = \frac{\text{Number of neutrons produced per fission}}{\text{Number of neutrons producing fission}}$$

(a) When K = 1, in this type of reaction mass of U^{235} = critical mass
(minimum mass which can cause chain fission reaction
(b) When K < 1, in this type of reaction mass of U^{235} = subcritical mass
(mass < critical mass, cannot cause chain fission reaction
(c) K > 1, in this type of reaction mass of U^{235} = super critical mass
(mass > critical mass, can cause uncontrolled chain fission reaction and leads to explosion as in atomic bomb)

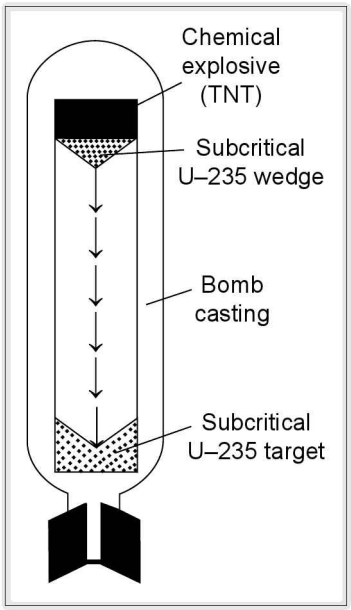


Fig. 4.28 A simple design of atomic bomb

(ii) **Controlled Fission Reaction**
The fission reaction can proceed at steady and slow rate by absorbing 2 of the 3 secondary neutrons by cd or B rods. Since it produced controlled quantity of heat, this energy can be converted into electricity with the help of atomic power plant.

The amount of energy released during nuclear fission can be calculated as in example by finding the accompanying mass change and then using the Einstein mass-energy relationship discussed in the previous section. When calculating the mass change, it is simplest to use the masses of the atoms corresponding to the relevant nuclei, rather than the masses of the nuclei themselves, because the number of electrons is the same in both reactants and products and thus cancels from the calculation.



Worked-out Examples

67. How much energy (in kj/mol) is released by the fission of uranium-235 to form barium-142 and krypton-91? The fragment masses are ^{235}U (235.0439 amu), ^{142}Ba (141.9164 amu), ^{91}Kr (90.9234 amu), and n (1.008 66 amu).

$$_0n^1 + {}_{92}U^{235} \rightarrow {}_{56}Ba^{142} + {}_{36}Kr^{91} + 3\ {}_0n^1$$

Solution First calculate the mass change by subtracting the masses of the products from the mass of the ^{235}U reactant:

Mass of ^{235}U = 235.0439 amu
- Mass of ^{142}Ba = –141.9164 amu
- Mass of ^{91}Kr = –90.9234 amu

- Mass of 2 n = –(2)(1.008 66 amu) = –2.0173 amu
Mass change: = 0.1868 amu (or 0.1868 g/mol)
Next, use the Einstein equation to convert the mass loss into an energy change:
$\Delta E = \Delta mc^2$
$= (0.1868 \text{ g/mol})\ (1 \times 10^{-3} \text{ kg/g})\ (3.00 \times 10^{8} \text{ m/s})$
$= 1.68 \times 10^{13} \text{ kg . m}^2/(\text{s}^2 \text{ . mol}) = 1.68 \times 10^{10} \text{ kJ/mol}$ Nuclear fission of 1 mol of ^{235}U releases 1.68×10^{10} kJ.

68. An alternate pathway for the nuclear fission of ^{235}U produces tellurium-137 and zirconium-97. How much energy (in kJ/mol) is released in this fission pathway?

$$_0n^1 + {}_{92}U^{235} \rightarrow {}_{52}Te^{137} + {}_{40}Zr^{97} + 2{}_0n^1$$

The masses are ^{235}U (235.0439 amu), ^{137}Te (136.9254 amu), ^{97}Zr (96.9110 amu), and n (1.008 66 amu).

Solution 1.79×10^{10} kJ/mol

Nuclear reactors

The same fission process that can lead to a nuclear explosion when uncontrolled can be used for the generation of electric power when carried out in a controlled manner in a nuclear reactor (Figure 4.29). The principle behind a nuclear reactor is simple: Uranium fuel is placed in a containment vessel surrounded by circulating coolant, and control rods are added. Made of substances such as boron and cadmium that absorb and thus regulate the flow of neutrons, the control rods are raised and lowered as necessary to maintain the fission at a barely self-sustainable rate so that overheating is prevented. Energy from the controlled fission heats the circulating coolant, which in turn produces steam to drive a turbine and produce electricity.

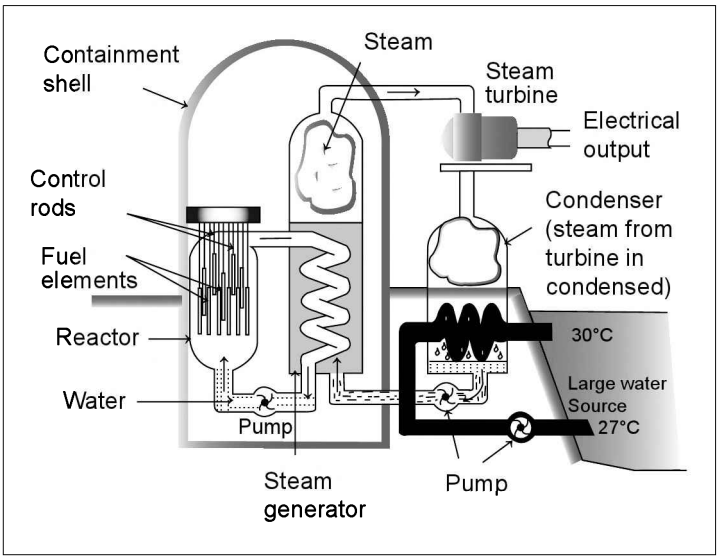
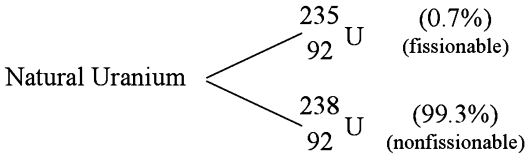


Fig. 4.29 A diagram of a nuclear power plant. Heat produced in the reactor core is transferred by coolant circulating in a closed loop to a steam generator, and the steam then drives a turbine to generate electricity.

Naturally occurring uranium is a mixture of two isotopes. The non-fissionable ^{238}U isotope has a natural abundance of 99.3%, while the fissio able ^{235}U isotope is present only to the extent of 0.7%. The fuel used in nuclear reactors is typically made of compressed pellets of UO2 that have been isotopically enriched to a 3% concentration of ^{235}U and then encased in zirconium rods. The rods are placed in a pressure vessel filled with water, which acts as a moderator to slow the neutrons so that they can be captured more

readily. No nuclear explosion can occur in a reactor because the amount and concentration of fissionable fuel is too low. In a worst-case accident, however, uncontrolled fission could lead to enormous overheating that could melt the reactor and surrounding containment vessel, thereby releasing large amounts of radioactivity to the environment.

Breeder reactor



Scientists have been trying to build reactors in which the neutrons produced from the fission of ^{235}U can be partially used to carry out the fission of ^{235}U and partially to produce fissionable Pu.239 and U.233 from U.238. This is done in reactors named as Breeder reactor which produces more fissionable material than it consumes.

What is nuclear fusion?

Nuclear fusion is a nuclear reaction in which lighter nuclei combine together (i.e., are fused together) to form a single heavy and more stable nucleus and a large amount of energy is also released (called fusion energy). For example, the following nuclear reaction which shows the formation of one helium nucleus, ${}^{4}_{2}He$ (heavy nucleus) by the combination (fusion) of two deuterons, ${}^{2}_{1}H$ (light nuclei) is a fusion reaction. In this reaction, energy equal to 23.75 MeV is also released.

$$ {}^{2}_{1}H + {}^{2}_{1}H \xrightarrow{\text{Fusion}} {}^{H}_{2}He + 23.7 \text{ MeV} $$

More examples of nuclear fusion reactions

The following nuclear reactions are the examples of fusion reactions:

$$ 4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2{}^{0}_{+1}e + 24.64 \text{ MeV.} $$

$$ {}^{1}_{1}H + {}^{1}_{1}H \longrightarrow {}^{2}_{1}H + {}^{0}_{+1}e + 0.42 \text{ MeV} $$

$$ {}^{2}_{1}H + {}^{1}_{1}H \longrightarrow {}^{3}_{2}He + 5.50 \text{ MeV.} $$

$$ {}^{13}_{6}C + {}^{1}_{1}H \longrightarrow {}^{14}_{7}N + 7.55 \text{ MeV} $$

$$ {}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{3}_{2}He + {}^{1}_{0}n + 3.3 \text{ MeV} $$

$$ {}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6 \text{ MeV} $$

Conditions necessary for fusion

(i) When the two lighter nuclei are brought closer to each other to combine together to form the heavy nucleus, the protons present in their respective nuclei repel each other. Hence, in order to overcome the repulsive forces, both the lighter nuclei should be given high kinetic energy, i.e., the nuclei should be fused at high temperature. Thus, nuclear fusion takes place only when the temperature is very high (4×10^6 degrees Celsius). Since nuclear fusion reactions require very high temperature, these reactions are also called thermo-nuclear reactions or temperature-dependent nuclear reactions

(ii) High pressure is also essential so that collisions are frequent. High temperature and high pressure both can be obtained only by the explosion of an atomic bomb. Therefore, on the earth, fusion reaction can take place during the explosion of an atom bomb. However, in the sun and stars high temperature is already there.

Energy released in the nudear fusion reactions

We have already said that in a nuclear fusion reaction, energy is released, i.e., nuclear fusion reaction is an exoergic raction. The energy released is called fusion energy.

The release of energy takes place because of the fact that in this reaction some mass is lost, since the sum of the masses of the reactants is greater than the sum of the masses of the products. The mass lost is converted into energy which is released in the reaction. The energy is calculated with the help of Einstein's mass energy relationship viz. $E = mc^2$ (E = energy, m = mass and c = velocity of light). If mass lost is in amu, then energy released

= Mass lost or loss in mass (in amu) × 931.5 MeV

= [(sum of the masses of the reactants) – (sum of the masses of the products)] × 931.5 MeV.

The magnitude of energy released in a nuclear fusion reaction is so high that scientists have not been able to control its magnitude as yet, i.e., in a nuclear fusion reaction an uncontrolled amount of energy is obtained and hence, this energy cannot be used for a peaceful purpose (example for the production of electricity). Note that the magnitude of energy obtained in the fission of ^{235}U nucleus by slow neutrons is also high but it can be converted into a controlled amount in a nuclear reactor and then can be converted into electricity.

Amount of energy released in the formation of one $_1^4He$ nucleus by the fusion of four $_1^1H$ nuclei

We know that the formation of one $_2^4He$ nucleus by the fusion of four $_1^1H$ nuclei can be shown as,

$$4\,{}_1^1H \longrightarrow {}_2^4He + 2\,{}_{+1}^0e \text{ (positrons)}$$

Mass of the reactants = 4 × mass of one H-atom

= 4 × 1.0078256 amu = 4.0313024 amu

Mass of the products = mass of He nucleus + 2 × mass of one positron

= (4.0026 + 2 × 0.0005486) amu = 4.0036972 amu

∴ Mass lost = (4.0313024 – 4.0036972) amu = 0.0276052 amu

∴ Energy released in the formation of one helium nucleus ($_2^4He$) = 0.0276052 × 931.5 MeV

= 25.7140 Mev

Energy released in the formation of one mole of helium nucleus from four moles of hydrogen,

$= 25.7140 \times 6.022 \times 10^{23}$ Mev = $25.7140 \times 6.022 \times 10^{23} \times 1.602 \times 10^{-16}$KJ

$= 248.0692 \times 10^7$ KJ ='4.806×10^8 KJ

Eriergy released in the fusion of one gram of hydrogen,

$$= \frac{24.806 \times 10^8}{4 \times 1.0078} \text{ KJ} = 6.153 \times 10^8 \text{ KJ}$$

Here, it may be noted that the burning of 1 g of coal in air produces only 0.350 KJ of heat energy. Obviously the difference between 6.153×10^8 and 0.350 is very high. **Origin of the energy of the sun and stars (stellar energy or solar energy).**

The temperature in the centre of the sun is extremely high (about 2×10^7 Kelvin). Sun has been providing us continuously heat and light for the last billion of years and will continue to do so for a similar another period, yet its temperature has never decreased nor it is likely to decrease even in the future. Now some questions arise: How is the energy produced in the sun? Why does the temperature of the sun not decrease?

It was in 1932 when Hans Bethe answered the above questions by proposing that the production of heat in the sun is due to the fusion reaction which is going on inside the sun (or stars) all the time.

Analysis of the spectrum of the light emitted by the sun has shown that the sun contains a tremendous quantity of $^{1}_{1}H$-atoms (Le., protons, $^{1}_{1}H$). According to Bethe, four hydrogen nuclei $(4\,^{1}_{1}H)$ combine together (i.e., are fused together) at high temperature prevailaing in the sun and form one $^{4}_{2}$ He nucleus (heavier nucleus) and two positrons ($^{0}_{+1}e$), and a large amount of heat and light energy is also produced.

$$4\,^{1}_{1}H \xrightarrow[\text{in the sun}]{\text{Fusion at high temperature}} {}^{4}_{2}He + 2\,{}^{0}_{+1}e + 24.64\ \text{MeV}.$$

It is this liberated energy which produces extremely high temperature in the sun and is also supplied in the form of heat and light by the sun to the earth. The above discussion shows that the sun may be regarded as a big thermonuclear furnace. Here, it should be noted that the conversion of four $^{1}_{1}H$ nuclei into one $^{4}_{2}$ He nucleus which is the source of the solar energy is so slow even at such a high temperature prevailing in the sun that it takes several million years for the conversion of one gram of hydrogen into helium. Why the sun produces energy at high rate is because of the enormous size of the sun.

The above hydrogen-helium fusion reaction does not take place through a single step; rather, it occurs through the following two types of cycles:

(i) Proton-proton cycle or (p-p) cycle. This cycle proceeds through the following three steps. In each step energy is released.

(a) $\left[{}^{1}_{1}H + {}^{1}_{1}H \rightarrow {}^{2}_{1}H + {}^{0}_{+1}e + 0.42\ \text{MeV}\right] \times 2$

(b) $[{}^{2}_{1}H + {}^{1}_{1}H \rightarrow {}^{3}_{2}He + 5.50\text{MeV}] \times 2$

(c) ${}^{3}_{3}He + {}^{3}_{2}He \rightarrow {}^{4}_{2}He + 2\,{}^{1}_{1}H + 12.80\ \text{MeV}$

On adding (a) × 2, (b) × 2 and (c), we get:

$$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{+1}e + (0.84 + 11.00 + 12.80)$$

or $\quad 4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{+1}e + 24.64\ \text{MeV}.$

(ii) Carbon-nitrogen cycle or (C–N) cycle. This cycle operates through the following six stes. In each step energy is also released.

$${}^{12}_{6}C + {}^{1}_{1}H \longrightarrow {}^{13}_{1}N\ (\text{unstable}) + 1.94\ \text{MeV}.$$

$${}^{13}_{7}N \longrightarrow {}^{13}_{6}C + {}^{0}_{+1}e + 1.20\ \text{MeV}.$$

$${}^{13}_{7}C + {}^{1}_{1}H \longrightarrow {}^{14}_{7}N + 7.55\ \text{MeV}.$$

$${}^{14}_{7}N + {}^{1}_{1}H \longrightarrow {}^{15}_{8}O\ (\text{unstable}) + 7.29\ \text{MeV}.$$

$${}^{15}_{8}O \longrightarrow {}^{15}_{7}N + {}^{0}_{+1}e + 1.74\ \text{MeV}.$$

$${}^{15}_{7}N + {}^{1}_{1}H \longrightarrow {}^{12}_{6}C + {}^{4}_{2}He + 4.96\ \text{MeV}.$$

On adding all the above six equation we get:

$$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{+1}e + (1.94 + 1.20 + 7.55 + 7.29 + 1.74 + 4.96)$$

or $\quad 4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{+1}e + 24.98\ \text{MeV}.$

In (C – N) cycle chain reactions $^{12}_{6}C$ acts as a sort of catalyst, since this istotope is regenerated at the end of these reactions. This cycle does not contribute much to the production of solar energy,

since the temperature at the sun's centre (of the order of 2×10^7 Kalvin) is too low for this reaction to proceed.

In certain more massive stars, the temperature prevailing is many times higher than the solar temperature. At these high temperatures (C – N) cycle chain reactions proceed very well and is the principal source of the energy of the massive stars.

An interesting problem

We have said above that the heat energy of the sun is generated by the fusion of four ${}_1^1H$ nuclei into one ${}_2^4He$ nucleus. Thus in the production of heat energy ${}_1^1H$ nuclei present in the sun are being consumed continuously due to their conversion into ${}_2^4He$ nuclei. Now, here a question arises. If the consumption of ${}_1^1H$ nuclei goes on continuously, then a day may come when all the stock of hydrogen in the sun will be consumed and no more fusion reaction will take place and hence no energy will be obtained.

The answer to the above question has been given as follows:

When all the ${}_1^1H$ nuclei are exhausted by their conversion into ${}_2^4He$ nuclei, the temperature and pressure in the sun will decrease and the sun will shrink in size under its own gravitational attraction. When the sun has considerably shrunk in its size, the temperature in the sun will again become high—so high that ${}_2^4He$ nuclei will fuse together to form ${}_6^{12}C$ isotope and a tremendous amount of energy will be liberated ($3\,{}_2^4He > {}_6^{12}C$ + Energy). In this way sun will regain its lost sun-shine and will become as bright as ever.

Hydrogen bomb

Hydrogen bomb consists of (deuterium + tritium) core, which is surrounded by an atomic bomb assembly. When atomic bomb is detonated, explosion takes place and extremely high temperature and pressure are attained. High temperature and high pressure thus obtained, make ${}_1^2H$ and ${}_1^3H$ nuclei to fuse together to produce helium nucleus (${}_2^4He$) and an uncontrolled amount of energy is also generated.

$$ {}_1^2H(\text{Deuterium}) + {}_1^3H(\text{Tritium}) \xrightarrow{\text{Fusion}} {}_2^4He + {}_0n^1 + 17.6\ \text{MeV}. $$

This reaction takes place at a very high speed which cannot be controlled, i.e., an uncontrolled fusion reaction takes place in hydrogen bomb. Since atomic bomb is used to produce high temperature and high pressure, which are essential for the fusion of ${}_1^2H$ and ${}_1^3H$ nuclei to produce ${}_2^4He$ nucleus, this bomb is named as trigger. Comparison between hydrogen bomb and atomic bomb

(i) We have already said that in an atomic bomb, uncontrolled fission reaction takes place. For the occurrence of such a reaction the mass of the fissionable material (like ^{235}U nucleus) should be greater than its critical mass. On the other hand, in a hydrogen bomb any amount of the fusible materials can be taken.

(ii) The amount of energy released in a hydrogen bomb is several times greater than that produced due to the explosion of atomic bomb.

Comparison between nuclear fission reactions and nuclear fusion reactions

(A) Similarity:

The only similarity between these two types of reactions is that the cause of the production of energy is the same and that is loss in mass (mass defect), *Le.,* energy is released because of the fact that the sum of the masses of the products Is less than the sum of the masses of the reactants. The mass which is lost is converted into energy and this energy is generated in the reaction.

(B) Dissimilarities:

(i) Nuclear fission is a nuclear reaction in which a heavier nucleus splits up into two lighter nuclei. On the other hand, nuclear fusion reaction is that nuclear reaction in which two lighter nuclei combine together (fuse together) to form a heavier nucleus.

(ii) Nuclear fission is a chain reaction while nuclear fusion is not so, since the product formed in this reaction is a single nucleus which is stable.

(iii) Nuclear fission is carried out by using slow moving neutrons while nuclear fusion reaction takes place at high tempurature and high pressure, since these are essential for overcoming the repulsive forces, existing between the protons present in the lighter nuclei which are fusing together to form the heavy nucleus.

(iv) The amount of energy produced in nuclear fusion reaction is much more than that generated in a fission reaction, since the loss in mass in a fusion reaction is greater than that in a fission reaction.

(v) The products (example $^{139}_{56}Ba$ and $^{94}_{36}Kr$) obtained in a nuclear fission reaction are radioactive and emit harmful radioactive radiations. Thus, these products are harmful. So the problem of the disposal of these harmful products arises. The products (example $^{4}_{2}He$) obtained in the fusion reaction are not radioactive and hence are harmless.

Uses of radioisotopes

The uses of radioisotopes are numerous, example carbon-14 is used to label organic molecules and its fate during subsequent breakdown of these molecules can be traced, thus allowing reaction mechanisms to be investigated; similarly, the labelling of phosphatic fertilizers with radioactive phosphorus-32 can be employed to determine the uptake of phosphorus by plants.



Worked-out Examples

69. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial velocity is ten times the permissible value, after how many days will it be safe to enter the room?

(a) 100 days (b) 1000 days

(c) 300 days (d) 10 days

Solution (a) Suppose activity of safe working = A

Given, $A_0 = 10A$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t_{1/2} = \frac{2.303}{\lambda} \log \frac{A_0}{A} = \frac{2.303}{0.693/30} \log \frac{10A}{A}$$

$$= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \text{ days.}$$

70. Which of the following nuclear reactions will generate an isotope?

(a) β-particle emission (b) Neutron particle emission

(c) Positron emission (d) α-particle emission.

Solution (b) Isotopes are atoms of same element having same atomic number but different atomic masses. Neutron has atomic number 0 and atomic mass 1. So loss of neutron will generate isotope. example,

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239}$$

71. An element $_{z}^{A}M$ undergoes an α-emission followed by two successive p-emissions. The element formed is .....

Solution $_{Z}M^{A-4}$

72. The number of neutrons in the parent nucleus which gives $_7N^{14}$ on beta emission is ..... **[IITJEE-1985]**

Solution 8; $_6C^{12} \rightarrow {}_7N^{14} + {}_{-1}e^0$

73. A radioactive nucleus decays emitting one alpha and two beta particles; the daughter nucleus is ..... of the parent.

Solution isotope

74. In p-emission from a nucleus the atomic number of the daughter element decreases by one. (1990-1 Marks)

Solution **False:** In β-emission ($_{-1}e^\circ$) the atomic number of the daughter nuclei increases by 1.

75. $_{13}Al^{27}$ is a stable isotope, is expected to disintegrate by

(a) α-emission (c) positron emission (b) β-emission (d) proton emission

Solution (b) The species $_{13}Al^{29}$ (Number of neutrons = 16) contains more neutrons than the stable isotope $_{13}Al^{27}$

(Number of neutrons =14).

Neutron on decomposition shows β-emission.

$$_0n^1 \rightarrow {}_{+1}p^1 + \underbrace{{}_{-1}e^0}_{\beta-\text{particle}}$$

76. The number of neutrons accompanying the formation of $_{54}Xe^{139}$ and $_{38}Sr^{94}$ a slow neutron by $_{92}U^{235}$ followed by nuclear fission is,

(a) 0 (b) 2 (c) 1 (d) 3

Solution (d) The guiding rule is:

The mass number and atomic numbers do not change in a nuclear reaction.

The given nuclear fission reaction is,

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{139}_{54}xe + {}^{94}_{38}Sr + 3{}^{1}_{0}n$$

77. ^{23}Na is the more stable isotope of Na. Find out the process by which i^4Na can undergo radioactive decay. **[IITJEE-2003]**

(a) β^- emission (b) α emission (c) β^+ emission (d) K electron cap

Solution (a) n/p ratio of ^{24}Na nuclide is 13/11 i.e., greater than unity and hence radioactive. To achieve stability, it would tend to adjust its n/p ratio to the proper value of unity. This can be done by breaking a neutron into proton and electron.

$$_0n^1 \rightarrow {}_{+1}p^1 + {}_{-1}e^0 \text{ or } \beta^-$$

The proton will stay inside the nucleus whereas electron which cannot exist in the nucleus, will be emitted out as β-ray.

78. Nuclear reactions accompanied with emission of neutron(s) are:

(a) $^{17}_{13}Al + {}^{4}_{2}H \rightarrow {}^{30}_{15}P$ (b) $^{12}_{6}C + {}^{1}_{1}H \rightarrow {}^{13}_{7}N$

(c) $^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^{0}_{1}e$ (d) $^{241}_{96}Am + {}^{4}_{2}He \rightarrow {}^{244}_{97}Bk + {}^{0}_{1}e$

Solution (a, d)

(a) $\mathbf{_{13}Al^{27} + {}_2He^4 \rightarrow {}_{15}P^{30} + {}_0n^1}$

(d) $\mathbf{_{96}Am^{241} + {}_2He^4 \rightarrow {}_{97}Bk^{244} + {}_1e^0 + {}_0n^1}$

79. A positron is emitted from $^{23}_{11}Na$. The ratio of the atomic mass and atomic number of resulting nuclide is **[IIT-2007]**

(a) 22/10 (b) 22/11

(c) 23/10 (d) 23/12

Solution (c) $^{23}_{11}Na \longrightarrow {}^{23}_{10}X + {}^{0}_{1}\beta$

80. The total number of α and β particles emitted in the nuclear reaction $^{238}_{92}U \rightarrow {}^{214}_{82}Pb$ is **[IIT-2009]**

Solution $_{92}U^{238} \rightarrow {}_{82}Pb^{214}$

Number of α particle $= \dfrac{238 - 214}{4}$

$= \dfrac{24}{4} = 6\alpha$

Number of β particle = 2β

Total particle = 6 + 2 = 8

ONE CORRECT OPTION TYPE QUESTIONS

1. The kinetic datas for the reaction: $2A + B_2 \longrightarrow 2AB$ are as given below:

[A] mol L^{-1}	[B_2] mol L^{-1}	Rate mol L^{-1} min^{-1}
0.5	1.0	2.5×10^{-3}
1.0	1.0	5.0×10^{-3}
0.5	2.0	1×10^{-2}

Hence, the order of reaction with respect to A and B_2 are, respectively,

(a) 1 and 2 (b) 2 and 1
(c) 1 and 1 (d) 2 and 2

2. Thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 minute show long will it take for 90% of the compound to decompose?

(a) 399 min (b 410 min
(c) 250 min (d) 120 min

3. Two substances A and B are present such that $[A_0] = 4[B_0]$ and half–life of A is 5 minutes and that of B is 15 minutes. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same.

(a) 15 minutes (b) 10 minutes
(c) 5 minutes (d) 12 minutes

4. For the first order reaction $A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$, the initial pressure is $P_A = 90$ mm Hg, the pressure after 10 minutes is found to be 180 mm Hg. The rate constant of the reaction is ($\log_{10}2 = 0.3$)

(a) 1.15×10^{-3} sec^{-1} (b) 2.3×10^{-3} sec^{-1}
(c) 3.45×10^{-3} sec^{-1} (d) 6×10^{-3} sec^{-1}

5. The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm the rate of reaction relative to the initial rate is

(a) 1/48 (b) 1/24
(c) 9/16 (d) 1/6

6. A catalyst lowers the activation energy of a reaction from 20 kJ $mole^{-1}$ to 10 kJ $mole^{-1}$. The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at 27°C is

(a) –123°C (b) 327°C
(c) 327°C (d) + 23°C

7. The inversion of cane sugar proceeds with half–life of 500 minute at pH 5 for any concentration of sugar. However if pH = 6, the half life changes to 50 minute. The rate law expression for the sugar inversion can be written as

(a) $r = K[sugar]^2[H]^6$ (b) $r = K[sugar]^1[H]^0$
(c) $r = K[sugar]^0[H^+]^6$ (d) $r = K[sugar]^0[H^+]^1$

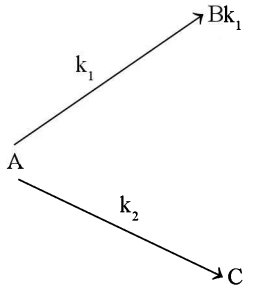
8. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{14} s^{-1} respectively the value of the rate constant as $T \rightarrow \infty$ is

(a) 2.0×10^{18} s^{-1} (b) 6.0×10^{14} s^{-1}
(c) ∞ (d) 3.6×10^{30} s^{-1}

9. A substance undergoes first order decomposition.

If follows two first order reactions as follow

$K_1 = 12.6 \times 10^{-4}$ s^{-1}



$K_2 = 3.8 \times 10^{-5} s^{-1}$.

(a) 75% B and 25% C
(b) 80% B and 20% C
(c) 68% B and 40% C
(d) 76.83% B and 23.17% C

10. At particular concentration, the half-life of the reaction is 100 minutes. When the concentration of the reactant becomes 10 times, the half-life of the reaction becomes 60 seconds, then what will be the order of the reaction?

(a) 1 (b) 2
(c) 0 (d) 3

11. $A \rightarrow$ Product, $\frac{dx}{dt} = k[A]^3$

If a is the initial concentration and (a – x) is the concentration of A after time t, then rate constant is given by:

(a) $k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$

(b) $k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$

(c) $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

(d) $k = \frac{x}{t}$

12. For the reaction,

$2H_2 + 2NO \rightarrow N_2 + 2H_2O$

the following mechanism has been proposed:

(i) $2NO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (fast)

(ii) $N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ (r.d.s)

(iii) $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

then what will be the rate law of this reaction?

(a) $r = k[NO]\,[H_2]^2$ (b) $r = k[NO]\,[H_2]$

(c) $r = k[NO]^0\,[H_2]^3$ (d) $r = k[NO]^2[H_2]$

13. The reaction: $A_2 + B_2 \rightarrow 2AB$ is bound to obey the following mechanism:

(i) $A_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A + A$ (fast)

(ii) $A + B_2 \xrightarrow{k_2} AB + B$ (slow)

(iii) $A + B \longrightarrow AB$ (fast)

the order of the over all reaction will be

(a) 3 (b) 2

(c) 2.5 (d) 1.5

14. The decomposition of ozone into oxygen gas i.e., $2O_3 \rightarrow 3O_2$ proceeds through the following mechanism.

(i) $O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ ...(fast)

(ii) $O + O_3 \xrightarrow{k_2} 2O_2$ ...(slow)

then what will be the order with respect O_3, O_2 and reaction respectively?

(a) 3, –1, 2 (b) 1, 2, 3

(c) 1, –2, 1 (d) 2, –1, 1

15. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6×10^{14} s^{-1} respectively. The value of the rate constant at

(a) 2.0×10^{18} s^{-1} (b) 6.0×10^{14} s^{-1}

(c) Infinity (d) 3.6×10^{30} s^{-1}

16. For the decomposition of $N_2O_5(g)$, it is given that:

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$;

Activation energy E_a

$N_2O_5(g) \rightarrow 2NO_2(g) + (1/2)O_2(g)$;

Activation energy E'_a

then:

(a) $E_a = E'_a$ (b) $E_a > E'_a$

(c) $E_a < E'_a$ (d) $E_a = 2E'_a$

17. It is observed that for reaction $x \rightarrow Y + Z$ rate increases by a factor 2.25 when the concentration of x is increased by a factor 1.5 at the same temperature. What is order of reaction with respect to X?

(a) 1 (b) 2

(c) 3/2 (d) $\frac{1}{2}$

18. If the activation energy of a reaction is zero (hypothetical) what will be the temperature coefficient of rate

(a) 1 (b) 2

(c) $\propto$ (d) zero

19. If the reactant A is simultaneously involved in the following elementary reactions,

$A \xrightarrow{k_1} B \quad 2A \xrightarrow{k_2} C \quad 3A \xrightarrow{k_3} D$

the rate of disappearance of A will be

(a) $-\frac{d[A]}{dt} = k_1[A] + k_2[A]^2 + k_3[A]^3$

(b) $-\frac{d[A]}{dt} = k_1[A] + 2k_2[A]^2 + 3k_3[A]^3$

(c) $-\frac{d[A]}{dt} = k_1[A] + \frac{1}{2}k_2[A]^2 + \frac{1}{3}k_3[A]^3$

(d) $-\frac{d[A]}{dt} = (k_1 + \frac{1}{2}k_2 + \frac{1}{3}k_3)[A]$

20. The hydrolysis of an estedr was carried our separately with 0.05 M HCl and 0.05 M H_2SO_4. Which of the following will be true?

(a) $k_{HCl} > k_{H_2SO_4}$

(b) $k_{HCl} < k_{H_2SO_4}$

(c) $K_{HCl} = k_{H_2SO_4}$

(d) $k_{H_2SO_4} = 2K_{HCl}$

21. If for a reaction 1 and 2, activation energies are E_A and E_{A_2} and rate constants are K_1 and K_2 at temperature T and K_1' and K_2' at temperature T' where T' is higher than T then which among the following is true if $E_{A_1} > E_{A_2}$?

(a) $\frac{K_1'}{K_1} > \frac{K_2'}{K_2}$

(b) $\frac{K_1'}{K_1} < \frac{K_2'}{K_2}$

(c) $\frac{K_1'}{K_1} = \frac{K_2'}{K_2}$

(d) None

22. On introducing a catalyst at 500 K the rate of a first order reaction increases by 1.718 times. The activation energy in presence of catalyst is 4.15 kJ mol^{-1}. The slope of the plot of ln k (in sec^{-1}) vs $\frac{1}{T}$ (T in Kelvin) in absence of catalyst is (R = 8.3 J $mol^{-1}K^{-1}$)

(a) + 1 (b) –1

(c) + 1000 (d) – 1000

23. The time taken for 90% of a first order reaction to complete is approximately

(a) 1.1 times that of half life

(b) 2.2 times that of half life

(c) 3.3 times that of half life

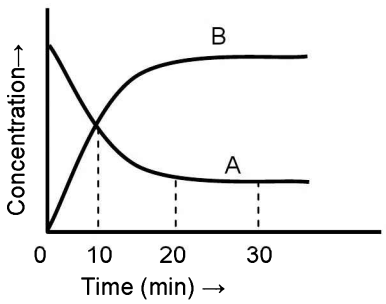
(d) 4.4 times that of half life

24. At 100°C, the gaseous reaction A → 2B + C is found to be of first order. Starting with pure A, if at the end of 10 min, the total pressure of the system is 176 mm and after a long time it is 270 mm, the partial pressure of A at the end of 10 min i

(a) 94 mm (b) 43 mm

(c) 47 mm (d) 176 mm

25. For a first order reaction, A ⟶ B, whose concentration vs time curve is as shown in the figure. The rate constant is equal to



(a) 41.58 h^{-1}

(b) 4.158 s^{-1}

(c) 1.155×10^{-3} s^{-1}

(d) 6.93 min^{-1}

26. The rates of a first order reaction are 0.1 mol $litre^{-1}$ S^{-1} and 0.001 mol $litre^{-1}$ S^{-} after 10 min. and 20 min. from the start of the reaction. The half life period of the reaction is

(a) 1.5 min (b) 10 min

(c) 5 min (d) 1 min

27. Consider the following two 1st order reactions

A → B ..... 1P → Q 2

The initial concentration of 'A'is twice that of 'p'. How long will it take for the two reactions to have equal rates

(Given half life period of reaction (1) and reaction (2) are 15 minand 30 min. respectively)

(a) 15 min (b) 30 min

(c) 60 min (d) 120 min

28. Consider the following elementary process:

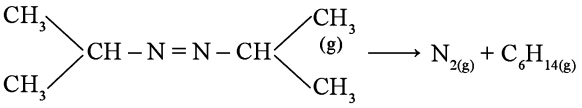
$\frac{1}{2} H_2 + \frac{1}{2} I_2 \longrightarrow HI$

The molecularity of the above reaction is

(a) 1 (b) $\frac{1}{2}$

(c) 2 (d) 4

29. Thermal decomposition of azo-isopropane to hexane and nitrogen follows a first order kinetics. If P_i is the initial pressure of azo isopropane and the pressure after time t sec is P, then the expression for rate constant 'k' can be given by:



(a) $\frac{1}{t} \ln \frac{P}{2P_i}$

(b) $\frac{1}{t} \ln \frac{P_i}{P}$

(c) $\frac{1}{t} \ln \frac{P_i}{2P_i - P}$

(d) $\frac{1}{t} \ln \frac{P}{2P_i - P}$

30. The rate constant for two parallel reactions were found tobe 1.0×10^{-2} dm^3 mol^{-1} s^{-1} and 3.0×10^{-2} dm^3 mol^{-1} s^{-1}. If the corresponding energies of activation of parallel reactions are 60.0 kJ mol^{-1} and 70.0 kJ mol^{-1} respectively, the apparent overall energyof activation is:

(a) 130.0 kJ mol^{-1}
(b) 67.5 kJ mol^{-1}
(c) 100.0 kJ mol^{-1}
(d) 65.0 kJ mol^{-1}

31. A certain reaction A + B → P is of first order with respect to each reactant. If $[A]_0 = 0.1$ M, $[B]_0 = 5.0$ M and the second order rate constant k is 6×10^{-3} M^{-1} s^{-1}, the half-life of the reaction in seconds is

(a) 23.5 (b) 27.7
(c) 33.3 (d) 115.5

32. The decomposition of NH_3 on finely divided platium follows the rate expression,

$$\text{Rate} = \frac{k_1[NH_3]}{1+k_2[NH_3]}$$

It is a first order reaction when concentration of NH_3 is

(a) very low (b) very high
(c) moderate (d) never

33. For a first order homogeneous gaseous reaction,

$A \longrightarrow 2B + C$

If the total pressure after time t was P_t and after long time ($t \longrightarrow \infty$) was P_∞ then k in terms of P_t, P_∞ and t is:

(a) $k = \frac{2.303}{t}\log\left(\frac{P_\infty}{P_\infty - P_t}\right)$

(b) $k = \frac{2.303}{t}\log\left(\frac{2P_\infty}{P_\infty - P_t}\right)$

(c) $k = \frac{2.303}{t}\log\left(\frac{2P_\infty}{3(P_\infty - P_t)}\right)$

(d) None of these

34. A(aq) ⟶ B(aq) + C(aq) is a first order reaction.

Time	t	∞
moles of reagent	n_1	n_2

Reaction progress is measure with the help of titration of reagent 'R'. If all A, B and C reacted with reagent and have 'n' factors [n factor; equation weight $= \frac{\text{mol. wt.}}{n}$] in ratio of 1: 2 : 3 with the reagent. The k in terms of t, n_1 and n_2 is:

(a) $k = \frac{1}{t}\ln\left(\frac{n_2}{n_2 - n_1}\right)$

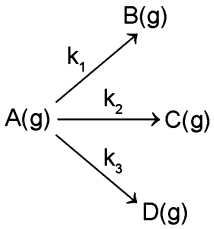
(b) $k = \frac{1}{t}\ln\left(\frac{2n_2}{n_2 - n_1}\right)$

(c) $k = \frac{1}{t}\ln\left(\frac{4n_2}{n_2 - n_1}\right)$

(d) $k = \frac{1}{t}\ln\left(\frac{4n_2}{5(n_2 - n_1)}\right)$

35. A gaseous compoud A reacts by three independent first order processes (as shown in figure) with rate constant 2×10^{-3}, 3×10^{-3} and 1.93×10^{-3} sec^{-1} for products B, C and D respectively.

If initially, pure A was taken in a closed container with P = 8 atm, then the partial pressure of B (in atm) after 100 sec from start of experiment.

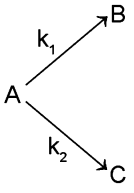


(a) 0.288 (b) 0.577
(c) 1.154 (d) none of these

36. The reaction cis-X ⇌ trans-X is first order in both directions. At 25°C, the equilibrium constant is 0.10 and the rate constant $k_f = 3 \times 10^{-4}$ s^{-1}. In an experiment starting with the pure cis-form, how long would it take for half of the equilibrium amount of the trans-isomer to be formed?

(a) 150 sec (b) 200 sec
(c) 240 sec (d) 210 sec

37. Consider the reaction.



The rate constant for two parallel reactions were found to be 10^{-2} dm^3 mol^{-1} s^{-1} and 4×10^{-2} dm^3 mol^{-1} s^{-1}. If the corresponding energies of activation of the parallel reaction are 100 and 120 kJ/mol respectively, what is the net energy of activation (E_a) of A?

(a) 100 kJ/mol
(b) 120 kJ/mol
(c) 116 kJ/mol
(d) 220 kJ/mol

38. A reaction takes place in various steps. The rate constant for first, second, third and fifth steps are k_1, k_2, k_3 and k_5 respectively. The overall rate constant is given by,

$$k = \frac{k_2}{k_3}\left(\frac{k_1}{k_5}\right)^{1/2}$$

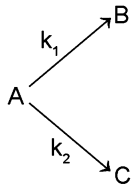
if activation energy are 40, 60, 50 and 10 kJ/mol respectively, the overall energy of activation (kJ/mol) is:

(a) 10 (b) 20
(c) 25 (d) None of these

39. The reaction, Sucrose $\xrightarrow{H^+}$ Glucose + Fructose, takes place at certain temperature while the volume of solution is maintained at 1 litre. At time zero the initial rotation of the mixture is 34°. After 30 minutes the total rotation of solution is 19° and after a very long time, the total rotation is –11°C. Find the time when solution was optically inactive.

(a) 135 min
(b) 103.7 min
(c) 38.7 min
(d) 45 min

40. For first order parallel reaction k_1 and k_2 are 4 and 2 min^{-1} respectively at 300 K. If the activation energies for the formation of B and C are respectively 30,000 and 38,314 joule/mol respectively. The temperature at which B and C will be obtained in equimolar ratio is:



(a) 757.48 K
(b) 378.74 K
(c) 600 K
(d) none of these

41. Two substances A and B are present such that $[A_0] = 4[B_0]$ and half–life of A is 5 minute and that of B is 15 minute. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same?

(a) 15 minute
(b) 10 minute
(c) 5 minute
(d) 12 minute

42. Fill in the blank

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ? + ^{92}_{36}Kr + 3^{1}_{0}n$$

(a) $^{141}_{56}Ba$ (b) $^{139}_{56}Ba$
(c) $^{139}_{54}Ba$ (d) $^{141}_{54}B$

ANSWER KEYS

1. (a)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (d)	**6.** (b)	**7.** (b)	**8.** (b)	**9.** (d)	**10.** (d)
11. (b)	**12.** (d)	**13.** (d)	**14.** (d)	**15.** (b)	**16.** (a)	**17.** (b)	**18.** (a)	**19.** (b)	**20.** (b)
21. (a)	**22.** (d)	**23.** (c)	**24.** (c)	**25.** (c)	**26.** (a)	**27.** (c)	**28.** (c)	**29.** (c)	**30.** (b)
31. (a)	**32.** (c)	**33.** (c)	**34.** (d)	**35.** (c)	**36.** (d)	**37.** (c)	**38.** (c)	**39.** (b)	**40.** (b)
41. (a)	**42.** (a)								

[redacted]TS AND EXPLANATIONS

1. (a) $2.5 \times 10^{-3} = K[0.5]^{\alpha}[1.0]^{\beta}$ ...(1)

$5 \times 10^{-3} = K[1.0]^{\alpha}[1.0]^{\beta}$ ...(2)

$1 \times 10^{-2} = K[0.5]^{\alpha}[2.0]^{\beta}$ ...(3)

Dividing equation (1) and (2),

$$\frac{1}{2} = \left[\frac{1}{2}\right]^{\alpha}$$

Hence $\alpha = 1$

Dividing equation (1) and (3),

$$\frac{2.5\times10^{-3}}{1\times10^{-2}} = \left(\frac{1.0}{2.0}\right)^{\beta}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^{\beta} \qquad \beta = 2$$

2. (a) $K = \dfrac{0.6932}{120}$ ...(1)

$$K = \frac{2.303}{t}\log\frac{a}{0.10a}$$

$$= \frac{2.303}{t}\log 10 \quad \text{...(2)}$$

Equating (1) and (2),

$$\frac{0.6932}{120} = \frac{2.303}{t} \quad t = 399 \text{ minutes}$$

3. (a) Amount of A left in n_1 halves $= \left(\frac{1}{2}\right)^{n_1}[A_0]$

Amount of B left in n_2 halves $= \left(\frac{1}{2}\right)^{n_2}[B_0]$

At the end, according to the question,

$$\frac{[A^0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}}$$

$$\Rightarrow \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, \quad [[A_0] = 4[B_0]]$$

$$\therefore \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1-n_2} = (2)^2 \therefore n_1 - n_2 = 2$$

$$\therefore \quad n_2 = (n_1 - 2) \quad \text{...(1)}$$

Also $t = n_1 \times t_{1/2(A)}$ $t = n_2 \times t_{1/2(B)}$

(Let concentration of both become equal after time t)

$$\therefore \quad \frac{n_1 \times t_{1/2(A)}}{n_2 \times t_{1/2(B)}} = 1 \Rightarrow \frac{n_1 \times 5}{n_2 \times 15} = 1 \Rightarrow \frac{n_1}{n_2} = 3 \quad \text{...(2)}$$

For equation (1) and (2),

$n_1 = 3, n_2 = 1$

$t = 3 \times 5 = 15$ minute

4. (a)

A	$\rightarrow$	2B	+	C
P		0		0
P – x		2x		x

At equilibrium,

$180 = P - \times + 2x + x$

$180 = 90 + 2x$

$2x = 90, \times = 45$

$$K = \frac{2.303}{t}\log\frac{P}{P-x}$$

$$= \frac{2.303}{10}\log\frac{90}{90-45} = \frac{2.303}{10}\log 2 = \frac{0.6932}{10}$$

$$= 0.6932 = \frac{0.06932}{60} = 1.1555 \times 10^{-3} \text{ sec}^{-1}$$

5. (d) $R_1 = K[A][B]$

$= K[0.6][0.80]^2$

After reaction,

A +	2B $\longrightarrow$	C +	D
0.6 – 0.2	0.8 – 0.4	0.2	0.2
0.4	0.4	0.2	0.2

$$\frac{R_2}{R_1} = \frac{K(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$$

6. (b) $\dfrac{E'a}{T_1} = \dfrac{E_a}{T_2} = \dfrac{10}{300} = \dfrac{20}{T_2}$

$\therefore \quad T_2 = 600 \text{ K} = 327°\text{ C}$

7. (b) Since $t_{1/2}$ does not depends upon the sugar concentration means it is first order respect to sugar concentration. $t_{1/2} \propto [\text{sugar}]^1$.

$t_{1/2} \times a^{n-1} = k$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[H^+]_1^{1-n}}{[H^+]_2^{1-n}}$$

$$\frac{500}{50} = \left(\frac{10^{-5}}{10^{-6}}\right)^{1-n}$$

$$10 = (10)^{1-n}$$

Hence, $n = 0$

8. (b) $K = Ae^{-Ea/RT}$

When, $T \to \infty$

$K \to A$

$A = 6 \times 10^{14}\ s^{-1}$

9. (d) The percentage distribution of B and C are in the ratio of their rate constants,

$$\% \text{ of } B = \frac{k_1}{k_1 \times k_2} \times 100$$

$$= \frac{(12.6 \times 10^{-4} s^{-1})}{(12.6 + 3.8) \times 10^{-4} s^{-1}} \times 100$$

$$= 23.17\%$$

$$\% \text{ of } C = 100 - 23.17$$

$$= 76.83\%$$

10. (d) $\therefore\ t_{1/2} \propto \frac{1}{C_0^{n-1}}$ where C_0 is the initial concentration.

$$\Rightarrow \frac{100}{1} = \left(\frac{10C_0}{C_0}\right)^{n-1}$$

or $10^2 = 10^{n-1}$

$\Rightarrow n = 3.$

12. (d) $\because k_{eqm} = \frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$ ...(i)

$\because$ Rate $= R = k_2 [N_2O_2] [H_2]$ ...(ii)

From equations (i) and (ii), we get,

$$R = k_2 \times \frac{k_1}{k_{-1}}[NO]^2[H_2] \quad = k[NO]^2[H_2]$$

13. (d) $\because \quad \frac{k_1}{k_2} = \frac{[A]^2}{[A_2]}$

$$\Rightarrow \quad [A] = \sqrt{\frac{k_1}{k_{-1}}[A_2]}$$

Now, rate $= r = k_2 [A] [B]_2$

$$= k_2 \times \sqrt{\frac{k_1}{k_{-1}}}\,[A_2]^{1/2}\,[B]^1$$

So, order to reaction will be $= 1 + 0.5 = 1.5$

14. (d) $\because \quad \frac{k_1}{k_{-1}} = \frac{[O_2][O]}{[O_3]}$

$$\Rightarrow [O] = \frac{k_1}{k_{-1}} = \frac{[O_3]}{[O_2]} \quad \text{...(i)}$$

$\because$ rate $= r = k_2[O_3][O]$ ...(ii)

From equation (i) and (ii), we get,

$$= k_2 [O_3]^2 [O_2]^{-1}$$

$\because$ Order with respect to O_3, O_2 and reaction are 2, –1, 1.

15. (b) $k = Ae^{-E_a/RT}$ (Arrhenius equation).

When $T \to \infty$

$k = Ae^0$,

or $k = A$

Thus $k = 6 \times 10^{14}\ s^{-1}$

16. (a) Energy of activation does not depend on the stoichiometry of change. It is characteristic value for a chemical reaction.

17. (b) $r_1 \propto [X]^n, \quad r_2 = 2.25\ r_1 \quad x_2 = 1.5 \times 1$

$$\frac{r_1}{r_2} = \left[\frac{x_1}{x_2}\right]^n, \quad \left(\frac{100}{2.25}\right) = \left(\frac{10}{1.5}\right)^n \quad \text{therefore, } n = 2$$

18. (a)

19. (b)

20. (b) H_2SO_4 is stronger than HCI

Also relative strength of two acids

$$= \frac{\text{rate constant by } H_2SO_4}{\text{rate constant by HCI}} \quad \text{or} \quad \frac{K_{H_2SO_4}}{K_{HCl}} > 1$$

21. (a) $$\log \frac{K_1'}{K_1} = \frac{E_{A_1}}{2.303R}\left(\frac{T' - T}{T'T}\right) \quad \text{....(1)}$$

$$\log \frac{K_2'}{K_2} = \frac{E_{A_2}}{2.303R}\left(\frac{T' - T}{T'T}\right) \quad \text{....(2)}$$

Dividing equation (1) by (2) $\dfrac{\log \frac{K_1'}{K_1}}{\log \frac{K_2'}{K_2}} = \dfrac{E_{A_1}}{E_{A_2}}$

$\because E_{A_1} > E_{A_2}$

$\therefore \quad \frac{K_1'}{K_1} > \frac{K_2'}{K_2}$

22. (d) $k = A\,e^{-Ea/RT} \qquad k' = A\,e^{-Ea'/RT}$

(Where k = rate constant for non catalysed reaction and k' = rate constant for catalysed reaction. Ea = activation energy for non-catalysed

reaction and Ea' = activation energy for catalysed reaction)

$\frac{k'}{k} = e^{Ea-Ea'}$; Also given k' = k + 1.718 k = 2.718 k

$\therefore \quad 2.718 = e^{\frac{Ea-Ea'}{RT}}$; $\log_e 2.718 = \frac{Ea - Ea'}{8.314\times10^{-3}\times500}$;

$Ea - Ea' = 4.11$;

$Ea' = 4.15 \quad \therefore Ea = 8.3\ KJ/mol^{-1}$; $\quad k = A\,e^{-Ea/RT}$

$\therefore \quad \log_e k = \log_e A - \frac{Ea}{RT}$

This is an equation for straight line with slope =

$-\frac{Ea}{R} = -\frac{8.3}{8.3\times10^{-3}} = -1000 \qquad \therefore$ (d)

23. (c) $t_{90\%} = \frac{2.303}{k}\log\frac{a}{a-0.9a} = \frac{2.303}{k}\log10\frac{2.303}{k}$

$t_{1/2} = \frac{2.303}{k}\log\frac{a}{a-a/2} = \frac{2.303}{k}\log 2$

$= \frac{2.303}{k}\times0.3010 \quad \therefore t_{90\%}/t_{1/2} = \frac{1}{0.3010} = 3.3$

i.e., $t_{90\%} = 3.3$ times $t_{1/2}$.

24. (c) After long time whole of A would change into B and C. On decomposition one mole of A changes into three moles of B and C. Therefore, Initial pressure of A = $\frac{270}{3}$ = 90 mm.

Suppose after 10 minutes pressure of A falls y x mm. In that case pressure of B and C would be 2x and x mm respectively.

Total pressure = (90 – x) + 2x + × = (90 + 2x) mm

90 + 2x = 176 mm

2x = (176 – 90) mm

x = 43 mm

Pressure of A after 10 minutes,

= (90 – x) mm = (90 –43) = 47 mm.

25. (c) From figure, the reaction seems to be first order whose half-life is 10 minutes

26. (c) $r_t = K[A]_t$

$\Rightarrow r_{10} = K\,[A]_{10}$

$r_{20} = K[A]_{20}$

$\frac{r_{10}}{r_{20}} = \frac{[A]_{10}}{[A]_{20}} = 10^2$

We know $\ln\left(\frac{[A]_0}{[A]_t}\right) = Kt$

Hence, $\ln\frac{[A]_{10}}{[A]_{20}} = 10\,K$ 1

and $\ln\frac{[A]_0}{[A]_{20}} = 20\,K$ 2

Equilibrium 2 – 1

$\ln\frac{[A]_{10}}{[A]_{20}} = 10K = \ln 10^2$

$\Rightarrow \quad K = \frac{\ln10}{5} = \frac{2.303}{5} = \frac{0.693}{t_{1/2}}$

$\Rightarrow \quad t_{1/2} = \frac{0.693\times5}{2.303} = 1.5$

Alternatively

$[A]_t = [A]_0\,e^{-Kt}$

$[A]_{10} = [A]_0\,e^{-10\,K}\ [A]_{20} = [A]_0\,e^{-20\,K}$

$\frac{[A]_{10}}{[A]_{20}} = e^{10K}\ 10^2$

$10^K = 2\ln10$

$K = \frac{2.303}{5} = \frac{0.693}{t_{1/2}} \Rightarrow t_{1/2} = 1.5$ min

Alternatively

$-\frac{d[A]}{dt} = K\,[A]$

$-\int_{[A]_{20}}^{[A]_{10}}\frac{d[A]}{[A]} = K\int_{10}^{20}dt$

$[A]_{10}\ln\frac{[A]_{10}}{[A]_{20}} = 10\,K = 10\times\frac{0.693}{t_{1/2}} = \ln10^2$

$t_{1/2} = 1.5$ min

27. (c) Initial Concent, $A \xrightarrow{K_1} B$ 1

2a –

Initial Concent, $P \xrightarrow{K_2} Q$ 1

a –

$K_1 = \frac{\ln2}{t_{1/2}} \qquad K_2 = \frac{\ln2}{t_{1/2}}$

$K_1 = \frac{\ln2}{15}\ min^{-1} \qquad K_2 = \frac{\ln2}{30}\ min^{-1}$

(Hence, $\frac{K_1}{K_2} = 2$)

$r_1 = r_t = K_1\,[A]_t \qquad r_2 = K_2\,[P]_t$

$\Rightarrow r_1 = K_1[A]_0 e^{-Kt} \Rightarrow r_2 = K_2[P]_o \quad e^{-K_2 t}$

$r_1 = r_2 \quad \Rightarrow 2K_1(2a)\, e^{-K_1 t} = K_2 a \quad e^{-K_2 t}$

$4\, e^{(K_2 - K_1)t} =$

$4 = e^{(K_1 - K_2)t} = 2^2$

$\Rightarrow (K_1 - K_2)t = 2 \ln 2 \Rightarrow \left(\frac{\ln 2}{15} - \frac{\ln 2}{30}\right) t = 2 \ln 2$

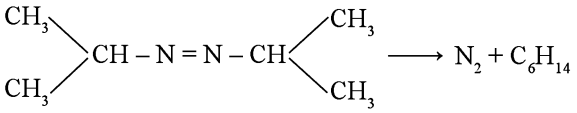
$\Rightarrow t = \left(\frac{15 \times 30 \times 2}{30 - 15}\right)$ min

$t = 60$ min

28. (c) Molecularity is always integer and its defined for the lowest integer value of he individual stoichiometric co-efficient of all the reactants. Hence the reaction for which its molecularity will be defined is,

$H_2 + I_2 \longrightarrow 2HI$

29. (c)



Initial pressure, $P_i \quad 0 \quad 0$

After time t sec, let p' be the decrease in pressure of azo-isopropane.

Hence, pressure after t sec.

$P_i - p' \quad p' \quad p'$

Total pressure $= P = p_{azopropane} + p_{N_2} + p_{C_6H_{14}}$

$= P = P_i - p' + p' + p'$

$\Rightarrow P = P_i + p'$ = partial pressure of azo-isopropane after time t seconds.

$p' = P - P_i$

$P_i - p' = P_i - (P - P_i) = 2.P_i - P$

Hence, $K = \frac{1}{t} \ln \frac{a}{a - x}$

$a \propto P_i \; (a - x) \propto P_i - p'$

$\Rightarrow k = \frac{1}{t} \ln \frac{P_i}{2P_i - P}$

It follows that (a), (b) and (d) are incorrect.

30. (b) $E_a = \frac{k_1 \times E_{a_1} + k_2 \times E_{a_2}}{k_1 + k_2}$

$= \frac{1.0 \times 10^{-2} \times 60 + 3.0 \times 10^{-2} \times 70}{1.0 \times 10^{-2} + 3.0 \times 10^{-2}} \quad 60 + 210 \quad 270$

$= \frac{60 + 210}{4} = \frac{270}{4}$

$= 67.5$ kJ mol^{-1}

31. For 2nd order reactions, $k = \frac{2.303}{t\{[A_0] - [B]_0\}} \log \frac{[B]_0[A]}{[A]_0[B]}$

when $t = t_{1/2}$, $[A] = [A]_0/2 = 0.1/2 = 0.05$

At that time $[B] = 5 - 0.05 = 4.95$ M

$\therefore \quad t_{1/2} = \frac{2.303}{6 \times 10^{-3}(0.1 - 5.0)} \log \frac{5 \times 0.05}{0.1 \times 4.95}$

$= \frac{2.303}{6 \times 10^{-3}(-4.9)} \log \frac{1}{2} \approx 23.5$ s

32. (c) $2NH_3 \xrightarrow{Pt} 1\, N_2 + 3H_2$

$-\frac{1}{2}\frac{d}{dt}[NH_3] = \frac{d}{dt}[N_2] = \frac{1}{3}\frac{d}{dt}[H_2]$

$\frac{-d}{dt}[NH_3]$ = Rate or decomposition of NH_3

$= k = 2.5 \times 10^{-4}$ Ms^{-1}

$\therefore \quad \frac{d}{dt}[N_2] = \frac{3}{2} \times 2.5 \times 10^{-4}$ Ms^{-1}

$= 3.75 \times 10^{-4}$ Ms^{-1}

33. (c)

	$A \longrightarrow$	$2B$	$+ C$
$t = 0$	p_i	0	0
t	$p_i - x$	$2x$	x
$t \to \infty$	0	$2p_i$	p_i

$P_\infty = 3P_i$ or $P_i = \frac{P_\infty}{3}$; $P_i + 2x = P_t \quad x = \frac{P_t - P_i}{2}$

As we know, $k = \frac{2.303}{t} \log\left(\frac{P_i}{P_i - x}\right)$

so $k = \frac{2.303}{t} \log\left(\frac{2P_\infty}{3(P_\infty - P_t)}\right)$

34. (d) Let n is the moles of reagent 'R' when R is reactant with A at time t = 0

	$A \longrightarrow$	$2B$	$+ C$
$t = 0$	n	0	0
At t	$n - x$	$2x$	$3x$
At $t \to \infty$	0	$2n$	$3n$

$\therefore \quad 5n = n_2 \Rightarrow n = \frac{n_2}{5} \qquad n + 4x = n_1 \Rightarrow x = \frac{n_1 - n}{4}$

$k = \frac{2.303}{t}\log\left(\frac{n}{n-x}\right)$

So, $\quad k = \frac{1}{t}\ln\left(\frac{4n_2}{5(n_2 - n_1)}\right)$

35. (c) Overall rate constant = $k = k_1 + k_2 + k_3$

$= 6.93 \times 10^{-3} t_{1/2} = \frac{0.693}{6.93 \times 10^{-3}} = 100$ sec;

After half-life, $P_B + P_C + P_D = 4$ atm

$$\frac{P_B}{P_B + P_C + P_D} = \frac{k_1}{k_1 + k_2 + k_3} = \frac{200}{693}$$

$$P_B = 4 \times \frac{200}{693} = 1.154 \text{ atm}$$

36. (d) $\underset{k_b}{\text{cis-X}} \rightleftharpoons \text{trans-X}$

Initial a 0; $K_{(aq)} = \frac{3 \times 10^{-4}}{0.1} = 3 \times 10^{-3}$

At time t, $a - x$ x

At equilibrium $a - x_e$ x_e

As we know $(k_f + k_b) = \frac{1}{t}\ln\left(\frac{x_e}{x_e - x}\right)$

Given, $x = \frac{x_e}{2} \qquad \therefore \quad (k_f + k_b) = \frac{1}{2}\ln 2$

or $\quad (3 \times 10^{-3} + 3 \times 10^{-4}) = \frac{0.693}{t} \quad t = 210$ sec

37. (c) For parallel reaction $E_a = \frac{k_1 E_{a_1} + k_2 E_{a_2}}{k_1 + k_2}$

$= \frac{10^{-2} \times 100 + 4 \times 10^{-2} \times 120}{10^{-2} + 4 \times 10^{-2}} \quad E_a = 116$ kJ/mol

38. (c) $k = A.e^{-E_a/(RT)} \quad \therefore$ Effective overall energy of activation $E_a = E_{a(2)} - E_{a(3)} + \frac{1}{2}E_{a(1)} - \frac{1}{2}E_{a(5)}$

$= 60 - 50 + \frac{1}{2} \times 40 - \frac{1}{2} \times 10 = 25$ kJ/mol

39. (b) $k = \frac{2.303}{t}\log\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right) = \frac{2.303}{30}\log\left(\frac{-11 - 34}{-11 - 19}\right)$

$= 1.35 \times 10^{-2}$ min^{-1}

When solution is optically inactive $r_t = 0; \quad t = \frac{1}{k}$

$\ln\left(\frac{-45}{-11}\right) = 103.7$ min

40. (b) $\ln\frac{k_1'}{k_1} = \frac{E_1}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ .... (i)

$\ln\frac{k_2'}{k_2} = \frac{E_2}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ ....(ii)

Solving we get (ii) – (i),

$\ln\frac{k_2'}{k_2} = \frac{k_1'}{k_1} = \left(\frac{E_2 - E_1}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

(for equimolar formation of B and C, $k_2' = k_1'$)

$\ln\left(\frac{k_1}{k_2}\right) = \left(\frac{8314}{8.314}\right)\frac{(T_2 - 300)}{300 \times T_2}$

$\ln 2 = (1000)$

$\left(\frac{T_2 - 300}{300 \times T_2}\right) \quad T_2 = 378.74$ K

41. (a) Amount of A left in n_1 halves $= \left(\frac{1}{2}\right)^{n_1}[A_0]$

Amount of B left in n_2 halves $= \left(\frac{1}{2}\right)^{n_2}[B_0]$

At the end, according to the question,

$$\frac{[A^0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}}$$

$\Rightarrow \quad \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, \quad [[A_0] = 4[B_0]]$

$\therefore \quad \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1 - n_2} = (2)^2 \therefore n_1 - n_2 = 2$

$\therefore \quad n_2 = (n_1 - 2)$ ...(1)

Also $\quad t = n_1 \times t_{1/2(A)} \quad t = n_2 \times t_{1/2(B)}$

(Let concentration of both become equal after time t)

$\therefore \frac{n_1 \times t_{1/2(A)}}{n_2 \times t_{1/2(B)}} = 1 \Rightarrow \frac{n_1 \times 5}{n_2 \times 15} = 1 \Rightarrow \frac{n_1}{n_2} = 3$ ...(2)

For equation (1) and (2),

$n_1 = 3, n_2 = 1$

$t = 3 \times 5 = 15$ minute

42. (a) $92 + 0 = Z + 36 + 0$

$\Rightarrow Z = 56$

$235 + 1 \longrightarrow A + 92 + 3$

$\therefore \quad A = 144$

Missing nuclide is $^{141}_{56}Ba$

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. $2N_2O_5 \rightarrow 4NO_2 + O_2$

If $-\frac{d[N_2O_5]}{dt} = K_1[N_2O_6] + \frac{d[NO_2]}{dt} = K_2[N_2O_5]$

$+ \frac{d[O_2]}{dt} = K_3[N_2O_5]$

What is the relation between, K_1, K_2 and K_3?

(a) $K_1 = K_2 = K_3$ (b) $2K_1 = K_2 = 4K_3$

(c) $2K_1 = K_2 = K_3$ (d) none

2. Which of the following relations is/are correct?

(a) $\frac{d\ln K}{dT} = \frac{Ea}{RT^2}$

(b) $\frac{dK_{eq}}{dT} = \frac{\Delta H K_{eq}}{RT^2}$

(K = rate constant)

(K_{eq} = eq^m constant)

(c) $\frac{dK}{dT} = \frac{Ea}{RT^2}$

(d) $\frac{dK_{eq}}{dT} = \frac{\Delta H}{RT^2}$

(K = rate constant)

3. For zeroth order reaction: A $\rightarrow$ Products

(a) The rate of reaction is independent of concentration.

(b) The concentration of reactant does not change with time.

(c) The half life period depends upon the concentration of reactant.

(d) The rate constant is numerically equal to the rate of the reaction.

4. For the following reaction P $\longrightarrow$ Q the rate constant at 27° is found to be 2×10^{-3} mol^{-1} litre s^{-1}. Hence,

(a) The half life time when the initial concentration of 'p' is 10 M is 50 seconds.

(b) When concentration of 'p' is doubled the rate of reaction is doubled as well.

(c) The rate does not depend on the concentration of 'p'

(d) The half life period decreases with the increasing concentration of reactants.

5. For a first order reaction

(a) the time required for 99% completion is twice the time required for 90% completion.

(b) The degree of dissociation is equal to $(1-e^{-kt})$

(c) The plot of reciprocal of concentration of reactant against time gives a straight line.

(d) The rate and rate constant have the same unit.

6. The value of rate constant of the above written reaction is

(a) 2×10^{-3} L^2 mol^{-2} S^{-1}

(b) 10^{-3} S^{-1}

(c) 2×10^{-3} S^{-1}

(d) 10^{-3} L^2 mol^{-2} S^{-1}

7. For the reaction A $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ B if 'a' is the initial concentration of A and n is the number of moles of A reacting, if initially no B was present then

(a) $\frac{dx}{dt} = k_1(a-x) - k_2x$ initially

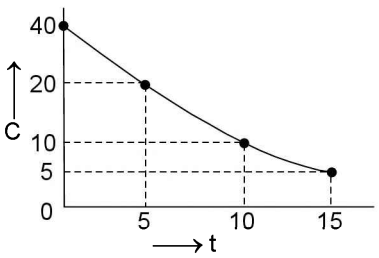
(b) $0 = k_1(a - x_e) - k_2x_e$ at equilibrium

(c) $k_1 + k_2 = k_1 \frac{a}{x_e}$

(d) $(k_1 + k_2) = \frac{1}{t} \ln \frac{x_e}{x_e - x}$

Where x_e = equilibrium concentration of B and n = number of moles of A reacting

8. For a reaction a graph was plotted between reactant concentration C and time as shown in figure. Which of the following statements is/are correct?



(a) The reaction in a first order reaction.

(b) The concentration of reactant cannever be theoretically zero.

(c) The rate of the reaction does not change with time.

(d) The half life period is constant and independent of concentration of reactant.

9. For the reaction A $\longrightarrow$ B, the rate law expression is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of A is A_0. Which of the following statements is/are true regarding this reaction?

(a) The plot of $\sqrt{A}$ against 't' will be linear

(b) The half life period is $t_{1/2} = \frac{\sqrt{2}(\sqrt{2}-1)}{K}\sqrt{A_0}$

(c) The linear decreases of rate of reaction with time.

(d) The integrated form of rate expression is $\sqrt{A} = -\frac{K}{2}t + \sqrt{A_0}$

10. The nuclei of two radioactive isotopes of same substance X^{236} and X^{234} are present in the ratio of 4 : 1 in a ore obtained from some other source. Their half lives are 30 min. and 60 min. respectively. Both isotopes are a⁻emitters and activity of isotope with half life 30 min. s 10^6 dps. Which of the following statement is/ are correct?

(a) After 60 minute the their number of nuclei will same

(b) After 180 minute their activities will be same

(c) After 120 minute their number of nuclei will be same.

(d) After 240 minute their activities will be same.

ANSWER KEYS

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

HINTS AND EXPLANATIONS

1. (b)

2. (a, b)

3. (a, c, d)

$t_{1/2} = \frac{a}{2K}$ and $r = K[A]^o = K$

4. (a, d)

5. $\ln\left(\frac{1}{1-\phi}\right) = Kt \Rightarrow \phi = (1 - e^{-Kt})$

$\ln\left(\frac{1}{1-0.9}\right) = Kt_{0.9} = \ln 10$

$\ln\left(\frac{1}{1-0.99}\right) = Kt_{0.99} = \ln 100$

$= 2\ln 10 = 2Kt_{0.9}$

$t_{0.99} = 2\, t_{0.9}$

6. $r = \frac{1}{2}\frac{d[XY]}{dt} = K[X_2]\,[Y_2]^2$

$\frac{1}{2}(2 \times 10^{-3}) = K \quad 1 \times 1^2 \quad K = 10^{-3}\, L^2\, mol^{-2}\, L^{-1}$

7. (a), (b), (c) and (d)

8. (a, b, d)
From the graph it is evident that concentration of 40 reduces to 20 in 5 minute 20 reduced to 10 in 5 minute and 10 reduces to 5 in again 5 minute, which shows that half life period is independent of concentration, a charactristic of a first order reaction. In a first order reaction the concentration of the reactant can never be theoretically zero. For first order reaction rate of reaction decreases with time.

9. (a, b, d)

(a) $-\frac{d[A]}{dt} = k[A]^{1/2}$

$$\text{or } -=\frac{dA}{[A]^{1/2}} = Kdt$$

on integrating $\int -[A]^{-1/2}dA = K\int dt$

$$-2A^{1/2} = Kt + C \quad \text{.....(1)}$$

at $t = 0$; $A = A_0$ $C = -2A_0^{1/2}$ .....(2)

By Eqs. (2) and (1),

$-2A^{1/2} = Kt - 2A_0^{1/2}$

or $Kt = 2\,[A_0^{1/2} - A^{1/2}]$ .....(3)

(b) plot of $A^{1/2}$ vs. t will be linear because Eq. (3) yields,

$2A^{1/2} = -Kt + 2A_0^{1/2}$

or $A^{1/2} = -\frac{K}{2}t + A_0^{1/2}$ (similar to y = mx + C)

(c) If $t =_{1/2}$ $A = A_0/2$

By Equation (3), $Kt^{1/2} = 2\left[A_0^{1/2} - \frac{A_0}{2}\right]^{1/2}$

$$= 2A_0^{1/2} \times \frac{1}{\sqrt{2}}$$

$$Kt_{1/2} = \frac{2[\sqrt{2}-1]}{\sqrt{2}} A_0^{1/2} = \sqrt{2}(\sqrt{2}-1)A_0^{1/2}$$

$$\therefore \quad t_{1/2} = \frac{\sqrt{2}(\sqrt{2}-1)}{K}A_0^{1/2}$$

10. (c) Let the nuclei of X^{236} initially be N_0

the nuclei of X_{234} initially will be $\frac{N_0}{4}$

Initial activity of $X_{236} = 10^6 = \frac{0.693 \times N_0}{30 \times 60}$

Initial activity of $X^{234} = \frac{0.693 \times N_0}{60 \times 60 \times 4} = \frac{0.693 \times N_0}{30 \times 60}$

$\times \frac{1}{8} = \frac{10^6}{8}$

Now for X^{236}, $A_t = A_0 e^{-\lambda t}$

$$A_t = 10^6 e^{-0.693 \times \frac{t}{30}}$$

For X^{234}, $A_t = \frac{10^6}{8}\ \frac{10^6}{8} e^{-0.693 \times \frac{t}{60}}$

Since the activities are to be equal,

$$10^6 e^{-0.693 \times \frac{t}{30}} = \frac{10^6}{8}\ e^{-0.693 \times \frac{t}{60}}$$

$\therefore$ t = 180 mins

For the number of nuclei to be same,

For X^{236}, $N_t = N_0 e^{-0.693 \times \frac{t}{30}}$

For X^{234}, $N_t = \frac{N_0}{4} e^{-0.693 \times \frac{t}{60}}$

$$\therefore \quad N_0 e^{-0.693 \times \frac{t}{30}} = \frac{N_0}{4} e^{-0.693 \times \frac{t}{60}}$$

$\therefore$ **t = 120 mins.**

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

For the following first order gaseous reaction

$$R \rightarrow P$$

Normal energy of R is = 40 kJ

Normal energy of P is = 20 kJ

Threshold energy of the uncatalysed forward reaction at 500 K is 140 kJ. The reaction is carried out in presence of the positive catalyst at 300 K temperature in a such a way so that the rate of the catalysed reaction becomes equal to the rate of the uncatalysed reaction.

Assume $\log_e x = 2.5 \log_{10} x$, R = 8 J/mol/K

1. What will be the value of the activation energy of the catalysed backward reaction?

(a) 55 kJ (b) 60 kJ

(c) 45 kJ (d) 80 kJ

2. What percentage fraction of the uncatalysed reacting molecules, will cross over the energy barrier as given in the data?

(a) 1% (b) 10^{-5}%

(c) 90% (d) 10^{-8}%

3. What percentage fraction of the catalysed reacting molecules will cross over the energy barrier as given in the data?

(a) 3% (b) 5%

(c) 10^{-5}% (d) 10^{-8}%

COMPREHENSION-II

Read the paragraph carefully and answer the following questions:

A catalyst increases the rate of chemical reaction by providing an alternative reaction pathway which lowers the activation energy than the reaction pathway in its absence. A catalyst is not consumed and therefore does not appear in the chemical equation for the reaction. A homogeneous catalyst is in the same phase as the reactants whilst a heterogeneous catalyst is in a different phase.

The complex $[Co(NH_3)_5F]^{2+}$ reacts with water according to the equation;

And Rate = k [complex]^a $[H^+]^b$

The reaction is acid catalysed, i.e., $[H^+]$ does not change during the reaction. Thus, rate = k'[complex]^a where, k' = $[H^+]^b$

Complex	$[H^+]$	$t_{1/2}$(hr)	$t_{3/4}$ (hr)
0.1	0.01	1	2
0.2	0.02	0.5	1

4. For the above data, value of a is

(a) 1 (b) 2

(c) 0 (d) $\frac{1}{2}$

5. Overall order of reaction is

(a) 1 (b) 2

(c) 0 (d) $\frac{1}{2}$

6. If 'a' is the initial concentration and k is the rate constant of a zero order reaction, the time for the reaction to go to completion will be

(a) $\frac{k}{a}$ (b) $\frac{a}{k}$

(c) $\frac{a}{2k}$ (d) $\frac{k}{2a}$

ANSWER KEYS

1. (d) **2.** (d) **3.** (d) **4.** (a) **5.** (b) **6.** (b)

HINTS AND EXPLANATIONS

1. (d) Activation energy of the catalysed backward reaction

$= E_{ab} - x = 120 - 40 = 80$ kJ

2. (d) % fraction of the uncatalysed reacting molecules crossing over the energy barrier is $100 \times e^{-\frac{E_a}{RT}}$

$= 100 \times e^{-\frac{100,000}{8\times500}}$

$= 100 \times 10^{-10} = 10^{-8}\%$

3. (d) Because rate of reaction is same, so same fraction of the molecules will cross over the energy barrier in presence of the catalyst i.e., $10^{-8}\%$

4. (a) Because $t_{3/4} = 2t_{1/2}$ for any set of data

5. (b) When concentrations of the reactants were doubled, the $t_{1/2}$ decreased to half of the initial value.

For 2nd order reaction $t_{½} = \frac{1}{Ka} \Rightarrow t_{½} \propto \frac{1}{a}$

6. (b)

MATCH THE COLUMN TYPE QUESTIONS

1. C_o = Initial concentration of reactant; C = Concentration of reaction at any time t; k = rate constant. Match the following:

Plot	Slopes
(i) C Vs t (abscissa) for zero order	(a) Unity
(ii) log C Vs t (abscissa) for first order	(b) Zero
(iii) $\left(-\frac{dc}{dt}\right)$ Vs C for zero order	(c) – k
(iv) ln (–dc/dt) Vs ln C for first order	(d) –k/2.303

2.

Column-I	Column-II
(a) α-emission	(p) Change in mass number
(b) β-emission	(q) No change in atomic number and mass number
(c) γ-emission	(r) Atomic number decreases
(d) β^+(Positron) emission	(s) Atomic number increases

ANSWER KEYS

1. (i) c; (ii) d; (iii) b; (iv) a **2.** (a); (p, r) (b); (s) (c); (q) (d); (s)

TRUE/FALSE TYPE QUESTIONS

1. A first-order reaction takes 100 minutes for 99.9% reaction, if it is 75% completed in 20 minutes.

2. For a given reaction constant is 1.0×10^{-2} M s^{-1}, then its half life period is proportional to the molar concentration of the reactant.

3. For a given reaction, rate is 1×10^{-2} M s^{-1} and rate constant is 1×10^{-4} M^{-1} s^{-1} hence, concentration of the reactant is 10 M.

4. Arrhenius equation gives variation of k with temperature as,

$$\frac{d \log_e k}{dT} = \frac{E_a}{2.303RT^2}$$

5. Based on half-life period order of the reaction is,

$$n = 1 + \frac{\log\left(\frac{T_1}{T_2}\right)}{\log\left(\frac{a_2}{a_1}\right)}$$

Where T_1 and T_2 are half-life periods at concentrations a_1 and a_2.

ANSWER KEYS

1. T **2.** T **3.** T **4.** F **5.** T

ASSERTION/REASON TYPE QUESTIONS

1. **Statement I:** The rate of a multistep reaction depends upon the slowest step known as rate determining step.

   Statement II: The rate constant of the slowest step is the rate constant of the overall reaction.
   Statement 'I' is correct but 'Statement II' is incorrect.

ANSWER KEYS

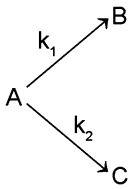
1. (a)

SUBJECTIVE QUESTIONS

1. | A (mol L^{-1}) | B (mol L^{-1}) | r_0 (mol $l^{-1}s^{-1}$) |
   |---|---|---|
   | 0.1 | 0.1 | 0.05 |
   | 0.2 | 0.1 | 0.10 |
   | 0.1 | 0.2 | 0.05 |

   Find (i) The rate law and
   (ii) The rate constant **[IIT-JEE 2004]**

2. Show that $t_{1/2}/t_{3/4}$ for nrd order reaction is a function of 'n' alone. $t_{3/4}$ is the time required for concentration to become ¼ of original concentration.

3. 

   Let $k_1:k_2 = 1:10$. Calculate the ratio, $\frac{[C]}{[A]}$ at the end of one hour assuming that $k_1 = \times\ hr^{-1}$

4. The reaction mentioned below is first-order w.r.t. sucrose and zero order with respect to water since water is in large excess as compared to sucrose. That is, it is an example of pseudo unimolecular reaction. Sucrose, glucose and fructose all are optically active substance. So, the progress of the reaction can be followed by measuring angle of rotations of the reaction mixture at various time intervals.

   During the reaction angle of rotation goes on decreasing and after sometime there is reversal of the direction of rotation i.e., from dextro to laevo and hence the reaction is called ***"inversion of cane sugar"*** or inversion of sucrose.

   $$\underset{\text{d-Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{d-Glucose}}{C_6H_{12}O_6} + \underset{\text{l-Furctose}}{C_6H_{12}O_6}$$

Initially	a	Excess	0	0
After time t	a – x	constant	x	x
At infinit	0	constant	a	a

   Angle of optical rotation is measured by means of an instrument called polarimeter. Optical rotation is mathematically expressed as,

   $$R_{obs} = l.C.\ [\alpha]_D^t$$

   Where, l = length of the polarimeter tube

   C = concentration of test solution

   $[\alpha]_D^t$ = specific rotation

   For a given sample and polarimeter, l and $[\alpha]_D^t$
   $r_{obs} \propto C$, or $r_{obs} = kC$, k – proportionality constant

   If r_0, r_t and r_∞ be the observed angle of rotations of the sample at zero time, time t and infinity

respectively, and k_1, k_2 and k_3 be the proportionately in terms of sucrose, glucose and fructose, respecting.

Then,

$$r_0 = k_1 a$$

$$r_t = k_1(a - x) + k_2 x + k_3 x$$

$$r_\infty = k_2 a + k_3 a$$

From these equations it can be shown that,

$$\frac{a}{a-x} = \frac{r_0 - r_\infty}{r_t - r_\infty}$$

So, the expression for the rate constant of this reaction in terms of the optical rotational data may be put as,

$$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

5. ***A ⟶ B +C***

Time	0	t
Volume of reagent	V_1	V_2

Reagent reacts with all of them (A, B and C). A,B and C have 'n' factors in the ratio of 1:2:3 with the reagent (assuming its n factor remains same with all of them). Find k.

Now consider this situation A ⟶ B+C

Time	T	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A,B and C and have 'n' factors in the ratio of 1:2:3 with the reagent. Find k.

	A ⟶	B	+	C
At t = 0	V_1		0	0
At t = t	$V_1 - x$		2 x	3x
At t =∞	0	$2V_1$	$3V_1$	

$\therefore \quad 5V_1 = V_3 \qquad V_1 = V_3/5$

$V_1 + 4 \times = V_2 \qquad x = \dfrac{V_2 - V_1}{4}$

$$\therefore \quad V_1 - x = \frac{V_3}{5} - \frac{V_2}{4} + \frac{V_3}{20} = \frac{5V_3 - 5V_2}{20}$$

$$\therefore \quad k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{V_3/5}{5V_3 - 5V_2/20}$$

$$k = \frac{1}{t} \ln \frac{4V_3}{5(V_3 - V_2)}$$

Now, we will consider a reaction A $\xrightarrow{D}$ B+C which is catalysed by D. We will assume in this problem that the concentration of the catalyst remains constant throughout. The data given to us is

Time	0	t	∞
Volume of reagent	V_1	V_2	V_3

The reagent reacts with all (A,B,C and D). Assume that 'n' factor of A,B and C are in the ratio of 1:1:1 and that of D is not known. Find k.

Let V_A be the volume of the reagent required by A initially and V_D be the volume required by D.

$$\therefore \quad V_1 = V_A + V_D$$

$V_2 = (V_A - x) + \times + \times + V_D$ (x is the volume of the reagent required for those moles of A that have reacted to give B and C).

$$V_3 = 2V_A + V_D$$

We can see that, $V_3 - V_1 = V_A$

And, $V_3 - V_2 = V_A - x$

$$\therefore \quad k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t} = \frac{1}{t} \ln \frac{(V_3 - V_1)}{(V_3 - V_2)}$$

6. For the decomposition of dimethyl ether, A in the Arrhenious equation $K = Ae^{-E/RT}$ has a value of 1.26×10^{13} and E_a value of 58.5 kcal. Calculate half life period for first order decomposition at 527°C.

7. For the reaction —

$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ at 900 K, the following data are obtained:

Initial pressure of NO (atm)	*Initial pressure of H_2(atm)*	*Rate (atm min^{-1})*
0.150	0.400	0.020
0.075	0.400	0.005
0.150	0.200	0.010

Find the rate law and the value of rate constant.

8. ^{227}Ac has a half-life of 22.0 years with respect to radioactive decay. The decay follows two parallel paths, one leading to ^{222}Th and the other to ^{223}Fr. The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths?

9. The nucleidic ratio of $^{3}_{1}H$ to $^{1}_{1}H$ in a sample of water is 8.0×10^{-18}:1. Tritium undergoes decay with half life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contains 40 years after the original sample in collected?

10. On analysis, a sample of Uranium was found to contain 0.277 g of $_{82}Pb^{206}$ and 1.667 g of $_{92}U^{238}$. The half life period of $_{92}U^{238}$ is 4.51×10^{9} years. If all the lead were assumed to have come from decay of $_{92}U^{238}$, what is the age of the earth?

11. Gram atoms of an α -active radio isotope are disintegrating in a sealed container. In one hour the helium gas collected at STP is 11.2 cm^3. Calculate the half-life of the radio-isotope.

12. A carbon radio isotope $_{Z}X^{A}$ (half life 10 days) decays to give $_{Z-2}Y^{A-4}$. If 1.00 g atom of $_{Z}X^{A}$ is kept in a sealed tube, how much helium will accumulate in 20 days ? Express the result in cm^3 at STP.

13. Radioactive decay is a first order process. Radioactive carbon wood sample decays with a half life of 5770 years. What is the rate constant in $(years)^{-1}$ for the decay? What fraction would remain after 11540 years?

14. A sample of $_{53}I^{131}$, as iodide ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? Given $T_{1/2}$ I^{131} = 8 days.

HINTS AND EXPLANATIONS

1. When concentration of A is doubled keeping the concentration of B constant, the rate is doubled so

$r \propto [A]$ when [B] is constant.

When conc. of B is doubled keeping the concentration of A constant, the rate remains unchanged.

So $r \propto [B]^0$, when [A] is constant.

Hence, the overall rate law is:

$$\text{Rate} \propto [A]$$

$$\text{Rate} = k[A]$$

$$0.05 = k \times 0.1$$

$$\therefore \quad k = 0.5\ s^{-1}$$

2. $A \rightarrow$ Products

$$-\frac{dC_A}{dt} = KC_A^n \qquad (\because \text{ order is n})$$

$$\text{On integrating } \frac{-(C_A)^{1-n}}{1-n} = Kt + \text{constant} \qquad ...(1)$$

$$\text{at } t = 0,\ C_A = C_0 \qquad \therefore \text{ constant} = -\frac{C_0^{1-n}}{1-n} \qquad ...(2)$$

$\therefore$ By equations (1) and (2),

$$-\frac{C_A^{1-n}}{1-n} = Kt - \frac{C_0^{1-n}}{1-n}$$

$$\text{or} \qquad Kt = \frac{1}{(n-1)}[C_A^{1-n} - C_0^{1-n}] \qquad ...(3)$$

$$\text{if } C_A = \frac{C_0}{2} \text{ at } t = t_{1/2} \text{ then by Eq. (3)}$$

$$Kt_{1/2} = \frac{1}{(n-1)}\left[\left(\frac{C_0}{2}\right)^{1-n} - (C_0)^{1-n}\right]$$

$$= \frac{1(C_0)^{1-n}}{(n-1)} \times [2^{n-1} - 1] \qquad ....(4)$$

Similarly, if $C = \frac{C_0}{4}$ at $t = t_{3/4}$, then by Eq. (3)

$$Kt_{3/4} = \frac{C_0^{1-n}}{(n-1)}[4^{n-1} - 1] \qquad ....(5)$$

By Eqs. (4) and (5),

$$\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1} - 1}{4^{n-1} - 1}$$

Thus the ratio depends only on 'n'.

3. $$\frac{-d[A]}{dt} = (k_1 + k_2)[A]$$

$$\therefore \quad \frac{-d[A]}{[A]} = (k_1 + k_2)\, dt$$

Integrating with in the required limits, we get,

$$\ln\frac{[A]_0}{[A]_t} = (k_1 + k_2)t$$

$$\therefore \quad \ln\frac{[A]_t + [B] + [C]}{[A]_t} = (k_1 + k_2)\, t$$

Since, $\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{1}{10}$

$\therefore \quad \ln \frac{[A]_t + \frac{[C]}{10} + [C]}{[A]_t} = 11x$

$$\frac{[C]}{[A]_t} = \frac{10}{11}(e^{11x} - 1)$$

6. Taking logarithm of Arrhenious equation $K = Ae^{-E/RT}$ we get,

$$\log K = \log A - \frac{E}{2.303RT} \quad \ldots (i)$$

Given $A = 1.26 \times 10^{13}$

$E = 58.5$ kcal

$T = 527 + 273 = 800$ K

Substituting these value in equation (i), we get,

$$\log K = \log (1.26 \times 10^{13}) - \frac{58.5 \times 10^2}{2.303 \times 1.987 \times 800}$$

$= 13.1003 - 15.9799$

$= -2.8796$

$K = 1.3194 \times 10^{-3}$ sec^{-1}

$$t_{1/2} = \frac{0.693}{1.3194} \times 10^3 \text{ sec} = 525 \text{ sec}$$

7. Let order with respect to NO(g) is 'm' and order with respect to H_2(g) is 'n'

Then, Rate $= K[P_{NO}]^m[P_{H_2}]^n \quad \ldots (1)$

$0.020 = K\,[0.15]^m\,[0.40]^n \quad \ldots (2)$

$0.005 = K\,[0.075]^m\,[0.40]^n \quad \ldots (3)$

$0.010 = K\,[0.15]^m\,[0.2]^n \quad \ldots (4)$

Dividing equation (2) by (3), we get,

$$\frac{0.020}{0.005} = \left(\frac{0.15}{0.075}\right)^m$$

$m = 2$

Dividing Equations (2) by (4), we get,

$$\frac{0.020}{0.010} = \left(\frac{0.4}{0.2}\right)^n$$

$n = 1$

Rate $= [P_{NO}]^2[P_{H_2}]^1$

Substituting the values of m, n in Eq. (2), we get

$0.020 = K\,(0.15)^2\,[0.40]$

$K = 2.22$ atm^{-2} min^{-1}

8. The rate constant of the decay is $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{22}$;

If k_1 and k_2 are the rate constants of the reactions leading to ^{222}Th and ^{223}Fr, respectively we have $k_1 + k_2 = \frac{0.693}{22}$; $\frac{k_1}{k_2} = \frac{2}{98}$; On solving for k_1 and k_2, we get; $k_2 = 0.03087$ y^{-1}; $k_1 = 0.00063$ y^{-1}

9. 18 g H_2O has 2H atom in it $= 6.023 \times 10^{23} \times 2$; 18 g H_2O has $^3_1$H atoms $= 8 \times 10^{-18} \times 6.023 \times 10^{23} \times 2$ $\therefore$ 10 g H_2O has $^3_1$H atoms $= \frac{8 \times 10^{-18} \times 6.023 \times 10^{23} \times 2 \times 10}{18}$

i.e., No of $^3_1$H $= 5.354 \times 10^6$ atoms $40 = \frac{2.303 \times 12.3}{0.693}$

$$\log \frac{5.354 \times 10^6}{N} = 5.624 \times 10^5 \text{ atoms}$$

10. $_{92}U^{238} = 1.667$ g $= \frac{1.667}{238}$ mole;

$_{82}Pb^{206} = 0.227$g $= \frac{0.227}{206}$ mole

$\because$ All the lead have come from decay of U.

$\therefore$ Moles of Pb formed $= \frac{0.277}{206}$

$\therefore$ moles of U decayed $= \frac{0.277}{206}$ $\therefore$ Total moles of Uranium $= \frac{1.667}{238} + \frac{0.277}{206}$, i.e., N_0;

Also, N for $U^{238} = \frac{1.667}{238}$ $\because$ for U^{238}

$$t = \frac{2.803}{k} \log \frac{N_0}{N} = \frac{2.303 \times 4.51 \times 10^9}{0.693} \log \frac{\frac{1.667}{238} + \frac{0.277}{206}}{\frac{1.667}{238}};$$

$t = 1.143 \times 10^9$ yrs .

11. Number of atoms of helium is 11.2 cc at NTP

$= \frac{11.2}{22400} \times 6.02 \times 10^{23} = 3.01 \times 10^{20}$ atoms

Since, helium atom corresponds to α-particle.
Thus, Rate of disintegration
$= 3.01 \times 10^{20}$ per hour.

We know, Rate = Rate constant × concentration in atom

$3.01 \times 10^{20} = K \times 10 \times 6.02\ 10^{23}$

$K = 0.05 \times 10^{-3}$ hour^{-1}

$$T_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.05 \times 10^{-3}} = 13860 \text{ hours}$$

$$T_{1/2} = \frac{13860}{24 \times 365} = 1.58 \text{ years}$$

12. Initial concentration (N_0) of radio-isotope is 1 g atom. Concentration remained after 20 days may be calculated as,

$$N_t = N_0\left(\frac{1}{2}\right)^n$$

Where n = n_0 of half lives = 20/10 = 2 = $1\left(\frac{1}{2}\right)^2 = \frac{1}{4}$

Concentration decayed to α-particles = $1 - \frac{1}{4} = \frac{3}{4}$ g atom. An α-particle takes 2 electron from air and from helium gas. Thus,

Helium formed $= \frac{3}{4}$ g atom $= \frac{3}{4} \times 22400$ cc

$= 16800$ cc

13. $K = \frac{0.693}{T_{1/2}} = \frac{0.693}{5770}$

$= 1.201 \times 10^{-4}$ year^{-1}

$$K = \frac{2.303}{t}\log\frac{N_0}{N_t}$$

$$1.201 \times 10^{-4} = \frac{2.303}{11540}\log\frac{N_0}{N_t}$$

$$4.002 = \frac{N_0}{N_t}$$

$$\therefore \quad \frac{N_t}{N_0} \text{ (Remaining fraction)} = \frac{1}{4.002}$$

14. We know,

$$\frac{0.693}{T_{1/2}} = \frac{2.303}{t}\log_{10}\left[\frac{N_0}{N}\right]$$

$$\frac{0.693}{8} = \frac{2.303}{4}\log_{10}\left[\frac{N_0}{N}\right]$$

$$\frac{N}{N_0} = 0.707$$

$\Rightarrow$ 70.7% of initial activity is present. Given that 67.7% activity is migrated to thyroid gland.

Thus, weight of I^- migrated to thyroid gland may be calculated as,

$$\frac{67.7}{70.7} \times 100 = 95.75\%$$

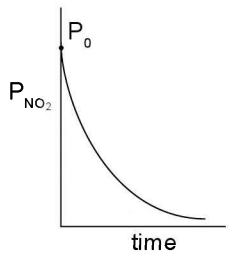
i.e., $0.1 \times \frac{95.75}{100} = 0.09575$ mg

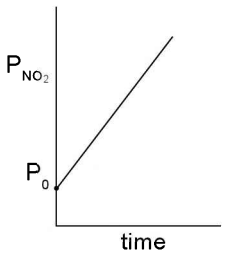
Question Bank

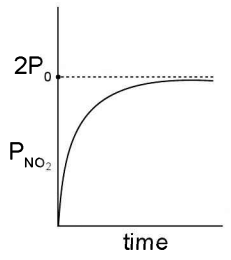
STRAIGHT OBJECTIVE TYPE QUESTIONS

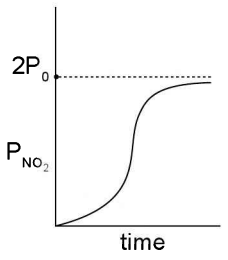
1. $N_2O_5 \rightarrow 2NO_2 + O_2$

When N_2O_5 decompose, its t_{12} does not change with its changing pressure during the reaction, so which one is the correct representation for "pressure of $2NO_2$" vs lime° during the reaction when initial N_2O_5 is equals to P_0.

(a) 

(b) 

(c) 

(d) 

2. In a hypothetical reaction

A(aq) 2B(aq) + C(aq) (1st order decomposition)

'A' is optically active (dextro-rototory) while 'B' and 'C' are optically inactive but 'B' takes part in a titration reaction (fast reaction) with H_2O_2. Hence the progress of reaction can be monitored by measuring rotation of plane polarized light or by measuring volume of H_2O_2 consumed in titration.

In an experiment the optical rotation was found to be O = 30° at t = 20 min and 8 =15° at t = 50 min. from start of the reaction. If the progress would have been monitored by titration method, volume of H_20_2 consumed at t = 30 min. (from start) is 30 ml, then the volume of H_2O_2 consumed at t = 90 min will be:

(a) 60 ml (b) 45 ml

(c) 52.5 ml (d) 90 ml

3. The elementary reaction A + B → products has $k = 2 \times 10^{-5}\ M^{-1}\ S^{-1}$ at a temperature of 27°C. Several experimental runs are carried out using stoichiometric proportion. The reaction has a temperature coefficient value of 2.0. At what temperature should the reaction be carried out if inspite of halving the concentrations, the rate of reaction is desired to be 50% higher than a previous run. (Given $\frac{\ell n6}{\ell n2} = 2.585$).

(a) 47 °C (b) 53 °C

(c) 57 °C (d) 37 °C

4. The high temperature (≈1200K) decomposition of CH_3COOH) occurs as follows as per simultaneous 1st order reactions.

$CH_3COOH \xrightarrow{k_1} CH_4 + CO_2$

$CH_3COOH \xrightarrow{k_2} CH_2C0 + H_20$

What would be the % of CH_4 by mole in the product mixture (excluding CH_3COOH)?

(a) $\frac{50k_1}{(k_1+k_2)}$

(b) $\frac{100k_1}{(k_1+k_2)}$

(c) $\frac{200k_1}{(k_1+k_2)}$

(d) it depends on time

5. A reaction takes place in three steps; the rate constants are B_r, k_2 and k_3. The overall rate constant $K = \frac{k_1k_3}{k_2}$ If energies of activation are 40, 30 and 20 kJ, the overall energy of activation is (assumming 'A' to be constant for all)

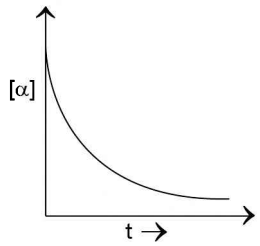
(a) 10 (b) 15

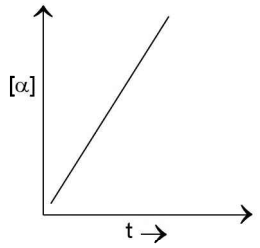
(c) 30 (0) 60

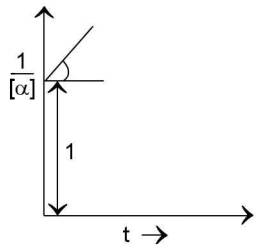
6. The inversion of cane sugar proceeds with half life of 600 minute at pH = 5 for any concentration of sugar. However, at pH = 6, the half life changes to 60 minutes, the rate law expression for sugar inversion can be written as

(a) $r = k\,[sugar]^2\,[H+]^\circ$
(b) $r = k\,[sugar]'\,[Hl^\circ$
(c) $r = k\,[sugar]^2\,[H^+]^1$
(d) $r = k[sugar]^\circ[H+]^{-1}$

7. Some graphs are sketch for the reaction A → B (assuming different orders). Where 'α' represent the degree of dissociation.

(a)


(b)


(c)


The order of reaction is respectively.
(a) 0, 1, 2 (b) 1, 0, 2
(c) 2, 0, 1 (d) 1, 2, 0

8. A hypothetical reaction:
$A_2 + B_2 \xrightarrow{K_C} 2AB$ Follows mechanism as given below:

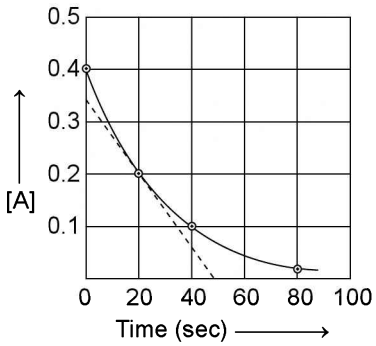
$A_2 \underset{K_{2122}}{\rightleftharpoons} A + A$ (fast) (K_c - is equilibrium constant)

$A + B_2 \xrightarrow{k_1} AB + B$……(slow) ($k_1$ - rate constant)

$A + B \underset{K_{322}}{\rightleftharpoons} AB$ (fast) (k_2, k_3 - are rate constant)

The order of overall reaction is:
(a) 2.5 (b) 1
(c) 3/2 (d) Zero

9. A certain reaction A-3 B follows the given concentration (Molarity)-time graph. Which of the following statement is true?



(a) The reaction is second order with respect to A
(b) The rate for this reaction at 40 seconds will be approximately $3.5 \times 10^{-3}\ Ms^{-1}$
(c) The rate for this reaction at 80 seconds will be $1.75 - 10^{-3}\ Ms^{-1}$
(d) The [B] will be 0.25 Matt = 60 seconds

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

10. For the consectutive reaction $A \xrightarrow{k_1(time^{-1})} B \xrightarrow{k_2(time^{-1})} C$ following curves were obtained depending upon the relative values of k_1 & k_2
Now which of the following is the correct match?
(a) figure 1 — ($k_1 < k_2$)
(b) figure 2 — ($k_1 < k_2$)
(c) figure 2 — ($k_1 \gg k_2$)
(d) figure 1 — ($k_1 \gg k_2$)

11. For a certain reaction A → products, the $t_{1/2}$ as a function of $[A]_0$ is given as below:

Which of the following is true:
(a) The order is $\frac{1}{2}$
(B) t_{112} would be $100\sqrt{10}$ min for $[A]_0 = 1M$
(c) The order is 1
(d) t_{112} would be 100 min for $[A]_0 = 1$ M

12. Decomposition of 3A(g) → 2B(g) + 2C(g) follows first order kinetics. Initially only A is present in the container. Pressure developed after 20 min. and infinite time are 3.5 and 4 atm respectively. Which of the following is true.

(a) t_{50} = 20 min (b) t_{ams} = 40 min
(c) $t_{99\%}$ = 64/3 min (d) $t_{8,\ 5\%}$ = 60 min

13. The reaction $2NO + Br_2 \rightarrow 2NOBr$ follows the mechanism:

(1) $NO + Br_2 \xrightarrow{Fast} NOBr_2$
(2) $NOBr_2 + NO \xrightarrow{Slow} 2NOBr$

Which of the following is/are true regarding this:
(a) The order of the reaction with respect to NO is two
(b) The molecularly of the steps (1) and (2) are two each.
(c) The molecularly of the overall reaction is three.
(d) The overall order of the reaction is three.

14. In the following gaseous phase first order reaction,

$A(g) \rightarrow 2B(g) + C(g)$

initial pressure was found to be 400 mm of Hg and it changed to 1000 mm of Hg after 20 min. Then:
(a) Half life for A is 10 min
(b) Rate constant is 0.0693 min^{-1}
(c) Partial pressure of C at 30 min is 350 mm of Hg
(d) Total pressure after 30 min is 1150 mm of Hg

15. The polarimeter readings in an experiment to measure the rate of inversion of cane suger (1st order reaction) were as follows

time (min) :	0	30	co
angle (degree) :	30	20	–15

Identify the true statement (s) log 2 = 0.3, log 3 = 0.48, log 7 = 0.84 , $\log_e$ 10 = 2.3
(a) The half life of the reaction is 75 min
(b) The solution is optically inactive at 120 min.
(c) The equimolar mixture of the products is dextro-rotatory
(d) The angle would be 7.5° at half time

16. Identify the true statement(s)
(a) A catalyst is chemically unchanged at the end of a reaction
(b) A catalyst may appear in the kinetic rate equation of the reaction
(c) A catalyst will not affect the composition of an equilibrium mixture
(d) A catalyst cannot cause a non-spontaneous ($\Delta G > 0$) reaction to proceed

17. The half – period T for the decomposition of ammonia on tungsten wire, was measured for different initial pressure P of ammonia at 25°C. Then

P (mm Hg)	11	21	48	73	120
T (sec)	48	92	210	320	525

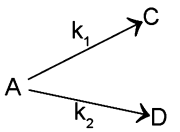
(a) Zero order reaction
(b) First order reaction
(c) Rate constant for reaction is 0.114 seconds
(d) Rate constant for reaction is 1.14 seconds.

18. The ozone layer in the earth's upper atmosphere is important in shielding the earth from very harmful ultraviolet radiation. The ozone, O_3, decomposes according to the equation $2O_3(g) \rightarrow 3O_2(g)$. The mechanism of the reaction is thought to proceed through an initial fast, reversible step and then a slow second step.

Step 1: Fast, reversible $O_3(g) \quad O_2(g) + O(g)$
Step 2: Slow $O_3(g) + O(g) \rightarrow 2O_2(g)$

The which of the following is correct?
(a) Step 2 is rate determining step
(b) the rate expression for step 2 is $-\frac{dt}{dt}[O_3] = k[O_3][O]$
(c) For Step 1, molecularity is 1
(d) For Step 2, molecularity is 2

19. Consider the following case of COMPETING 1st ORDER REACTIONS



After the start of the reaction at t = 0 with only A, the [C] is equal to the [D] at all times. The time in which all three concentrations will be equal is given by

(a) $t = \frac{1}{2k_1}\ell n3$ (b) $t = \frac{1}{2k_2}\ell n3$
(c) $t = \frac{1}{3k_1}\ell n2$ (d) $t = \frac{1}{3k_2}\ell n2$

20. Rate of a chemical reaction 2A (g) → B (g) is defined as

$$'r_B' = \frac{1}{V}\frac{dn_B}{dt}$$

Where n_B = number of moles of B formed and C_B = concentration of B then which of the following relation is correct.

(a) $r_B = \frac{dC_B}{dt} + \frac{C_B}{v}\frac{dv}{dt}$ (If volume V is not constant)
(b) $r_B = \frac{dC_B}{dt}$ (If volume V is constant)
(c) $r_B = \frac{dC_B}{dt} - \frac{C_B}{v}\frac{dv}{dt}$ (If volume V is not constant)
(d) $r_B = -\frac{dC_B}{dt} + \frac{C_B}{v}\frac{dv}{dt}$ (If volume V is not constant)

ASSERTION/REASON TYPE QUESTIONS

21 **Statement-1:** If the activation energy of reaction is zero, temperature will have no effect on the rate constant.

Statement-2: Lower the activation energy fasten is the reaction.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

22. **Statement-1:** If the order of reaction is zero then the degree of dissociation will be independent upon initial concentration.

Statement-2: The degree of dissociation of Zero order reaction is given by $\alpha = \frac{kt}{c_0}$

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

TRUE AND FALSE TYPE QUESTIONS

23. The rate of the reaction A → B having the rate law $-\frac{d[A]}{dt} = k\,[A]\,[B]$ when plotted against time will exhibit maximum at some time.

24. A catalyst in a chemical reaction increases the forward E_a and decreases the backward E_a.

25. For a first-order reaction, the time required to reduce successively the concentration of reactant by a constant fraction is always same.

26. As a first order reaction proceeds at a constant temperature, the ode rewislis constant

27. Generally the rate of reaction decreases with decrease in temperature.

28. The rate law of the elementary reacton; $2A \rightarrow B + C$, must be $r = k\,[A]^2$.

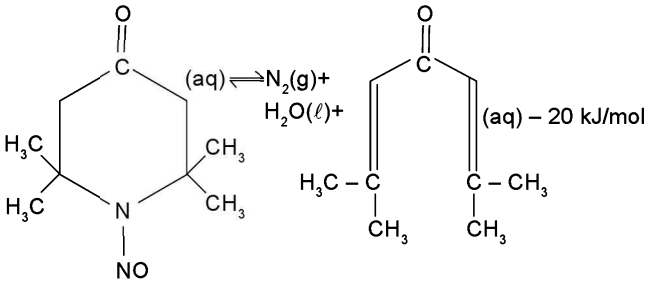
29. Generally the rate of reaction depends upon the surface area of the solid reactants.

30. Zero order reaction is uniform rate reaction but it can not be elementry reaction (single step reaction).

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

Consider the inter conversion of nitrosotnacetoamine into nitrogen phorone and water.



The reaction is 1st order in each direction, with an equilibrium constant of 10^4, the activation energy for the forward reaction is 11usactivation energy for the forward reaction is 57.45 kJ/mol. Assuming arrehemus preexponetial factor of $10^{12}\ S^{-1}$

31. What is the expected forward constant at 300K, if we initiate this reaction starting with only reactant

(a) 10^2 (b) 10^6
(c) 10^6 (d) 10^4

32. If the change in entropy of the reaction is 0.07 KJ. K^{-1} mol^{-1} at 1 atm pressure. Calculate upto which temperature the reaction would not be spontaneous. (For forward reaction)

(a) T < 285.7 K
(b) T > 250 K
(c) T < 340.2 K
(d) T > 200 K

33. Calculate Kp of the reaction at 300 K

(a) 2.4×10^4 atm^{-1}
(b) 10^4atm
(c) 24.6×10^4atm
(d) 2.82×10^2 atm^1

COMPREHENSION-2

PSEUDO-MOLECULAR REACTIONS

There are many reactions which obey a first order rate equation, although in reality they are bi- or ter-molecular. As an example of these may be taken the decomposition of Carbonyl sulfide in wate , namely,

$$COS + H_20 \rightarrow 00_2 + H_2S$$

According to the law of mass action this reaction should be second order with the rate dependent on the concentration of both the carbonyl sulfide and the water. Actually However, the rate is found to be first order with respect to the carbonyl sulfide and independent of the water reactions exhibiting such behaviour are said to be pseudo-molecular.

The pseudo-unimolecular nature of this reaction is explainable by the fact that water is present in such excess that its concentration remains practically constant during the course of the reaction. Under these condition b x = b, and the rate equation becomes

$$\frac{dx}{dt} = k_2(a-x)b$$

On integration this leads to

$$k = bk_2 = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$$

which is the equation for a first order reaction. It is evident, that now constant k is not independent of the concentration, as is the case with true first order constants, but may vary with b if the latter is changed appreciably, When such is the case, the true constant k_2 can be obtained from k by dividing the latter by b.

Pseudo-molecular reactions are encountered whenever one or more of the reactants remain constants during the course of an experiment. This is the case with reactions conducted in solvents which are themselves one of the reactants, as in the decomposition of carbonyl sulfide in water, or in the esterification of acetic anhydride in alcohol

$$(CH_3C0)_20 + 2C_2H_5OH \rightarrow 2CH_3C00C_2H_5 + H_20$$

Again, this is also true of reactions subject to catalysis, in which case the concentration of the catalyst does not change. The decomposition of diacetone alcohol to acetone in aqueous solution is catalyzed by hydroxyl ions, with the rate proportional to the concentration of the alcohol and that of the base. Since the concentration of the base does not change within any one experiment, however, the rate equation reduces to one of first order with respect to the alcohol. But the rate constant k obtained for various concentrations of base are not identical, as may be seen from table. To obtain from these the true second order velocity constant, the k's must be divided by the hydroxyl ion concentration. When this is done excellent k2 values result, as column 3 indicates.

Table: Decomposition of diacetone alcohol in water at 25°C (Catalyst : NaOH)

C Conc. of NaOH	k (min^{-1})	$k_2 = k/C$
0.0205	0.0455	2.22
0.0292	0.0651	2.23
0.0518	0.1160	2.24
0.0710	0.1576	2.22
0.1045	0.2309	2.21

34. Which of k or k_2 is dependent on concentration?

(a) only k
(b) only k_2
(c) both k and k_2
(d) neither k nor k_2

35. By what factor does the rate of reaction of diacetone alcohol in water solution change if pOH is increased by 2 units other things remaining same?

(a) increases 100 times
(b) decreases 100 times
(c) increases 2 times
(d) decreases 2 times

36. For the reaction A + B → C; r = k [A] [B] with $[A]_0$ = 0.001 M and $[B]_0$ = 10 M, the time in which the concentration of A becomes 0.005 M will be nearly

(a) $\frac{0.693}{10k}$ (b) $\frac{0.693}{k}$
(c) $\frac{6.93}{k}$ (d) $\frac{693}{k}$

COMPREHENSION-3

From the following data answer the questions :
Reaction: $A + B \rightarrow P$

[A] M	*[B] M*	*Initial rate M sec^{-1}*	
		300 K	***400 K***
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	

37. The order w.r.t A is
(a) 1 (b) 2
(c) 3 (d) –1

38. The value of rate constant at 300 K is (M^{-2} sec^{-1})
(a) 2.667×10^{8} (b) 2.667×10^{5}
(c) 2.667×10^{5} (d) 2.667×10^{9}

39. The energy of activation for reaction (KJ/mol) is
(a) 20.83 (b) 13.83
(c) 15.23 (d) 10.23

MATCH THE COLUMN TYPE QUESTIONS

40. For $A + B \rightarrow C$ in column-II the graphs given can be from any of these four types.

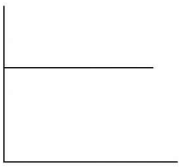
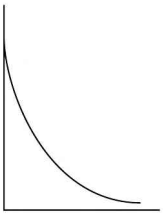
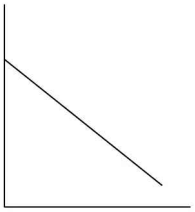
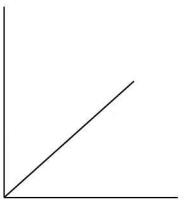
(a) $-\frac{dA}{dt}$ Vs time (x axis)

(b) $t_{1/12}$ Vs initial concentration (x axis)

(c) $\left(\frac{C_0 - C_t}{C_t}\right)$ Vs time (x axis)

(d) Concentration Vs time (x axis)

Match the graphs in Column-II for the given order of reactions in Column-I

Column-I	**Column-II**
(a) 1st order	(p) 
(b) Zero order	(q) 
(c) 2nd order	(r) 
(d) Pseudo first order	(s) 

41. Match the following:

Column-I	**Column-II**
(a) $2N_2O_5(g) \xrightarrow{1^{st}\ order} 4NO_2(g) + O_2(g)$	(p) All the gaseous products are para-magnetic in nature
(b) $2H_2O_2(aq) \xrightarrow{1^{st}\ order} 2H_2O(aq) + O_2(g)$	(q) Hybridization of reactant involves only s & p orbitals
(c) $2NH3(g) \xrightarrow{Zero\ order} N_2(g) + 3H_2(g)$	(r) As the reaction proceeds half life or reactant changes with time
(d) $2Cl_2O_7(g) \xrightarrow{Zero\ order} 4C1O_2(g) + 3O_2(g)$	(s) rate of production of gases decreases with the increase in concentration of products.

42. Match the following

Column-I	**Column-II**
(a) If the activation energy is 65 kJ, then how much time faster a reaction will proceed at 25°C than at 0°C	(p) 5
(b) Rate constant of a first-order reaction is 0.0693 min^{-1}. If we start with 20 mol L^{-1}, it is reduced to 2.5 mol L^{-1} in how many minutes	(q) 11

(c) Half-lives of first-order and zeroth order reactions are same. Ratio of rates at the start of reaction is how many times of 0.693. (r) 30

(d) The half-life periods are given, (s) 1/4

[A] (M)	0.0677	0.136	0.272	(t) 2
$t_{1,2}$ (sec)	240	480	960	(u) 1

order of thre reaction is (v) 0

SUBJECTIVE ANSWER TYPE QUESTIONS

SHORT SUBJECTIVE

43. Reaction A → B carried inside a container concentration varies as $A_t = a + bt$. Rate of reaction can be expressed in term of pressure at temperature T = 300 K take b = 4, R = $\frac{1}{12}$ atm $mol^{-1}k^{-1}$

44. The graph between log k and A $\frac{1}{T}$ [K is rate constant (sec^{-}) and T the temperature]. (K) is a straight line with OX = 5 and $\theta = \tan^{-1}\left(\frac{1}{2.303}\right)$. Calculate the value of E_a is cal.

45. For the reaction A → products, the following data is given for a particular run.

time (min.) :	0	5	15	35
$\frac{1}{[A]}(M^{-1})$:	1	2	4	8

Determine the order of the reaction.

LONG SUBJECTIVE

46. The rate constant of 1st order decomposition reaction of an organic compound (X) into another organic compound Y and an inorganic compound (gas) (Z) may be given $\log_{10} k\,(sec^{-1}) = 12.37 - \frac{1.25\times10^4}{T(\text{inkelvin})}$

Find the activation energy and rate constant at 750 K and indicate your answer as the product of Ea (in Joules moll and rate constant (in unit sec^{-1}) and fill the answer as a nearest whole number.

Take R = 8.3 $JK^{-1}mo1^{-1}$, {antismog (-4.3) = 5 x 10^{-5}}

47. For the same first-order reaction, A → B + C, occurring in solution phase, now let us assume that the reagent reacts with all the species A, B and C. The 'n' factor of A, B and C with the regent is α, β and γ respectively and that of the reagent with A, B and C is a, b, and c.

Time	*0*	*t*
Volume of reagent	V_0	V_1

Calculate the expression of rate constant.

ANSWER KEYS

1. (c)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (b)	**7.** (b	**8.** (c)	**9.** (b)
10. (b, d)	**11.** (a, b)	**12.** (a, b, d)	**14.** (a, b, c, d)	**15.** (a, b, d)	**16.** (a, b, c, d)	**17.** (a, c)	**18.** (a, b, c, d)	**19.** (a, b)
20. (a, b)	**21.** (b)	**22.** (d)	**23.** (True)	**24.** (False)	**25.** (True)	**26.** (False)	**27.** (True)	**28.** (True)
29. (True)	**30.** (True)	**31.** (b)	**32.** (a)	**33.** (c)	**34.** (a)	**35.** (b)	**36.** (a)	**37.** (b)
38. (a)	**39.** (b)	**40.** (a – p, q), (b – p, r, s), (d – p, q)			**41.** (a – p, q, s), (b – p, q, s), (c – q, r), (d – p, q, r)			
42. (a – q), (b – r), (c – t), (d – v)								

HINTS AND EXPLANATIONS

2. (b) As only A is optically active. So concentration of A at t = 20 min ∝ 30°
While concentration of A at t = 50 min ∝ mc 15°
So concentration has decreased to half of its value in 30 min, so $t_{1/2}$ = 30 min.

So, volume consumed of H_2O_2 at t = 30 min = $t_{1/2}$, is according to 50% production of B. at t = 90 min. production of B = 87.5% (Three half lives)

So, volume consumed = (30 ml) + $\left(\frac{30}{2}\text{ml}\right)$ + $\left(\frac{30}{4}\right)$ ml = 52.5 ml.

3. (b) $r_2 = k_2 [A]_2^1 [B]_2^1$ for a certain run
$r_1 = k_1 [A]_1^1 [B]_1^1$ for a previous run

$$\frac{r_2}{r_1} = \frac{k_2}{k_1}\frac{[A]_2}{[A]_1}\frac{[B]_2}{[B]_1}$$

Substituting the given information

$$1.5 = 2^{\left(\frac{t_2-27}{10}\right)} \times \frac{1}{2} \times \frac{1}{2}$$

$$\Rightarrow 6 = 2^{\frac{t_2-27}{10}}$$

$$\Rightarrow \frac{t_2-27}{10}\ell n2 = \ell n6$$

$$\Rightarrow \frac{t_2-27}{10} = \frac{\ell n6}{\ell n2}$$

$$\Rightarrow \frac{t_2-27}{10} 2.585$$

$$\Rightarrow t_2 = 52.85°C$$

$$\sqcup 53°C$$

4. (a) $$\frac{n_{CH_4}+n_{co_2}}{n_{CH_2CO}+n_{H_2O}} = \frac{k_1}{k_2}$$

$$\Rightarrow \frac{n_{CH_4}+n_{CO_2}}{n_{CH_4}+n_{CO_2}+n_{CH_2CO}+n_{H_2o}} = \frac{k_1}{k_1+k_2}$$

$$\Rightarrow \frac{2n_{CH_4}}{n_{total}} = \frac{k_1}{(k_1+k_2)}$$

$$\Rightarrow \frac{n_{CH_4}}{n_{total}} = \frac{k_1}{2(k_1+k_2)}$$

$$\Rightarrow \frac{n_{CH_4}}{n_{total}} \times 100 = \frac{50k_1}{(k_1+k_2)}$$

5. (c) $$K = \frac{k_1k_3}{k_2}$$

$\therefore \ \ell n\, K \ \ell n\, K_1 + \ell n\, K_3 - \ell n\, K_2$

But $\ell n\, K = -\frac{E}{RT} + \ell n\, A$

$$\therefore -\frac{E}{RT} + \ell n\, A = -\frac{E_1}{RT} + \ell n\, A$$

$$-\frac{E_3}{RT} + \ell n\, A + \frac{E_2}{RT} - \ell n\, A$$

or $E_{Total} = E_1 + E_3 - E_2 = 40 + 20 - 30 = 30$ KJ.

6. (b) At pH = 5 the $t_{1/2} \propto$ [sugar]° or the reaction is first order w.r.t. sugar because $t_{1/2}$ remains same forany concentration of sugar.

so rate = k [sugar]^1 [H$^+$]^0 [n = order w.r.t. H$^+$ ion]

Also $t_{1/2}$ for $[H^+] \propto \frac{1}{[C_0]^{n-1}} \propto C_o^{1-n}$

$\therefore \ 600 \propto [10^{-5}]^{1-n}$

$60 \propto [10^{-6}]^{1-n}$

or $10 = (10)^{1-n}$ or $1 - n = 1$

$n = 0$

7. (b) (a) $\alpha = 1 - e^{-kt}$

$t = 0, \alpha = 1 \Rightarrow$ **Ist order**

(b) $\alpha = \frac{kt}{C_0}$ for **Zero order**

α is directly proportional to 't' so 0°

(c) $$\alpha = \frac{C_0kt}{C_0kt+1}$$

$$\frac{1}{\alpha} = 1 + \frac{1}{(C_0k)}\frac{1}{t}$$ for **IInd order.**

8. (c) Rate is governed by slowest step

$$A + B_2 \xrightarrow{K1} AB + B$$

From $A_2 \overset{K_c}{\rightleftharpoons}$ ..... (i)

$$k_C = \frac{[A]^2}{[B_2]}$$ ..... (ii)

$[A] = \sqrt{k_c}\ [A_2]^{1/2}$

$r = k_1 \sqrt{k_c}\ [A_2]^{1/2} [B_2]$ order is $= \frac{1}{2} + 1 = \frac{3}{2}$

9. (b) Rate is slope of curve

at 20 sec $\frac{y_2 - y_1}{x_2 - x_1} = \frac{0.35}{50}$ (approve) = 7 × 10^{-3}M sec^{-1}

at 40 sec rate become half because of first orde

$r_{40\ sec} = 3.5 \times 10^{-3}$ M sec^{-1}

$r_{60\ sec} = 1.75 \times 10^{-3}$ M sec^{-1}

$r_{80\ sec} = \frac{1.75}{2} - 10^{-3}$

$$A \longrightarrow B$$

$t = 0 \quad 0.4$

$t = 60 \quad 0.4 - x \ \ x$

$= 0.05$

$50\ x = 0.35$

11. (a, b)

$100 \propto (0.1)^{1-n}$

$50 \propto (0.025)^{1-n}$

divide $2 = 4^{1-n}$

$\Rightarrow \log 2 = (1-n)\log 4$

$\Rightarrow 1 = -\dfrac{\log 2}{\log 4}$

$\Rightarrow n = 1 - \dfrac{\log 2}{\log 4} = 1 - \dfrac{\log 2}{\log 2} = 1 - \dfrac{1}{2} = \dfrac{1}{2}$

$100 \propto (0.1)^{1/2}$

$t^{1/2} \propto (1)^{1/2}$

divide $\dfrac{t_{1/2}}{100} = \left(\dfrac{1}{0.1}\right)^{1/2}$

$t_{1/2} = 100\sqrt{10}$ min.

12. (a, b, d) $3A(g) \longrightarrow 2B(g) + 2C(g)$

$t = 0$	P_0		
$t = 20$	$P_0 - x$	$\dfrac{2x}{3}$	$\dfrac{2x}{3}$
$t = \infty$		$\dfrac{2P_0}{3}$	$\dfrac{2P_0}{3}$

$\Rightarrow \dfrac{4P_0}{3} = 4$

$P_0 = 3$ atm.

$P_0 + \dfrac{x}{3} = 3.5 \Rightarrow t_{50\%} = 20$ is the half life.

$t_{75\%} = 2 \times 20 = 40$ min

$t_{78.5\%} = 3 \times t_{50\%}\ 3 \times 20 = 60$ min

$t_{99\%} = \dfrac{2}{3} \times t_{99.9\%}\ \dfrac{2}{3} \times 10 \times t_{50\%} = \dfrac{400}{3}$

14. (a, b, c, d)

$A(g) \rightarrow 2B(g) + C(g)$

$t = 0$	400	0	0
$t = 20$ min	$400 - p$	$2p$	p

given $400 - p + 2p + p = 1000$

$400 + 2p = 1000$

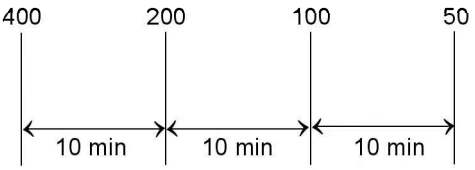
$p = 300$ mm

$k = \dfrac{1}{20} \text{ In } \dfrac{400}{400-300} = \dfrac{1}{20} \ell n\ 4$

$k = \dfrac{\text{In}2}{10}$ min^{-1}

$t_{1/2} = 10$ min

After 30 min Partial Pressure of A is 50 mm
After 30 min Partial Pressure of B is 700 mm
After 30 min Partial Pressure of C is 350 mm
After 30 min total Pressure become 1150 mm



15. (a, b, d)

0	30	∞
30	20	-15

$k = \dfrac{1}{30}\ 2.3 \log \dfrac{30-(-15)}{20-(-15)} = \dfrac{1}{30} 2.3 \log \dfrac{45}{35}$

$\therefore$ t1/2 = 75 min

$k = \dfrac{1}{t}\ 2.3 \log \dfrac{45}{0-(-15)}$

$t = 120$ min

$\dfrac{30-(-15)}{x-(-15)} = 2$ at half time

$\Rightarrow \dfrac{45}{x+15} = 2 \Rightarrow x + 15 = \dfrac{45}{2}$

$\Rightarrow x = 22.5 - 15 = 7.5°$

17. (a, c) $t_{1/2} \propto (a)^{1-n}$

or $(1-n) = \dfrac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''}$

$t_{1/2} \propto \dfrac{1}{P^{n-1}} \Rightarrow \dfrac{21}{11} = \left(\dfrac{49}{92}\right)^{n-1}$ n = 0 for zero order

$t_{1/2} = \dfrac{P}{2K} \Rightarrow K = \dfrac{P}{2t_{1/2}}$

$K = \dfrac{11}{2 \times 48} = 0.114$ sec.

18. (a, b, c, d)

Slow step is rate determining step, from slow step

$-\dfrac{d}{dt}[O_3] = k[O_3][O]$

Molecularity for step 1 is 1 and for step 2 is 2 as shown in above given reaction.

19. (a, b) $k_1 = k_2$

$\Rightarrow \dfrac{2}{3}$rd A has reacted for [A] = [C] = [D]

$$\therefore \quad k_1 + k_2 = \frac{1}{t} \text{ In } \frac{[A]_0}{\frac{1}{3}[A]_0}$$

$$\Rightarrow \quad t = \frac{1}{k_1 + k_2} \text{ In } 3 = \frac{1}{2k_1} \text{ In } 3 = \frac{1}{2k_2} \text{ In } 3$$

20. (a, b) $r_B = \frac{dC_B}{dt} = \frac{1}{V}\frac{dn_B}{dt} = \frac{1}{V}\frac{d(C_B V)}{dt}$

$$= \frac{V}{V}\frac{dC_B}{dt} + \frac{C_B}{V}\frac{dV}{dt} = \frac{dC_B}{dt} + \frac{C_B}{V}\frac{dV}{dt}.$$

21. (b) According to arrhenius equation $K = Ae^{-Ea/RT}$ when, $E_a = 0$, $K = A$.

22. (d) For zero order reactions $\alpha = \frac{kt}{c_0}$. They depend upon initial concentration.

23. **True** Because rate = 0 at t = 0 and t = ∝

24. **False** It decreases both by equal amount.

25. **True** Such as $t_{1/2}$ is constant for 1st order reaction

26. **False** Rate of Is' order always decreases with time.

27. **True**

28. **True**

29. **True**

30. **True**

31. (b) $\log K_b = \log A - \frac{E_a}{2.303RT} \Rightarrow \log K_b = 12$

$$- \frac{57450}{2.303 \times 8.314 \times 300}$$

$\text{Log } K_b = 2$
$K_b = \text{Antilog } 2$
$K_b = 10^2$

$$K_c = \frac{K_F}{K_b} \Rightarrow 10^4 = \frac{K_F}{10^2} \Rightarrow K_F = 10^6$$

32. (a) $\Delta G = \Delta HD - T\Delta S$
$\Delta G = 20 - T \times 0.07$
For non-spontaneous process $\Delta G > 0$
hence $0 < 20 - T \times 0.07$

$$T < \frac{20}{0.07} \Rightarrow T < 285.7 \text{ K}$$

33. (c) $Kp = Kc(RT)^{\Delta n} = 10^4 (0.082 \times 300)^1 = 24.6 \times 10^4$

35. (b) If $[OH^-]$ is decreased by 100 times pOH increases by 2 units. Hence, the rate decreases by 100 times.

36. (a) $r \cong 10k\,[A]$

$$\therefore \quad 10k = \frac{0.693}{t_{1.2}}$$

$$\Rightarrow \text{t1/2} = \frac{0.693}{10k}$$

37. (b) $R = k\,[A]^m\,[B]^n$

$5 \times 10^{-4} = k\,[2.5 \times 10^{-4}]^m\,[3 \times 10^{-5}]$" ...(i)

$4 \times 10^{-3} = k\,[5 \times 10^{-4}]^m\,[6 \times 10^{-5}]^n$ ... (ii)

$1.6 \times 10^{-2} = k\,[1 \times 10^{-3}]^m\,[3 \times 10^{-4}]^n$ ... (iii)

From it m = 2.

38. (a) $K_{300} = \frac{5 \times 10^{-4}}{(2.5 \times 10^{-4})(3 \times 10^{-5})} = 2.677 \times 10^8$

39. (b) $K = A \,.\, e^{-Ea/RT}$

$$\ell n \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{300} - \frac{1}{400}\right]$$

$E_a = 13.83$

40. (a – p, q), (b – p, r, s), (c – s), (d – p, q)

41. (a – p, q, s), (b – p, q, s), (c – q, r), (d – p, q, r)

42. (a – q), (b – r), (c – t), (d – v)

(a) $2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \Rightarrow \frac{K_2}{K_1} = 11$

$T_2 = 298$ K; $T_1 = 273$ K, $E_a = 65000$ J, R = 8.314 J/(mol K)

(b) $\frac{2.5}{20} = \frac{1}{8} = \left(\frac{1}{2}\right)^n \Rightarrow n = 3$

$$\Rightarrow t = 3 \times \frac{0.693}{0.0693} = 30$$

(c) Zero order: $t_{1/2} = \frac{a}{2K}$

I order: $t_{1/2} = \frac{0.693}{K}$

$$\frac{1}{2K_1} = \frac{0.693}{K_2}$$

$$\Rightarrow \quad \frac{K_2}{K_1} = 2 \times 0.693$$

(d) $t_{1/2} \propto (a)1\text{-}n$ or $(1-n) = \dfrac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''}$

$t_{1/2} \propto \dfrac{1}{a^{n-1}} \Rightarrow \dfrac{480}{240} = \left(\dfrac{0.0577}{0.136}\right)^{n-1}$ $n = 0$

43. $A \rightarrow B$

$Ct = a + b\,t$

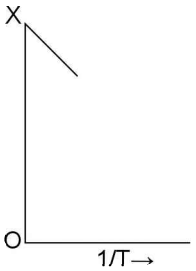
$p = (a + b\,t)\,RT$

$\dfrac{dp}{dt} = bRT = 44 \times \dfrac{1}{12} \times 300 = 100$ atm sec^{-1}

44. $2.303 \log K = -\dfrac{E_a}{RT} + 2.303 \log A$

Thus, $-\dfrac{E_a}{2.303R} = \tan\theta = -\dfrac{1}{2.303}$

$\therefore$ $E_a = R = 2$. Cal.



45.

t:	0	5	15	35
[A]:	1	0.5	0.25	0.125

IInd order of the reaction

46. Arrhenius equation $k = Ae^{-Ea/RT}$

or $\log_{10} k = \log A - \dfrac{Ea}{2.303RT}$ ..... (i)

Comparing the given equation with equation (i),

$\dfrac{Ea}{2.303RT} = \dfrac{1.25 \times 10^4 (K)}{T}$

$\Rightarrow$ $Ea = 2.303 \times 1.25 \times 10^4 \times 8.3 = 238936.25$ J mol^{-1}

Rate constant at 750 K is

$k = \text{antilog}\left[12.37 - \dfrac{1.25 \times 10^4}{150}\right]$

$= \text{antilog}\,(-4.3)$ sec^{-1}

$= 5 - 10^{-5}$ sec^{-1}

$\therefore$ $Eak = 238936.25 \times 5 \times 10^{-5}$ 11.95 $\Rightarrow$ 12

Hence **12**

47. $A \rightarrow B + C$

V

$V - x$ x x

$\alpha V \propto aV_0$ ... (i)

$\Rightarrow \dfrac{\alpha}{a} V \propto V_0$

$\alpha(V - x) \propto aV_1$

$\beta x \propto bV_2$

$\gamma x \propto CV_3$

$\dfrac{\alpha}{a}(V - x) + \dfrac{\beta}{b} x + \dfrac{\gamma}{c} x \propto V_t$

$\dfrac{\alpha V}{a} + x\left(\dfrac{\beta}{b} x + \dfrac{\gamma}{c} - \dfrac{\alpha}{a}\right) \propto V_t$

$x\left(\dfrac{\beta}{b} + \dfrac{\gamma}{c} - \dfrac{\alpha}{a}\right) \propto V_t - V_0$

$x \propto \dfrac{V_t - V_0}{\left(\dfrac{\beta}{b} + \dfrac{\gamma}{c} - \dfrac{\alpha}{a}\right)}$; $V = \dfrac{aV_0}{\alpha}$

$k = \dfrac{1}{t} \ell n \dfrac{\dfrac{av_0}{\alpha}}{\dfrac{av_0}{\alpha}} - \dfrac{v_t - v_0}{\left\{\dfrac{\beta}{b} + \dfrac{\gamma}{c} - \dfrac{\alpha}{a}\right\}}$

STRAIGHT OBJECTIVE TYPE QUESTIONS

1. Which of the following statements about physical adsorption is not correct?

(a) It is usually monolayer

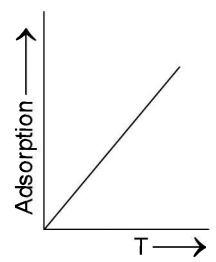
(b) It is reversible in nature

(c) It involves Van der Waals interactions between adsorbent and adsorbate

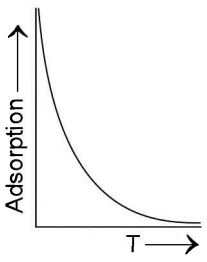
(d) It involves small value of adsorption

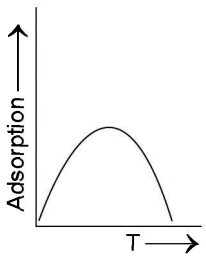
2. Following is the variation of physical adsorption with temperature:

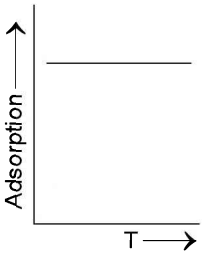
(a)



(b)



(c) 

(d) 

3. A colloidal solution can be purified by following the method of
   (a) 4 dialysis (b) peptization
   (c) filtratio (d) oxidation

4. Gold number of a lyophilic solution is such property that:
   (a) the larger its value, the greater is the peptizing power
   (b) the lower its value, the greater is the peptizing power
   (c) the lower its value, the greater is the protecting power
   (d) the larger its value, the greater is the protecting power

5. Size of colloidal particles may range from
   (a) 1 to 1000 nm (b) 10 to 100 pm
   (c) 1 to 1001.1M (d) 1 to 10 mm

6. Select correct statement (s):
   (a) hydrophilic colloid is a colloid in which there is a strong attraction between the dispersed phase and water
   (b) hydrophobic colloid is a colloid in which there is a lack of attraction between the dispersed phase and water
   (c) hydrophobic soils are often formed when a solid crystallizes rapidly from a chemical reaction or a supersaturated solution
   (d) all of the above

7. Which one of the following statements is false for hydrophilic soils?
   (a) they do not require electrolytes for stability
   (b) their coagulation is reversible
   (c) their viscosity is of the order of that of water
   (d) their surface tension is usually lower than that of dispersion medium.

8. Which one of the following statements is correct:
   (a) Brownian movement is more pronounced for smaller particles than for bigger ones
   (b) Soils of metal sulphides are lyophilic
   (c) Schulze-Hardy law states, the bigger the size of the ion, the greater is its coagulating power
   (d) Onewould expect charcoal to adsorb chlorine more strongly than hydrogen sulphide.

9. What can adsorb larger volume of hydrogen gas:
   (a) Colloidal solution of palladium
   (b) Finely divided nickel
   (c) Finely divided platinum
   (d) Colloidal $Fe(OH)_3$.

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

10. Which of the following are correct statements
   (a) Spontaneous adsorption of gases on solid surface is an exothermic process as entropy decreases during adsorption
   (b) Formation of micelles takes place when temperature is below Kraft Temperature (T_k) and concentration is above critical micelle concentration (CMC)
   (c) A colloid of $Fe(OH)_3$ is prepared by adding a little excess (required to completely precipitate Fe^{3+} ions as $Fe(OH)_3$)) of NaOH in $FeCI_3$ solution the particles of this solution will move towards cathode during electrophoresis.
   (d) According to Hardy-Schulze rules the coagulation (flocculatin) value of Fe^{3+} ion will be more than Ba^{2+} or Na^+

11. Which of the following statements are true for physisorption?
   (a) Extent of adsorption increases with the increase in pressure.
   (b) It needs activation energy

(c) It can be reversed easily
(d) It occurs at high temperature.

12. Which of the following are incorrect statements?
(a) Hardy schulze rule is related to coagulation
(b) Brownian movement and Tyndall effect are the characteristic of colloids.
(c) In gel, the liquid is dispersed in liquid
(d) Lower the gold number, more is the protective power of lyophillic soils.

13. The origin of charge on colloidal solution is
(a) Frictional rubbing
(b) Electron capture during Bredig's arc method
(c) Selective adsorption of ion on their surface
(d) It is due to addition of protective colloids

ASSERTION/REASON TYPE QUESTIONS

14. **Statement-1:** All colloidal dispersions give very low osmotic pressure and show very small freezing point depression or boiling point elevation.

Statement-2: Tydall effect is due to scattering of light from the surface of colloidal particles.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

15. **Statement-1:** The Brownian movement is due to the bombardment of collodial particles by the molecules of dispersion medium which are in the constant motion like molecules in a gas.

Statement-2: Brownian movement provides a visible proof of the random kinetic motion of molecules in a liquid.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

16. **Statement-1:** In the coagulation of negatively charged arsenic sulphide soil, the coagulating power decreases in the order, $Al^{3+} > Ba^{2+} > Na^{+}$.

Statement-2: Generally greater the valence of coagulating ion, the greater is its power of coagulation.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

17. **Statement-1:** Isoelectric point is pH at which colloidal can move towards either of electrode

Statement-2: At isoelectric point, colloidal solution become electrically neutral
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

18. **Statement-1:** Medicines in the colloidal state are more effective.

Statement-2: In the colloidal state, the medicines are easily assimilated by the body.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

The clouds consist of charged particles of water dispersed in air. Some of them are +vely charged, others are –vely charged. When +vely charged clouds come closer, they cause lightening and thundering, whereas, when +ve and –ve charged clouds come closer, they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus, coagulating the mist hanging in air.

19. When excess of AgNO3 is treated with KI solution, Agi forms
- (a) +vely charged soil
- (b) –vely charged soil
- (c) neutral soil
- (d) true solution

20. AO helps in artificial rain because:
- (a) it helps in condensation process
- (b) it helps in dispersion process
- (c) it helps in coagulation
- (d) all of them

COMPREHENSION-2

Adsorption is the presence of excess concentration of any particular component at the surface of liquid or solid phase as compared to bulk. This is due to presence of residual forces at the surface of body. In the adsorption of hydrogen gas over a sample of charcoal, 1.12cm^3 of H_2(g) measured over S.T.P. was found to adsorb per gram of charcoal. Consider only monolayer adsorption. Density of H_2 is 0.07gm/cc. In another experiment same 1 gm charcoal adsorbs 100m1 of 0.5M CH_3COOH to form monolayer and thereby the polarity of CH3COOH reduces to 0.49.

(3 × 47.73)1/3
47t = 2.24.
(2.24)2 = 5

21. Numbers of molecules of hydrogen over 1 gram charcoal are —
- (a) 3.01 × 1015
- (b) 3.01 × 1013
- (c) 3.01 × 1021
- (d) 3.01 × 1022

22. What is the radius of adsorb hydrogen molecule
- (a) 2.24 × 10-7 cm
- (b) 2.24 × 10-5 cm
- (c) 2.24 × 10-gcm
- (d) 2.24 × 10-15cm

23. Specific surface area of charcoal is (cm^2/gm) —
- (a) 4.72 × 103
- (b) 4.72 × 104
- (c) 4.72 × 105
- (d) 4.72 × 106

24. Molecule of acetic acids adsorbed —
- (a) 6.023 × 1025
- (b) 6.023 × 1021
- (c) 6.023 × 1022
- (d) 6.023 × 1023

25. Surface area of charcoal adsorbed by each molecule of (acetic acid) is —
- (a) 7.8 × 10–9 cm^2
- (b) 7.8 × 10–15 cm^2
- (c) 7.8 × 10–17 cm^2
- (d) 7.8 × 10–16 cm^2

MATCH THE COLUMN TYPE QUSTIONS

26. Match list I with list II and select the correct answer:

List I	List II
(a) Coagulation	(p) Scattering of light
(b) Dialysis	(q) Washing of precipitates
(c) Peptization	(r) Purification of colloid
(d) Tyndall effect	(s) Electrolyte

27. Match list I (Colloidal system) with list II (Example) and select the correct answer:

List I	List II
(a) Emulsifie	(p) Colloidal solution
(b) Xerogel	(q) Soaps
(c) Colloidal electrolyte	(r) Foil of cellophane
(d) Purple of Cassius	(s) Dextrin

SUBJECTIVE TYPE QUESTIONS

SHORT SUBJECTIVE

28. 5 ml of standard gold solution needs 0.5 mg of gelatin for its protection from coagulation, calculate the gold number of gelatin.

29. 100 ml of a colloidal solution is completely precipitated by addition of 0.5 ml of 1M NaCI solution, calculate the coagulation value of NCI.

30. On addition of the 1 ml. solution of 10% NCI to 10 ml gold solution in the presence of 0.00399 gm of starch, calculate the gold number.

31. Coagulation experiment, 5 ml of As_2S_3 is mixed with distilled water and 0.01 M solution of an electrolyte AB, so that total volume is 10 ml. It was found that all the solutions containing more than 5 ml of AB coagulate within 5 min. What is the Flocculation value of AB for As_2S_3 solution.

ANSWER KEYS

1. (a)	**2.** (b)	**3.** (a)	**4.** (c)	**5.** (a)	**6.** (d)	**8.** (a)	**9.** (a)	**10.** (a, c)	
11. (a, c)	**12.** (c, d)	**13.** (a, b, c)	**14.** (b)	**15.** (b)	**16.** (a)	**17.** (b)	**18.** (a)	**19.** (a)	
20. (c)	**21.** (b)	**22. (b)**	**23.** (b)	**24.** (a)	**25.** (c)	**26.** (a – s), (b – r), (c – q), (d – p)			
27. (a – s), (b – r), (c – q), (d – p)									

HINTS AND EXPLANATIONS

1. (a) Physical adsorption is a multilayer phenomenon

2. (b) Rate of physical adsorption gradually decreases with increase the temperature.

4. (c) Lower is the value gold number; greater will be the protecting power.

9. (a) It is because of more surface area of colloidal Pd

10. (a, c) (a) $\Delta G = \Delta HD - T\Delta BS < O$ as $\Delta S < 0$ so ΔH has to be negative
(b) Micelles formation will take place above T_k and above CMC
(c) This solution will be negatively charged.
(d) Fe^{3+} ions will have greater flocculatibility power, so smaller flocculating value.

12. (c, d) In gel, liquid is dispersed in solid,

26. (a – s); (b – r); (c – q); (d – p)

27. (a – s); (b – r); (c – q); (d – p)

28. 5 ml of gold solutions, required gelatin for protection from

28. 5 ml of gold solutions, required gelatin for protection from coagulation = 0.5 mg.

10 ml of gold soil. " " " $= \frac{0.5\times10}{5} = 1$

29. M Mole of NaCl = M × V = 0.5 × 1 = 0.5

$\frac{0.5\times1000}{100} = 5$

Coagulation Value = 100

30. Gold number = 1000 × 0.00399 = 4

31. A minimum of 5 ml of AB is required to coagulate the soil, the moles of AB in sol. is $= \frac{5\times0.01}{10} = 0.005$ moles this means that a minimum of 0.005 moles or 0.005 × 1000 = 5 milli moles are required for coagulation 1 litre of solution. flocculation value of AB for As_2S_3 solution = 5.

HINTS AND EXPLANATIONS

14. The abundance of three isotopes of oxygen, each containing 8, 9, 10 neutrons respectively has the % of one isotope (containing 8 neutrons) 9%. What are the other % if the at weight of oxygen is 16.12?

Sol. Mass number of isotope of O with 8 neutrons = 16 and is 90%.
Mass number of isotope of O with 9 neutrons = 17
Let a%

Mass number of isotope of O with 10 neutrons = 18

$\therefore$ (10–a) %

$\therefore$ Average atomic weight of O ($\overline{A}$) = $\Sigma A_1X_1/\Sigma X_{Total}$

$$= \frac{\%\text{ of } O^{16} \times \text{its mass} + \%\text{ of } O^{17} \times \text{its mass} + \%\text{ of } O^{18} \times \text{its mass}}{100}$$

$$\therefore \quad 16.12 = \frac{90\times16+17(a)+18(10-a)}{100} \qquad \therefore \ a = 8$$

$\therefore$ % of O^{17} = 8% % of O^{18} = 10 – 8 = 2%

35. Calculate the order of reaction for which rate becomes half if volume of container having same amount of reactant is doubled. (Assume gaseous phase reaction)

Sol. Rate = K[ ]^n

For Case I: Let a mole of reactant in vessel of V litre

$$\therefore \quad r_1 = K\left[\frac{a}{V}\right]^n \qquad ...(1)$$

For Case II: The volume is doubled, rate becomes half

$$\therefore \quad \frac{r_1}{2} = K\left[\frac{a}{2V}\right]^n \qquad ...(2)$$

$\therefore$ By Eqs. (1) and (2) or $2 = n(2)^n$ $\therefore$ n = 1

NOTE: The above fact is not valid for solution phase reactions.

36. For the reaction, $2NO + H_2 \rightarrow N_2O + H_2$, the value of $-\frac{dP}{dt}$ was found to be 1.5 Pa s^{-1} for a pressure of 359 Pa of NO and 0.25 Pa s^{-1} for a pressure of 152 Pa of NO. The pressure of H_2 being constant. If pressure of NO was kept constant, the value of $-\frac{dP}{dt}$ was found 1.60 Pa s^{-1} for a pressure of H_2 289 Pa and 0.79 Pa s^{-1} for a pressure of 147 Pa of H_2. Calculate the order of reaction.

Sol. Rate of reaction $= -\frac{1}{2}\frac{dP_{NO}}{dt} = -\frac{dP_{H_2}}{dt}$

For P_{H_2} constant: $-\frac{1}{2}\frac{dP_{NO}}{dt} = 1.5 = K(359)^m(P_{H_2})^n$

$$-\frac{1}{2}\frac{DP_{NO}}{dt} = 0.25 = K(152)^m\,(P_{H_2})^n$$

$$\therefore \quad \frac{1.5}{0.25} = \left(\frac{359}{152}\right)^m$$

$\therefore$ m = 2

For P_{NO} constant: $-\frac{dP_{H_2}}{dt} = 1.60 = (P_{NO})^m\,(289)^n$

$$-\frac{dP_{H_2}}{dt} = 0.79 = (P_{NO})^m\,(147)^n$$

$$\therefore \quad \frac{1.60}{0.79} = \left(\frac{289}{147}\right)^n$$

$\therefore$ n = 1

$\therefore$ Rate = $K[P_{NO}]^2\,[P_{H_2}]^1$

$\therefore$ Order of reaction = 2 + 1 = 3

37. The chemical reaction between $K_2C_2O_4$ and $HgCl_2$ is,

$2HgCl_2 + K_2C_2O_4 \longrightarrow 2KCl + 2CO_2 + Hg_2Cl_2$

The weight of Hg_2Cl_2 are precipitated from different solutions in given time are as:

Time	$HgCl_2$ (mol litre^{-1})	$K_2C_2O_4$ (mol litre^{-1})	Hg_2Cl_2 formed (mol litre^{-1})
60	0.0418	0.404	0.0032
65	0.0836	0.404	0.0068
120	0.0836	0.202	0.0031

Calculate order of reaction.

Sol. Rate = $K[HgCl_2]^m\,[K_2C_2O_4]^n$

$$\therefore \quad \frac{0.0032}{60} = K[0.0418]^m\,[0.404]^n \qquad ...(1)$$

$$\frac{0.0068}{65} = K[0.0836]^m\,[0.404]^n \qquad ...(2)$$

$$\frac{0.0031}{120} = K[0.0836]^m\,[0.202]^n \qquad ...(3)$$

Solving Eqs. (1), (2) and (3), we get

m = 1 n = 2 $\therefore$ O.R. = m + n = 1 + 2 = 3

38. The half period and initial concentration for a reaction are as follows. What is order of reaction?

Initial concentration	350	540	158
$t_{1/2}$	425	275	941

Sol. $t_{1/2} \propto (a)^{1-n}$

For I $\therefore$ $425 \propto (350)^{1-n}$

For II $\therefore$ $275 \propto (540)^{1-n}$

For III $\therefore$ $941 \propto (158)^{1-n}$

By Eqs. (1) and (2); $\frac{425}{275} = \left(\frac{350}{540}\right)^{1-n}$

Taking log, $\log\frac{425}{275} = (1-n)\log\frac{350}{540}$

$\therefore$ n = 2

39. The following data was obtained for the decomposition of NO in contact with gold surface at 900°C. Find the O.R.

Time (in minute)	15	30	45	65	80
% decomposition	17	32	44.5	57	65

Sol. $K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$ ... (1)

Case I: $K = \frac{2.303}{15}\log_{10}\frac{100}{100-17}\left(\begin{array}{c}\text{if } a = 100\\ x = 17 \text{ at } t = 15\end{array}\right)$

$= 1.24 \times 10^{-2}$

Case II: $K = \frac{2.303}{30}\log_{10}\frac{100}{100-32}$ (x = 32 at t = 30)

$= 1.28 \times 10^{-2}$

Case III: $K = \frac{2.303}{45}\log_{10}\frac{100}{100-44.5}$ (x = 44.5 at t = 45) $= 1.31 \times 10^{-2}$

Thus, all the values of K are same and hence equation (1) is valid, i.e., **reaction obeys Ist order kinetics.**

40. While studying the decomposition of N_2O_5 (g), it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameter can be obtained from this?

Sol. Consider Ist order reaction:

$$Kt = 2.303 \log_{10}\frac{a}{(a-x)}$$

or $Kt = 2.303 \log_{10} a - 2.303 \log_{10}(a-x)$ ...(1)

In terms of pressure Eq. (1) may be written as,

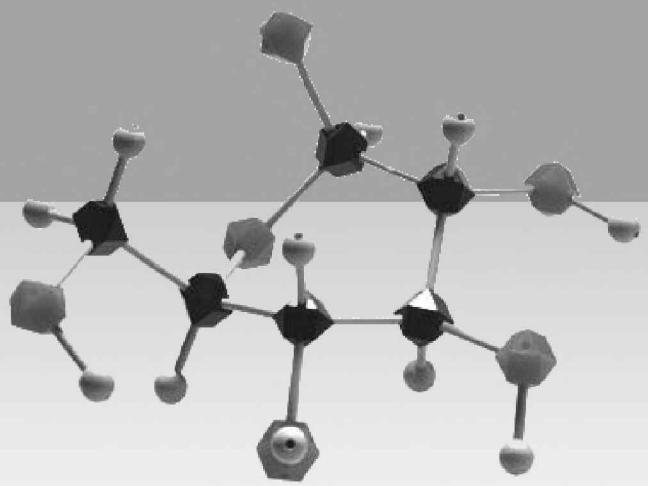
$\because\ a \propto P_0 \quad (a-x) \propto P$

$$Kt = 2.303 \log_{10} P_0 - 2.303 \log_{10} P$$

or $\log_{10} P = -\frac{K}{2.303}t + \log_{10} P_0$

Thus, log P vs. time graph is linear with intercept equal to log P_0 and slope equal to $-\frac{K}{2.303}$. Since linear results are given and thus, decomposition may be said **to be of Ist order.**

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CHAPTER 5

Thermodynamics

INTRODUCTION

Thermodynamics (from the Greek *therme,* meaning "heat" and, *dynamis,* meaning "power") is the study of energy conversion between heat and mechanical work, and subsequently the macroscopic variables such as temperature, volume and pressure.

Thermodynamics reflects of effect of work, heat and energy on the system.The study of thermodynamics is based on large scale observations.

A **thermodynamic system**, originally called a **working substance**, is defined as that part of the universe that is under consideration.

A hypothetical boundary separates the system from the rest of the universe, which is referred to as the environment, surroundings, or reservoir.

A useful classification of thermodynamic systems is based on the nature of the boundary and the quantities flowing through it, such as matter, energy, work, heat, and entropy. A system can be anything, for example, a piston, a solution in a test tube, a living organism, an electrical circuit, a planet, etc.

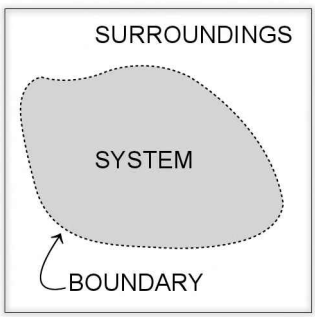


Fig. 5.1

Thermodynamics is basically concerned with the flow and balance of energy and matter in a thermodynamic system. Three types of thermodynamic systems are distinguished depending on the kinds of interaction and energy exchange taking place between the system and its surrounding environment:

- **Isolated systems** are completely isolated in every way from their environment. They do not exchange heat, work or matter with their environment. An example of an isolated system would be an insulated rigid container, such as an insulated gas cylinder.

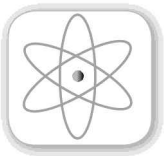
- **Closed systems** are able to exchange energy (heat and work) but not matter with their environment. A greenhouse is an example of a closed system exchanging heat but not work with its environment. Whether a system exchanges heat, work or both is usually thought of as a property of its boundary.
- **Open systems** are able to exchanging energy (heat and work) and matter with their environment. A boundary allowing matter exchange is called *permeable*. The ocean would be an example of an open system.

In reality, a system can never be absolutely isolated from its environment, because there is always at least some slight coupling, even if only via minimal gravitational attraction. In analysing a system in steady-state, the energy into the system is equal to the energy leaving the system.

In true sense, a **boundary** is a real or imaginary volumetric demarcation region drawn around a thermodynamic system across which quantities such as heat, mass, or work can flo . In short, a thermodynamic boundary is a division between a system and its surroundings. A boundary may be adiabatic, isothermal, diathermal, insulating, permeable, or semipermeable. Boundaries can also be fixed (example a constant volume reactor) or moveable (example a piston)

For an engine, a fixed boundary means the piston is locked at its position; as such, a constant volume process occurs. In that same engine, a moveable boundary allows the piston to move in and out. For closed systems, boundaries are real while for open system boundaries are often imaginary.

THERMODYNAMIC STATE



A **thermodynamic state** is a set of values of properties of a thermodynamic system that must be specified to reproduce the system. The individual parameters are known as **state variables**, **state parameters** or **thermodynamic variables**. Once a sufficient set of thermodynamic variables have been specified, values of all other properties of the system are uniquely determined. The number of values required to specify the state depends on the system, and is not always known.

Thermodynamic Variables

Thermodynamic variables, also known as state variables or state parameters, describe the momentary condition of a thermodynamic system. Regardless of the path by which a system goes from one state to another—i.e., the sequence of intermediate states—the total *change* in any state variable will be the same as long as initial and final states are fixed. This means that the incremental changes in such variables are *exact differentials*. Examples of state variables include:

- Density (ρ)
- Energy (E)
- Helmholtz free energy (A)
- Gibbs free energy (G)
- Enthalpy (H)
- Internal energy (U)
- Mass (m)
- Pressure (p)
- Entropy (S)
- Temperature (T)
- Volume (V)
- The amounts of each of the chemical components $\{ n_i \}$, expressed as numbers of moles or molecules

Path function (path variables)

Thermodynamic variables or properties which depend upon the path of the transformation are known as path function or path variable. So, a path variable can have different values for the same state depending on the path of transformation through which the state has been attained. Work and heat are path variables. They are not exact differential.

Equilibrium State

Systems found in nature are often dynamic and complex, but in many cases their states are amenable to description based on proximity to ideal conditions. One such ideal condition is that of a stable equilibrium

state. Based on many observations, thermodynamics postulates that all systems having no effect on the external environment will change in such a way as to approach unique stable equilibrium states.

Closed Simple System

A common example in which the state can be succinctly described is a closed simple system in an equilibrium state. A closed simple system is an ideal system devoid of any internal adiabatic, rigid, or impermeable boundaries and not being acted upon by any external force fields or inertial forces. Based on observation, scientists and engineers have postulated that the state of a simple system at equilibrium can be completely characterized by specifying two independent property variables, such as temperature and pressure, and the masses of the particular chemical species in the system. Relying on this postulate, for many chemical species, phase distribution and intrinsic phase properties such as density, heat capacity, thermal conductivity, viscosity, enthalpy, and entropy have been reproducibly measured and catalogued as functions of temperature and pressure.

A thermodynamic process may be defined as the energetic evolution of a thermodynamic system proceeding from an initial state to a final state. Paths through the space of thermodynamic variables are often specified by holding certain thermodynamic variables constant. It is useful to group these processes into pairs, in which each variable held constant is one member of a conjugate pair.

The pressure-volume conjugate pair is concerned with the transfer of mechanical or dynamic energy as the result of work.

Thermodynamic process

- An **isobaric process** occurs at constant pressure. An example would be to have a movable piston in a cylinder, so that the pressure inside the cylinder is always at atmospheric pressure, although it is isolated from the atmosphere. In other words, the system is **dynamically connected**, by a movable boundary, to a constant pressure reservoir.
- An **isochoric process** is one in which the volume is held constant, meaning that the work done by the system will be zero. It follows that, for the simple system of two dimensions, any heat energy transferred to the system externally will be absorbed as internal energy. An isochoric process is also known as an **isometric** process or an **isovolumetric** process. An example would be to place a closed tin can containing only air into a fire. To a first approximation, the can will not expand, and the only change will be that the gas gains internal energy, as evidenced by its increase in temperature and pressure.
- An **isothermal process** occurs at a constant temperature. An example would be to have a system immersed in a large constant temperature bath. Any work energy performed by the system will be lost to the bath, but its temperature will remain constant. In other words, the system is **thermally connected**, by a thermally conductive boundary to a constant temperature reservoir.
- An **adiabatic process** is a process in which there is no energy added or subtracted from the system by heating or cooling. For a reversible process, this is identical to an isentropic process. We may say that the system is **thermally insulated** from its environment and that its boundary is a thermal insulator.

In thermodynamics, **work** performed by a system is the quantity of energy transferred by the system to another due to changes in the external parameters of the system. If these changes happen in a reversible way, then the performed work does not lead to a change of the entropy. It is a generalization of the concept of mechanical work in mechanics. In the SI system of measurement, work is measured in joules (symbol: J). The rate at which work is performed is power.

According to the *First Law of Thermodynamics*, it is useful to separate changes to the internal energy of a thermodynamic system into two sorts of energy transfers. **Work** refers to forms of energy transfer which can be accounted for in terms of changes in the *macroscopic* physical variables of the system, for example energy which goes into expanding the volume of a system against an external pressure, by driving a piston-head out of a cylinder against an external force. This is in contrast to **heat** energy, which is carried into or out of the system in the form of transfers in the *microscopic* thermal motions of particles.

The concept of thermodynamic work is slightly more general than that of mechanical work because it includes other types of energy transfers as well. The electrical work required to move a charge against

an external electrical field can be measured, as can the work required to move heat against a temperature gradient. An extremely important fact to understand is that thermodynamic work need not have any mechanical component to be considered such.

Mathematical Definition

According to the First Law of Thermodynamics, any net increase in the internal energy U of a thermodynamic system must be fully accounted for, in terms of heat δQ entering the system minus work δW done *by* the system.

The letter d indicates that internal energy U is a property of the state of the system, so changes in the internal energy are exact differentials; they depend only on the original state and the final state, and not upon the path taken. In contrast, the Greek delta's (δ's) in this equation reflect the fact that the heat transfer and the work transfer are *not* properties of the final state of the system. Given only the initial state and the final state of the system, one can only say what the total change in internal energy was, not how much of the energy went out as heat, and how much as work. This can be summarized by saying that heat and work are not state functions of the system.

Pressure-Volume Work

Chemical thermodynamics studies *PV work*, which occurs when the volume of a fluid changes. PV work is represented by the following differential equation:

where,

- W = work done on the system
- P = external pressure
- V = volume

The above equation of the Work is valid for reversible process of closed system.

Like all work functions, PV work is path-dependent. This means that the differential dW is an inexact differential; to be more rigorous, it should be written đW (with a line through the d).

In other words, from a mathematical point of view, đW is not an exact one-form. The line-through is merely a flag to warn us there is actually no function (0-form) W which is the potential of đW. If there were, indeed, this function W, we should be able to just use Stokes Theorem to evaluate this putative function, the potential of đW, at the boundary of the path, that is, the initial and final points, and therefore, the work would be a state function. This impossibility is consistent with the fact that it does not make sense to refer to *the work on a point* in the PV diagram; work presupposes a path.

PV work is often measured in the (non-SI) units of litre-atmospheres, where 1 L·atm = 101.325 J. The mathematical equation for the thermodynamical substance depends on the weight,mass and temperature of the thermodynamical substance.

Free Energy and Exergy

The amount of useful work which *can* be extracted from a thermodynamic system is discussed in the article *Second Law of Thermodynamics*. Under many practical situations this can be represented by the thermodynamic Availability or Exergy function. Two important cases are: in thermodynamic systems where the temperature and volume are held constant, the measure of "useful" work attainable is the Helmholtz free energy function; and in systems where the temperature and pressure are held constant, the measure of "useful" work attainable is the Gibbs free energy.

A **thermodynamic cycle** is a series of thermodynamic processes transferring heat and work, while varying pressure, temperature, and other state variables, eventually returning a system to its initial state. **State** Properties depend only on the thermodynamic state and cumulative variation of such properties add up to zero. **Path Quantities**, such as heat and work are process dependent, and cumulative heat and work are non-zero. The first law of thermodynamics dictates that the net heat input is equal to the net work output over any cycle. The repeating nature of the process path allows for continuous operation, making the

cycle an important concept in thermodynamics. Thermodynamic cycles often use quasistatic processes to model the workings of actual devices.

Two primary classes of thermodynamic cycles are power cycles and heat pump cycles. Power cycles are cycles which convert some heat input into a mechanical work output, while heat pump cycles transfer heat from low to high temperatures using mechanical work input. Cycles composed entirely of quasistatic processes can operate as power or heat pump cycles by controlling the process direction. On a pressure-volume or Temperature-entropy diagram, the clockwise and counterclockwise directions indicate power and heat pump cycles, respectively.

Thermodynamic power cycles

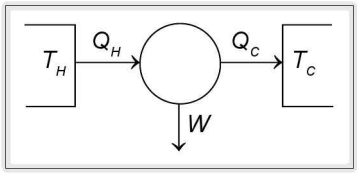


Fig. 5.2

Thermodynamic power cycles are the basis for the operation of heat engines, which supply most of the world's electric power and run almost all motor vehicles. Power cycles can be divided according to the type of heat engine they seek to model. The most common cycles that model internal combustion engines are the Otto cycle, which models gasoline engines and the Diesel cycle, which models diesel engines. Cycles that model external combustion engines include the Brayton cycle, which models gas turbines, and the Rankine cycle, which models steam turbines.

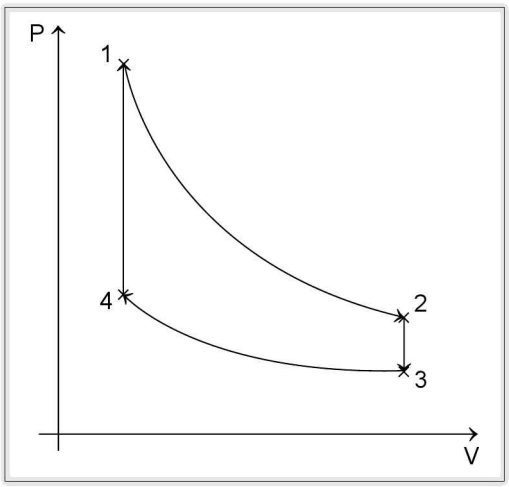


Fig. 5.3

The clockwise thermodynamic cycle indicated by the arrows shows that the cycle represents a heat engine. The cycle consists of four states (the point shown by crosses) and four thermodynamic processes (lines).

For example the pressure-volume mechanical work done in the heat engine cycle, consisting of 4 thermodynamic processes, is:

$$(3)\ W = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

$$W_{1\to2} = \int_{V_1}^{V_2} P\, dV, \text{ positive, gives work}$$

$$W_{2\to3} = \int_{V_2}^{V_3} P\,dV, \text{ zero work if V2 equal V3}$$

$$W_{3\to4} = \int_{V_3}^{V_4} P\,dv, \text{ negative, uses work}$$

$$W_{4\to1} = \int_{V_4}^{V_1} P\,dV, \text{ zero work if V4 equal V1}$$

If no volume change happens in process 4->1 and 2->3, equation (3) simplifies to

$$(4)\quad W = W_{1\to2} + W_{3\to4}$$

Thermodynamic heat pump and refrigeration cycle

Main article: Heat pump and refrigeration cycle

Thermodynamic heat pump and refrigeration cycles are the models for heat pumps and refrigerators. The difference between the two is that heat pumps are intended to keep a place warm while refrigerators are designed to cool it. The most common refrigeration cycle is the vapour compression cycle, which models systems using refrigerants that change phase. The absorption refrigeration cycle is an alternative that absorbs the refrigerant in a liquid solution rather than evaporating it. Gas refrigeration cycles include the reversed Brayton cycle and the Hampson-Linde cycle. Regeneration in gas refrigeration allows for the liquefaction of gases.

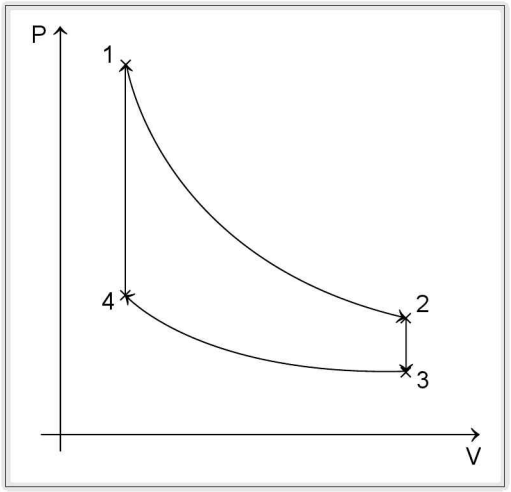


Fig. 5.4

Example of P-V diagram of a thermodynamic cycle.

A thermodynamic cycle is a closed loop on a P-V diagram. A P-V diagram's *Y* axis shows pressure (*P*) and *X* axis shows volume (*V*). The area enclosed by the loop is the work (*W*) done by the process:

$$(1)\quad W = \oint P\,dV\,.$$

This work is equal to the balance of heat (Q) transferred into the system:

$$(2)\quad W = Q = Q_{in} - Q_{out}\,.$$

Equation (2) makes a cyclic process similar to an isothermal process: even though the internal energy changes during the course of the cyclic process, when the cyclic process finishes the system's energy is the same as the energy it had when the process began.

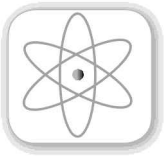
If the cyclic process moves clockwise around the loop, then it represents a heat engine, and W will be positive. If it moves counterclockwise then it represents a heat pump, and W will be negative.

Properties

Extensive and intensive properties: Properties of a substance which depend on the quantity of matter (or amount of the substance) are called extensive properties example Mass, volume and the various thermodynamic properties like internal energy enthalpy, entropy and free energy. Properties which do not depend on the quantity of matter are called intensive properties. Examples Pressure, temperature, density, refractive index, surface tension, viscosity, chemical potential etc. An extensive property may become an intensive property by specifying the quantity of the substance.

Example	Extensive property	Intensive property
	Mass	Density (or mass per unit volume)
	Heat capacity	Specific heat (or heat capacity per unit mass
	Free energy	Chemical potential (or free energy per mole)

ZEROTH LAW OF THERMODYNAMICS



The **zeroth law of thermodynamics** is a concoction about the thermal equilibrium among bodies, or thermodynamic systems, in contact. It results from the definition and properties of temperature.[1]

A system is said to be in thermal equilibrium when its temperature does not change over time. Let A, B, and C be distinct thermodynamic systems or bodies. The zeroth law of thermodynamics can then be expressed as:

"If A and C are each in thermal equilibrium with B, A is also in thermal equilibrium with C."[2]

The preceding sentence asserts that thermal equilibrium is a Euclidean relation between thermodynamic systems. If we also grant that all thermodynamic systems are (trivially) in thermal equilibrium with themselves, then thermal equilibrium is also a reflexive relation. Relations that are both reflexive and Euclidean are equivalence relations. One consequence of this reasoning is that thermal equilibrium is a transitive relation between the temperature T of A, B, and C:

if $T(A) = T(B)$
and $T(B) = T(C)$
then $T(A) = T(C)$.

Internal Energy

In thermodynamics, the **internal energy** of a thermodynamic system, or a body with well-defined boundaries, denoted by U, or sometimes E, is the total of the kinetic energy due to the motion of particles (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules or crystals. It includes the energy in all of the chemical bonds, and the energy of the free, conduction electrons in metals.

One can also calculate the internal energy of electromagnetic or black body radiation. It is a state function of a system, and is an extensive quantity. The SI unit of energy is the joule although other historical, conventional units are still in use, such as the (small and large) calorie for heat.

One can have a corresponding intensive thermodynamic property called **specific internal energy**, commonly symbolized by the lower-case letter u, which is internal energy per mass of the substance in question. As such, the SI unit of specific internal energy would be the J/kg. If intensive internal energy is expressed on an amount of substance basis, then it could be referred to as *molar internal energy* and the unit would be the J/mol.

Internal energy does not include the translational or rotational kinetic energy of a body *as a whole*. It also does not include the relativistic mass-energy equivalent $E = mc^2$. It excludes any potential energy a body may have because of its location in external gravitational or electrostatic fiel , although the potential energy it has in a field due to an induced electric or magnetic dipole moment does count, as does the energy of deformation of solids (stress-strain).

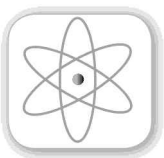
We can also say that Internal energy–the sum of all microscopic forms of energy of a system. It is related to the molecular structure and the degree of molecular activity and may be viewed as the sum of kinetic and potential energies of the molecules; it comprises the following types of energy:[15]

Type	*Composition of internal energy (U)*
Sensible energy	the portion of the internal energy of a system associated with kinetic energies (molecular translation, rotation, and vibration; electron translation and spin; and nuclear spin) of the molecules.
Latent energy	the internal energy associated with the phase of a system.
Chemical energy	the internal energy associated with the different kinds of aggregation of atoms in matter.
Nuclear energy	the tremendous amount of energy associated with the strong bonds within the nucleus of the atom itself.
Energy interactions	those types of energies not stored in the system (example heat transfer, mass transfer, and work), but which are recognized at the system boundary as they cross it, which represent gains or losses by a system during a process.
Thermal energy	the sum of sensible and latent forms of internal energy.

The principle of equipartition of energy in classical statistical mechanics states that each molecular quadratic degree of freedom receives $1/2\ kT$ of energy, a result which was modified when quantum mechanics explained certain anomalies; example, in the observed specific heats of crystals (when $h\nu > kT$). For monoatomic helium and other noble gases, the internal energy consists only of the translational kinetic energy of the individual atoms. Monoatomic particles, of course, do not (sensibly) rotate or vibrate, and are not electronically excited to higher energies except at very high temperatures.

From the standpoint of statistical mechanics, the internal energy is equal to the ensemble average of the total energy of the system. It is also called Intrinsic energy.

FIRST LAW OF THERMODYNAMICS



The **first law of thermodynamics**, an expression of the principle of conservation of energy, states that energy can be transformed (changed from one form to another), but cannot be created or destroyed. Alternatively: In any process in an isolated system, the total energy remains the same.

For a thermodynamic cycle the net heat supplied to the system equals the net work done by the system.

The First Law states that energy cannot be created or destroyed; rather, the amount of energy lost in a steady state process cannot be greater than the amount of energy gained. This is the statement of conservation of energy for a thermodynamic system. It refers to the two ways that a closed system transfers energy to and from its surroundings–by the process of heating (or cooling) and the process of mechanical work. The rate of gain or loss in the stored energy of a system is determined by the rates of these two processes. In open systems, the flow of matter is another energy transfer mechanism, and extra terms must be included in the expression of the first la .

The First Law clarifies the nature of energy. It is a stored quantity which is independent of any particular process path, i.e., it is independent of the system history. If a system undergoes a thermodynamic cycle, whether it becomes warmer, cooler, larger, or smaller, then it will have the same amount of energy each time it returns to a particular state. Mathematically speaking, energy is a state function and infinitesimal changes in the energy are exact differentials.

All laws of thermodynamics but the First are statistical and simply describe the tendencies of macroscopic systems. For microscopic systems with few particles, the variations in the parameters become larger than the parameters themselves, and the assumptions of thermodynamics become meaningless.

The internal energy is essentially defined by the first law of thermodynamics which states that energy is conserved:

$$\Delta E = \Delta U = Q + W + W'$$

where

ΔE or ΔU is the change in internal energy of a system during a process.

or Q is heat *added to* a system (measured in joules in SI); that is, a positive value for Q represents heat flow *into* a system while a negative value denotes heat flow *out of* a system.

W is the mechanical work *done on* a system (measured in joules in SI)

W' is energy added by all other processes

The first law may be stated equivalently in infinitesima terms as:

$$dE = dU = \delta Q + \delta W + \delta W'$$

where the terms now represent infinitesimal amounts of the respective quantities. The d before the internal energy function indicates that it is an exact differential. In other words, it is a state function or a value which can be assigned to the system. On the other hand, the δ's before the other terms indicate that they describe increments of energy which are not state functions but rather they are processes by which the internal energy is changed.

From a microscopic point of view, the internal energy may be found in many different forms. For a gas it may consist almost entirely of the kinetic energy of the gas molecules. It may also consist of the potential energy of these molecules in a gravitational, electric, or magnetic fiel . For any material, solid, liquid or gaseous, it may also consist of the potential energy of attraction or repulsion between the individual molecules of the material.

Expressions for the Internal Energy

The internal energy may be expressed in terms of other thermodynamic parameters. Each term is composed of an intensive variable (a generalized force) and its conjugate infinitesimal extensive variable (a generalized displacement).

For example, for a non-viscous fluid, the mechanical work done on the system may be related to the pressure p and volume V. The pressure is the intensive generalized force, while the volume is the extensive generalized displacement:

Taking the default direction of work, W, to be from the working fluid to the surroundings

$$\delta W = pdV .$$

p is the pressure

V is the volume

The first law of thermodynamics says that energy is conserved in any process involving a thermodynamic system and its surroundings. Frequently it is convenient to focus on changes in the assumed internal energy (U) and to regard them as due to a combination of heat (Q) added to the system and work done by the system (W). Taking dU as an incremental (differential) change in internal energy, one writes

$$dE = dU = \delta Q - \delta W$$

where δQ and δW are incremental changes in heat and work, respectively. Note that the minus sign in front of δW indicates that a positive amount of work done by the system leads to energy being lost from the system.

Note, also, that some books formulate the first law as

$$dE = dU = \delta Q + \delta \tilde{W}$$

where $\delta \tilde{W} = -\delta W$ is the work done **on the system** by the surroundings. [1]

When a system expands quasistatically, the work done on the system is $-PdV$ whereas the work done by the system while expanding is PdV. In any case, both give the same result when written explicitly as:

$$dE = dU = \delta Q - PdV$$

Work and heat are due to *processes* which add or subtract energy, while U is a particular *form* of energy associated with the system. Thus the term "heat energy" for δQ means "that amount of energy added as the result of heating" rather than referring to a particular form of energy. Likewise, "work energy" for δw means "that amount of energy lost as the result of work". Internal energy is a property of the system whereas work done and heat supplied are not. A significant result of this distinction is that a given internal energy change (dU) can be achieved by, in principle, many combinations of heat and work.

Reversible and irreversible processes

In a reversible process a the process can be reversed (i.e., system can be brought to the initial state) without causing any change in the surroundings.

A reversible process is that change in a system which can be made to proceed in the exactly reverse way by exactly reversing the conditions of the change. For example, if in a gaseous system at constant temperature, the volume changes by dV accompanying a decrease of pressure dP, then the original volume must be restored when the pressure is increased in the next stage by dP in order that the change may be a reversible one.

The idea of reversibility involves the idea of equilibrium of the system with its surroundings. If this equilibrium in respect of pressure and temperature is maintained, then and then only a system can change reversibly from one state to another. In order that during a change the system is always in pressure and temperature equilibrium with its surroundings, the change must be carried out infinitesimally slowly . Thus a reversible change is the sum of an infinite number of stages each of very small dimension. If at any stage, the change is appreciable the equilibrium is not maintained and the change becomes irreversible.

Let us try to make the concept clear by considering the isothermal expansion of a gas from volume V_1 to V_2 accompanying a change of pressure from P_1 to P_2, and then reversing the change by an isothermal compression. The work done at any stage is the product of the change of volume and the opposing pressure. In the present case the pressure is first reduced from $_1$ to P_2 and the volume allowed to expand

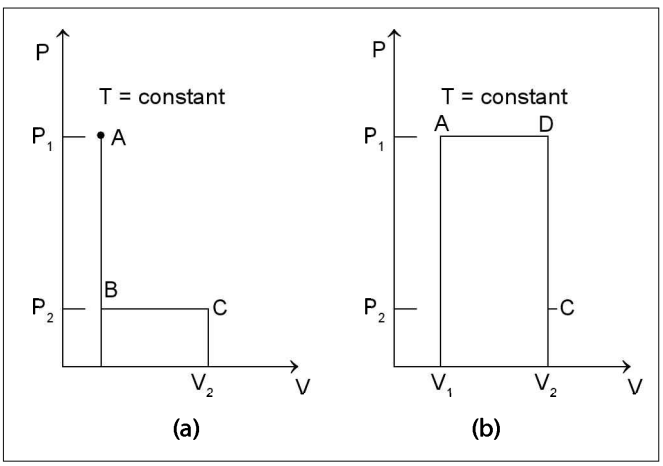


Fig. 5.5 (a)

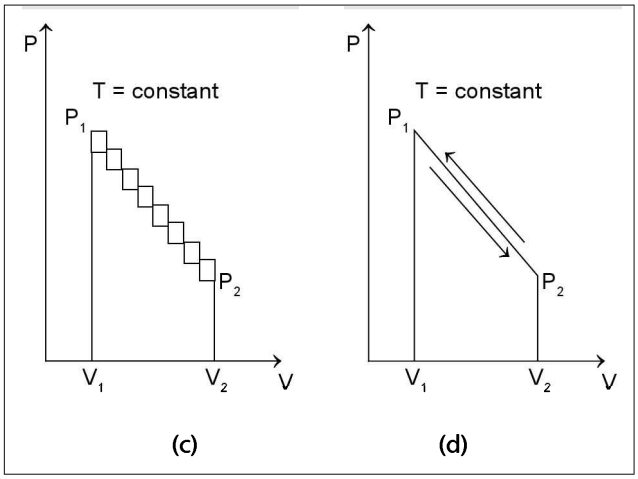


Fig. 5.5 (b)

from V_1 to V_2 so that the system moves from A to C through B (figure (a) The work done in this case is the area $BCV_1V_2[=P_2(V_2 - V_1)$. Now, the system can be pushed back to the initial state A by raising the pressure from P_2 to P_1, and allowing the volume to decrease from V_2 to V_1, so that the system moves from C to A through D and the work done in this case is the area AD V_2V_1 $[= -P_1(V_2 - V_1)]$ (Figure (b))

The magnitude of the latter work is obviously greater than the magnitude of the former and hence the system does not follow the same path in the backward direction as in the forward process. So the change is irreversible.

Now suppose that the pressure drops from P_1 to P_2 by a very small amount at a time. Then, the system follows the path below the line joining P_1P_2 and the work done in this case is the area enclosed by the zig-zag track and V_1V_2(Figure (c)). If the reverse process is carried out also in the same manner, i.e., by increasing the pressure by a small amount at a time, then the system will follow the zig-zag track above the line P_1P_2 and the work done in the area enclosed by this curve and V_1V_2. The magnitudes of these two works are not very different and in the limiting case these works are equal when the number of stages is increased enormously. Both the zig-zag curves will then be converted to the same straight line P_1P_2 and magnitudes of the work done in the forward and in the backward processes will be the same, being the area $P_1P_2V_2V_1$ (Figure (d)) The process has thus become reversible only under this limiting condition and the equilibrium exists at very stage between the system and the surroundings.

No process, however, can be ideally reversible. The number of stages in a process may be increased so that the change can approach reversibility. Since it is not physically possible to make the number of stages equal to infinit , therefore some amount of irreversibility will always remain in a process however slowly the process may be carried out. Scientists, of course, ignore the small amount of irreversibility and consider a process reversible when it occurs very slowly.

A reversible process may consist of more than one step, if necessary. For example, suppose we want to convert some amount of water at room temperature, say 298 K, and under normal atmospheric pressure to vapour at 400 K and half atmosphere. To carry out the process, first the liquid water should be heated reversibly at constant pressure until the temperature reaches 373 K. Then at 373 K the liquid is vaporized reversibly at constant pressure and temperature; and then the vapour is heated reversibly and isobarically upto 400 K and finally the pressure of the vapour is reduced reversibly and isothermally to half atmosphere. So, the process actually consists of four steps.

Worked-out Example

1. Describe a reversible process by which the temperature and pressure of one mole of helium may be changed from 300 K and 1 atmosphere to 500 K and 10 atmosphere respectively.

Solution The process, in short, may be represented as

$$\text{1 mole He (300 K; 1 atm)} \xrightarrow{\text{P Constant}} \text{1 mole He (500 K; 1 atm)} \xrightarrow{\text{T constant}} \text{1 mole He (500 K; 10 atm)}$$

Processes which occur spontaneously are irreversible in character, because, the processes occur rapidly so that equilibrium with the surroundings is never maintained. These processes always occur in a single direction and if conditions are changed by some external agency, the occurrence of the process in the reverse direction may become possible. Neverthless, the process remains irreversible because of the I reversible nature of the forward process. Natural changes occur spontaneously and hence all natural changes are irreversible.

It may be mentioned here that the work done by a system, example, work of expansion, is maximum for a reversible process as is evident from figures(a and d). The work done on a system, i.e., work of compression, is likewise mainium for a reversible process.

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

ISOTHERMAL PROCESS

An isothermal process is a change of a system, in which the temperature remains constant: $\Delta T = 0$. This typically occurs when a system is in contact with an outside thermal reservoir (heat bath), and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange. An alternative special case in which a system exchanges no heat with its surroundings ($Q = 0$) is called an *adiabatic process*. In other words, in an isothermal process, the value $\Delta T = 0$ but $Q \neq 0$, while in an adiabatic process, $\Delta T \neq 0$ but $Q = 0$.

Details for an ideal gas

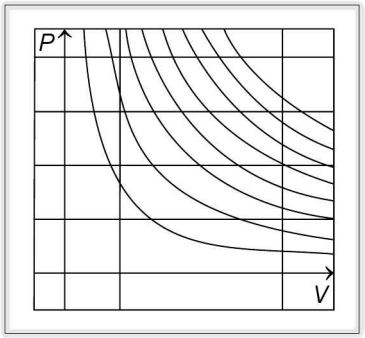


Fig. 5.6 Several isotherms of an ideal gas on a p-V diagram

For the special case of a gas to which Boyle's law applies, the product pV is a constant if the gas is kept at isothermal conditions. The value of the constant is nRT, where n is the number of moles of gas present and R is the ideal gas constant. In other words, the ideal gas law $pV = nRT$ applies. This means that

$$p = \frac{nRT}{V} = \frac{\text{constant}}{V}$$

holds. The family of curves generated by this equation is shown in the graph presented here. Each curve is called an isotherm. Such graphs are termed indicator diagrams and were first used by James Watt and others to monitor the efficiency of engines. The temperature corresponding to each curve in the figure increases from the lower left to the upper right.

Isothermal Expansion of a Gas

Let us enclose one mole of an ideal gas in a cylinder fitted with a weightless, frictionless piston. The pressure, volume and temperature of he gas are P_1, V_1 and T respectively. The volume is to be changed to V_2 at constant temperature. The pressure will naturally change to P_2. For expansion $V_2 > V_1$.

Calculation of work

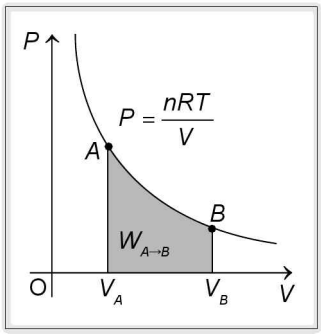


Fig. 5.7 The shaded area represents "work" for this isothermal change

If the gas is compressed, meaning ΔV = (final volume-initial volume) < 0, then the natural log term is negative and, therefore, W < 0. That is, during isothermal compression the gas does negative work, or, equivalently, the environment does positive work. Restated, the environment does work on the gas.

If the gas expands, meaning ΔV = (final volume-initial volume) > 0, then the natural log term is positive and, therefore, W > 0. That is, during isothermal expansion the gas does positive work, or, equivalently, the environment does negative work. Restated, the gas does work on the surroundings.

Case I

Suppose the process is carried out reversibly.

This can be done by placing the system in a large reservoir containing a liquid at temperature T and by pulling the piston upward very slowly. The energy required at any stage of expansion of the gas will be taken up by the system from the reservoir, but since the reservoir is large its temperature will not change to an appreciable extent. Thus, the process will be isothermal. Suppose that the pressure P of the system is decreased at any stage by a small amount dP resulting in a small voume change dV. The opposing pressure here is P – dP and hence the small amount of work dW done by the system is given by

$$dW = (P - dP)\, dV$$

Since both dP and dV are very small quantities, therefore their product dPdV must be smaller than either dP or dV and is negligible in comparison to pdV. Hence,

$$dW = (P - dP)\, dV = PdV = dPdV$$

or

For one mole of an ideal gas, $P = RT/V_m$, and hence

$$dW = RT \frac{dV}{V} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

To obtain the total work done for a change of volume from V_1 to V_2, Eq. (1) is to be integrated between limits V_1 and V_2. So

$$\int dW = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow \quad W = RT \ln \frac{V_2}{V_1} = 2.303\ RT \log \frac{V_2}{V_1}$$

For n moles of an ideal gas, P = nRT/V, and hence

$$W = nRT \ln \frac{V_2}{V_1} = 2.303\ nRT \log \frac{V_2}{V_1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Equation (3) represents the general expression for the work done by a gaseous (ideal) system due to reversible isothermal expansion.

The work W may also be expressed in terms of pressure. As at constant temperature, the Boyle's law is applicable, so $V_2/V_1 = P_1/P_2$ and hence

$$W = nRT \ln \frac{P_1}{P_2} = 2.303\ nRT \log \frac{P_1}{P_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Case II

Irreversible process

This can be of two types:

1. **Intermediate expansion**
   (Work done against a constant external pressure)
   Let us next find out the work (W_{ir}) done by the same expansion in an irreversible manner. Suppose that the pressure of the gas is reduced suddenly from P_1 to P_2 and the gas is allowed to expand from V_1 to V_2. The opposing pressure in this case is P_2 and the accompanying change of volume is $V_2 - V_1$. Therefore,

$$W_{ir} = P_2(V_2 - V_1) \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$= P_2\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right]$$

$$= nRT\left[1 - \frac{P_2}{P_1}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The difference between the work done by the gas under reversible, and irreversible conditions can be determined as follows. Equation (1) may be put in the form

$$W = nRT \ln \left(1 + \frac{P_1 - P_2}{P_2}\right)$$

Expanding the logarithmic term and neglecting higher powers of $(P_1 - P_2)/P_2$ when this quantity is less than unity, we get

$$W = nRT \frac{P_1 - P_2}{P_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

So, $$W - W_{ir} = nRT\left[\frac{P_1 - P_2}{P_2} - 1 + \frac{P_2}{P_1}\right]$$

$$= nRT\left[\frac{P_1 - P_2}{P_2} - \frac{P_1 - P_2}{P_1}\right]$$

$$= nRT(P_1 - P_2)\left(\frac{1}{P_2} - \frac{1}{P_1}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Since, $P_1 > P_2$, $W - W_{ir}$ is a positive quantity, meaning thereby that the work done by a gas in a reversible process is always greater than that down in an irreversible process.

That the reversible work is greater than the irreversible work may be shown in another way. Suppose that the isothermal expansion of a gas from V_1 to V_2 when the pressure changes from P_1 to P_2 is irreversibly brought about in one stage, and in another experiment in two stages.

When brought about in a single stage.

$$W_{ir} = P_2(V_2 - V_1) = \frac{nRT}{V_2}(V_2 - V_1) = nRT\left(1 - \frac{V_1}{V_2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

In the two-stage operation, suppose the pressure is first changed to P' when the volume is V' and then to P_2 when the volume is V_2. So,

$$W_1 = P'(V' - V_1) = nRT\left(1 - \frac{V_1}{V'}\right)$$

and $$W_2 = P_2(V_2 - V') = nRT\left(1 - \frac{V'}{V_2}\right)$$

The total work done in two step irreversible expansion is,

$$W_{ir}' = W_1 + W_2 = nRT\left(2 - \frac{V_1}{V'} - \frac{V'}{V_2}\right)$$

$$= nRT\left(2 - \frac{V_1V_2 + V'^2}{V'V_2}\right)$$

Remembering that $V_2 > V' > V_1$ it can be shown that $W_{ir}' > W_{ir}$. For example suppose that $V_1 = 1$ dm^3; $V_2 = 10$ dm^3 and $V' = 5$ dm^3, then

$$W_{ir} = nRT\left(1 - \frac{1}{10}\right) = \frac{9}{10}nRT = 0.9\ nRT$$

and $$W_{ir}' = nRT\left(2 - \frac{1 \times 10 + 25}{50}\right) = 1.3\ nRT$$

So, it is found that the amount of work in an isothermal expansion of a gas increases as the number of stages increases. As a reversible process consists of an infinite number of stages, so the reversible work is always greater than the irreversible work.

2. Free expansion

It is the expansion against zero external pressure,i.e., expansion against vacuum.

Hence work done, $W = P_{ext}\, dv = 0$

$$\Rightarrow \quad \Delta E_T = q - w = 0$$

$$\Rightarrow \quad q = w = 0$$

So, there will be no heat exchange between the system and surroundings.

Worked-out Example

2. One mole of helium is isothermally expanded at 27°C from 100 atmosphere to 1 atmosphere. Calculate the work done when the expansion is carried out (i) in a single stage (ii) in two stages; the intermediate pressure being 50 atmosphere and (iii) in four stages with intermediate pressure 75, 50 and 25 atmosphere respectively. Find out also the work done when the process is carried out reversibly.

Solution In an irreversible process for one mole of a gas

$$W_{ir} = nRT\left(1-\frac{P_2}{P_1}\right) = RT\left(1-\frac{P_2}{P_1}\right)$$

(i) $W_i = 8.314\ JK^{-1} \times 300\ K\left(1-\frac{1}{100}\right) = 2469\ J$

(ii) $W_1 = 8.314 \times 300\left(1-\frac{50}{100}\right) = 1247\ J$

and $W_2 = 8.314 \times 300\left(\frac{1}{50}\right) = 2444\ J$

Therefore,

$$W_{ii} = W_1 + W_2 = 3691\ J$$

(iii) $W_1 = 8.314 \times 300\left(1-\frac{75}{100}\right) = 623.5\ J$

$$W_2 = 8.314 \times 300\left(1-\frac{50}{75}\right) = 831.3\ J$$

$$W_3 = 8.314 \times 300\left(\frac{25}{50}\right) = 1247\ J$$

$$W_4 = 8.314 \times 300\left(1-\frac{1}{25}\right) = 2394\ J$$

Therefore,

$$W_{iii} = W_1 + W_2 + W_3 + W_4 = 5095.8\ J$$

For reversible work done,

$$W = 2.303\ RT \log -\frac{P_1}{P_2} = 2.303 \times 8.314 \times 300 \log 100 = 11488\ J$$

Enthalpy or Heat Content

If a system involves work of expansion only, then dW = PdV and the first law equation then become

$$\delta Q = dE + PdV \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

If the process is carried out at constant pressure, then for an appreciable chnge

$$Q_p = (E_2 - E_1) + P(V_2 - V_1)$$

$$Q_p = E_2 - E_1 + P_2V_2 - P_1V_1 \qquad [\text{when } P_1 = P_2 = P]$$

$$= (E_2 + P_2V_2) - (E_1 + P_1V_2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

E is a state function and P and V are parameters of the state, so E + PV is also a state function and its change during a process does not depend on the way of transformation. The E + PV has been given the symbol H, and is called the enthalpy or heat content of the system. Thus by definition

$$H = E + PV \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and dH is an exact differential.
Differentiating equation (3) we get

$$dH = dE + PdV + VdP \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

and at constant pressure

$$(dH)_P = dE + PdV \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

From Eqn. (1) and (5) we find that for a process occurring at constant pressure

$$(dH)_P = \delta Q_P \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

It may be noted that at constant volume, Eq. (1) gives

$$(dE)_v = \delta Q_V \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Degrees of Freedom and the Average Energy of a Molecule

A system consisting of N particles can be described by specifying three coordinates for each particle or a total of 3N coordinates. Even when these particles are undergoing motions, however complicated they may be, the system at any instant can be described by stating these 3N coordinates. Since any one of these components can vary by any amount, the system is said to possess 3N independent components of motion of degrees of freedom. If N particles are bound together to form a molecule, then the 3N coordinates and components of motion are conveniently chosen as follows.

Translational Motion

The translational motion of a molecule as a whole can be described by the motion of its centre of mass. Since three coordinates are required to describe the position of centre of mass, it follows that the energy (kinetic only) stored in the translational motion as given by equation

$$\bar{\varepsilon}_{trans} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

Rotational Motion

(a) Linear Molecule. Since a linear molecule can rotate around two axes, the energy stored in the rotational motion as gien by Eq. is

$$\bar{\varepsilon}_{rot} = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

(b) Nonlinear Molecule. Since a nonlinear molecule can rotate around three axes, the energy stored in the rotational motion as given by Eq. is

$$\bar{\varepsilon}_{rot} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

Thus a linear molecule contributes, on an average, kT and a nonlinear molecule (3/2)kT, towards the total average energy due to rotational motion.

Vibrational Motion

The remaining (3N–5) coordinates for a linear molecule and (3N–6) coordinates for a nonlinear molecule, describe the bond distances and bond angles within the molecule. Motion in these coordinates corresponds

to the vibrations (stretching or bonding) of he molecule. Thus, linear molecules have (3N–5) and nonlinear molecules (3N–6) vibrational modes. Vibrational energy stored in each of the vibrational mode as given by Eq. is given by

$$\bar{\varepsilon}_{vib} = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

Thus, each vibrational mode contributes on an average kT towards the total average energy. Thus, linear molecules contribute (3N–5) kT and nonlinear molecules contribute (3N–6) kT towards the total average energy due to their vibrational motions.

The total average energy contribution due of all the three modes is:

For linear molecule:

$$\bar{\varepsilon}_{linear} = \left(\frac{3}{2}kT\right)_{trans} + \left(\frac{2}{2}kT\right)_{rot} + \{(3N-5)kT\}_{vib}$$

For nonlinear molecule:

$$\bar{\varepsilon}_{nonlinear} = \left(\frac{3}{2}kT\right)_{trans} + \left(\frac{3}{2}kT\right)_{rot} + \{(3N-6)kT\}_{vib}$$

The total average energy stored by the molecules in one mole of the gas is

$$\bar{E}_{linear} = N_A \bar{\varepsilon}_{linear} = \frac{3}{2}RT + RT + (3N-5)RT$$

$$\bar{E}_{linear} = N_A \bar{\varepsilon}_{linear} = \frac{3}{2}RT + \frac{3}{2}RT + (3N-6)RT$$

For monatomic gases, N = 1, and thus the total degrees of freedom are three. These are the three translational motions along x-, y-, and z-axes

Thus $= \frac{3}{2}kT$ per molecule

or $\bar{E} = \frac{3}{2}RT$ per mole

Heat Capacity

The amount dq of heat added to an ideal gas at constant volume is utilized in increasing its internal energy, dU, i.e.,

$$dqv = dU$$

whereas at constant pressure, it increases not only its internal energy but also in doing the work of expansion, i.e.,

$$dq_p = dU + pd_v = dqV + nR\,dT$$

Heat capacity of a system is defined as the amount of heat required to increase its temperature by 1 kelvin. Thus one can have two heat capacities, (i) heat capacity C_v at constant volume condition and (ii) heat capacity C_p at constant pressure condition. These are represented as:

$$C_v = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_p = \frac{dp_p}{dT} = \frac{dq_v + nRdT}{dT} = \frac{dq_V}{dT} + nR$$

$$C_p = C_V + nR$$

For one mole of the gas

$$C_{p,m} = C_{V,m} + R$$

Molar heat capacity at constant volume of the gases can be obtained by differentiating the molar energies with respect to temperature. Thus, from Eq.s , we have:

Monatomic Gases

$$C_{V,m} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} R$$

$$C_{p,m} = \frac{5}{2} R$$

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{5}{3} \simeq 1.667$$

Polyatomic Gases

(Linear) $$C_{V,m} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} R + R + (3N - 5) R$$

(Nonlinear) $$C_{V,m} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R + \frac{3}{2}R + (3N - 6)R$$

The molar heat capacities for diatomic and triatomic molecules are as follows:

(i) Diatomic Molecule, N = 2, thus

$$C_{V,m} = \frac{3}{2} R + R + R = \frac{7}{2}R$$

$$C_{p,m} = \frac{9}{2} R$$

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{9}{7} \simeq 1.286$$

(ii) Triatomic Molecule, N = 3, thus

Linear $$C_{V,m} = \frac{3}{2} R + R + 4R = \frac{13}{2} R$$

$$C_{p,m} = \frac{15}{2} R$$

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{15}{13} \simeq 1.154$$

$$\text{Nonlinear } C_{V,m} = \frac{3}{2} + R + \frac{3}{2}R + 3R = 6R$$

$$C_{p,m} = 7R$$

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{7}{3} \simeq 1.167$$

Adiabatic Expansion of a Gas

P – V relation. For an adiabatic change $\delta Q = 0$ andhence from the first law of thermodynamics for the expansion of a gas

$$dE = -pdV \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Since E is independent of volume in the case of an ideal gas therefore, for one mole of a gas

$$dE = C_v dT$$

where C_V is the molar heat capacity of the gas at constant volume.
So

$$C_V\, dT = -PdV \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Again, for one mole PV = RT
Hence,

$$PdV + VdP = RdT \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

From (2) and (3)

$$C_v dT + RdT = VdP$$

$$(C_v + R)\, dT = VdP$$

or
$$C_P dT = VdP \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

From (3)

$$dT = \frac{PdV + VdP}{R} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Now from (2) and (5)

$$\frac{C_v}{R}(PdV + VdP) = -PdV \qquad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

or
$$\frac{C_V}{C_P - C_V}(PdV + VdP) = -PdV$$

or
$$PdV + VdP = \frac{(C_P - C_V)}{C_V} PdV = -\left(\frac{C_P}{C_V} - 1\right) PdV$$

or
$$PdV + VdP = -(\gamma - 1)\, PdV$$

or
$$\gamma PdV = -VdP$$

or
$$\gamma \frac{dV}{V} = -\frac{dP}{P}$$

Integrating we get,

$$\gamma \ln V = -\ln P + \text{constant}$$

or $$\ln V^{\gamma} + \ln P = \text{constant}$$

or $$\ln PV^{\gamma} = \text{constant}$$

or $$PV^{\gamma} = \text{constant} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Equation (7) is the P – V relation for an ideal gas during an adiabatic expansion. For a certain amount of gas under different conditions,

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$PV^{\gamma} = \text{constant} \Rightarrow \frac{nRT}{V} V^{\gamma} = \text{constant} \Rightarrow$$

$$TV^{(\gamma-1)} = \text{constant} \qquad (\because \text{n and R are constant}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$PV^{\gamma} = \text{constant} \Rightarrow P\left(\frac{nRT}{P}\right)^{\gamma} = \text{constant} \Rightarrow T^{\gamma}P^{(1-\gamma)} = \text{constant}$$



Worked-out Example

3. One mole of helium at 27°C and 1 atm pressure undergoes a reversible adiabatic expansion until the volume increases 100 times. Calculate the final pressure and temperature.

Solution He is a monoatomic gas. So, its $\gamma = 1.67$. For an adiabatic expansion

$$P_2V_2^{\gamma} = P_1V_1^{\gamma}$$

or $$P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma} = 1 \times \left(\frac{1}{100}\right)^{1.67}$$

$$P_2 = 4.57 \times 10^{-4} \text{ atmosphere}$$

And $$T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$$

or $$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 300 \times \left(\frac{1}{100}\right)^{1.67-1}$$

$$T_2 = 13.7 \text{ K} = -259.3°\text{C}$$

Slopes of adiabatic and isothermal curves

For an adiabatic process, $PV^{\gamma} = \text{constant}$.

Differentiation would show that $\frac{dP}{dV} = -\gamma\frac{P}{V}$ or $\left|\frac{dP}{dV}\right| = \gamma\frac{P}{V}$

For an isothermal process, $PV = \text{constant}$. $\therefore \left|\frac{dP}{dV}\right| = \frac{P}{V}$. Hence the adiabatic curve, relating P and V, is steeper than the isothermal curve, as shown in the following figure.

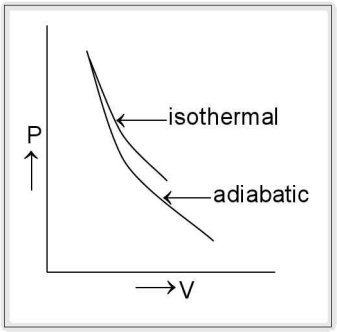


Fig. 5.8

This is an expression that describes the variation of ΔH of a reaction with temperature. Earlier, we have defined heat capacity of a substance at constant pressure as

Work due to Adiabatic Expansion

Adiabatic expansion of a gas is carried out by blanketing the container by some heat insulating material like wood wool etc. For a reversible adiabatic change, the small amount of work done in any stage is,

$$\delta W = PdV$$

The total work done is found by integrating this equation between the limits V_1 and V_2, i.e., between initial and final volumes

For an adiabatic change PV^{γ} = constant = K(say). Then,

$$P = K/V^{\gamma}$$

and, $$\delta W = \frac{KdV}{V^{\gamma}}$$

This gives,

$$W = K\int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

$$= \frac{1}{1-\gamma}(KV_2^{1-\gamma} - KV_1^{1-\gamma})$$

$$W = \frac{1}{1-\gamma}(P_2V_2^{\gamma}V_2^{1-\gamma} - P_1V_1^{\gamma}V_1^{1-\gamma})$$

$$W = \frac{1}{1-\gamma}(P_2V_2 - P_1V_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

An alternative expression for the adiabatic work can be established as follows. Since δQ = 0, from the first law one can writ

$$\delta W = -dE = -C_V\, dT$$

or $$W = -C_V(T_2 - T_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The above expressions for work are valid for the reversible changes only. Irreversible changes generally occur against a constant external pressure and in that case integration of PdV will give $P(V_2 - V_1)$ where P is the constant external pressure.

Some Practical Engines

This reduces both the efficiency of the engine and practical loss of heat. Vaporization of water in the boiler is an isobaric-isothermal process and is represented by AB. At B, the introduction of steam into the cylinder is cut off and the steam is adiabatically expanded along BC. CD represents the exhaust of the cooled steam during the return motion of the piston. The efficiency of a steam engine is 0.29–0.36 with saturated steam and 0.34–0.46 with superheated steam.

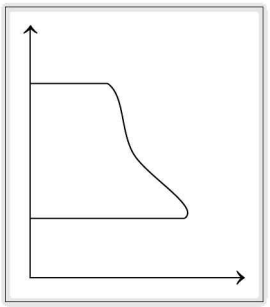
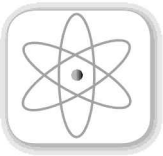


Fig. 5.9

The mechanism of the action of an internal combustion engine is given by the Diesel engine. (Fig. 5.9). At the start, the engine cylinder is full of air at atmospheric pressure (point C) hich is compressed adiabatically along CD and at D the fuel enters into the cylinder and gets ignited. Combustion of the fuel, being an isobaric process, takes place along DA. At A, the fuel admission is stopped and the remaining stroke of the piston causes adiabatic expansion AB. At B the spent fuel passes through an exhaust and the pressure rapidly falls along BC. For $T_2 = 2000$ K, $T_1 = 350$ K, $P_1 = 34$ atm and $P_2 = 0.56$ atm, the efficiency of the Diesel engine is .56.

THERMOCHEMISTRY



It is a common observation that whenever a chemical reaction takes place, energy is either absorbed or released. This might be in the form of heat, light or any other form of energy. A reaction is said to be exothermic if heat is evolved and is termed endothermic is heat is absorbed. These changes are obvious because all the chemical processes are accompanied by molecular rearrangement, which involves the disruption and simultaneous formation of certain chemical bonds. For example, in the reactions, at 298 K

$$C \text{ (graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -98.03 \text{ kcal}$$

$$C(\text{diamond}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -94.5 \text{ kcal}$$

C–C and O=O bonds are broken and C=O bonds are formed. The resultant of the energy requirement of the two processes appears in the form of heat energy.

It is quite apparent that the energy-changes depend upon the form and the physical state of the reactants and products. Chemical equations, when written so as to indicate the physical state of the reactants and products, and the amount of heat evolved or absorbed, during the change are called thermochemical equations. The heat changes, when stoichiometric amounts of the reactants, as represented by the balanced chemical equation, have completely reacted, is termed as the heat of reaction (ΔH_r). The amount of heat changes, however, depends upon the conditions under which the reaction is made to proceed.

For example, if a reaction is carried out at constant volume or at constant pressure, then the heat changes are given by,

$$Q_V = E_2 - E_1 = \Delta E$$

and

$$Q_P = H_2 - H_1 = \Delta H$$

Since these heat changes are equal to the changes in the internal energy or heat content, which are state functions of the system, therefore $Q_V(\Delta E)$, and $Q_P(\Delta H)$ also depend on the initial and the final states of the system, and not on the reaction path. The heat of reaction may thus be defined in two ways, viz.

The heat of reaction at constant volume is the increase in the total internal energy of the system accompanying the complete reaction at the constant volume and temperature.

The heat of reaction at constant pressure is the increase in the total enthalpy of the system accompanying the complete reaction at constant pressure and temperature.

It follows from the definition that the negative heat of reaction indicates an exothermic reaction and positive heat of reaction indicates an endothermic reaction.

The heat of a reaction, apart from volume and pressure (which canbe controlled, if desired) also depends upon the temperature and the physical state of the reactants and products. In order to standardize the thermochemical data, the heat changes are generally reported under some specified conditions of reactants and products. The standard conditions agreed to (though arbitrarily) are,

(i) a temperature of 298 K, or any specified temperatur
(ii) a pressure equal to 1 atmospheric pressure
(iii) the stable and the most common state at 298 K and 1 atm pressure for the reactants and products are taken as their standard states.

If the reactants and products are in their standard states, the heat of reaction is termed as the standard heat of reaction, represented as ΔE_r^o or ΔH_r^o.

Relation between the Heats of Reaction at Constant Volume and Constant Pressure

The relation between the two heats of reaction, i.e., the heat of reaction at constant pressure and that at constant volume, may be derived as follows.

We know that,

$$H = E + PV$$

or $$dH = dE + PdV + VdP$$

At constant pressure,

$$dH = dE + PdV$$

For an appreciable change, the above equation can be written as,

$$\Delta H = \Delta E + P\,\Delta V \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

If only solid and liquid substances take part in the reaction, then the change of volume is negligible, and hence,

$$\Delta H = \Delta E$$

For gases the change of volume is generally appreciable and cannot be neglected. If Δn is the change in the number of moles of he gaseous component due to the reaction, and V_m is the molar volume, then

$$\Delta V = \Delta n V_m$$

If gaseous component behaves ideally,

$$V_m = \frac{RT}{P}$$

Therefore,

$$\Delta H = \Delta E + P(\Delta n V_m)$$

$$= \Delta E + \Delta nRT \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

or $$= Q_P = Q_V + \Delta nRT \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

(2) or (3) gives the relation between the heats of a reaction at constant pressure and at constant pressure and at contant volume



Worked-out Example

4. Complete oxidation of one mole benzene is accompanied by the evolution of 781.0 kcal of heat at 298K at constant pressure. What is the value of the heat of the reaction at constant volume?

Solution The reaction for the oxidation of 1 mole of benzene is,

$$C_6H_6(l) + 7\frac{1}{2}\ O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l),\ Q_P = -781.0 \text{ kcal}$$

Since liquid molecules do not contribute towards volume change, hence

$$\Delta n = 6 - 7\frac{1}{2} = -1\frac{1}{2} = -1.5$$

Therefore,

$$Q_V = Q_P - \Delta nRT$$

$$= -781000 \text{ cal} - 2 \text{ cal } K^{-1} \text{ mole}^{-1} \times 298 \text{ K } (-1.5 \text{ mole})$$

$$= -780\ 106 \text{ cal}$$

$$= -780.1 \text{ kcal}$$

Various Heats of Reaction

Depending upon the nature of the chemical (or physical) change, the heats or reactions have been given various names. Some of them are;

Heat of formation. The heat of formation (ΔH_f) of a compound is defined as the enthalpy change accompanying the formation of one mole of the compound from its elements.

The amount of heat evolved or absorbed when one mole of a substance is formed from its constituent elements is called heat of formation.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g);\ \Delta H = -44 \text{ kcal}$$

Thus, enthalpy of formation of HCl is –22 kcal.

The formation reaction of a compound has only one mole of the compound and nothing else on the product side. Only elements in their stable states of aggregation appear on the reactant side.

Standard enthalpy of formation (H_f°)

It is enthalpy change of a reaction by which a compound is formed from its constituent elements, the reactants and products all being in a given, standard state (i.e., at 298 K and 1 atm pressure).

For example,

$$S(s) + O_2(g) \rightarrow SO_2(g)\ ;\ \Delta H_f^\circ = -296.9 \text{ kJ}$$

$$2Al(s) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s)\ ;\ \Delta H_f^\circ = -1669.8 \text{ kJ}$$

Let us considered a reaction, $C(s) + O_2(g) \rightarrow CO_2(g)\ ;\ \Delta H_f^\circ = -393.5$ kJ

$$\Delta H_f^\circ \quad H_P^\circ - H_R^\circ = -393.5 \text{ kJ}$$

Enthalpies of free elements in their standard states are assumed to be zero.

So, $\Delta H_f^\circ = \Delta H_p^\circ = -393.5$ kJ

The compounds having positive enthalpies of formation are called endothermic compounds and are less stable than the reactants and those having negative enthalpies of formation are known as exothermic compounds and are more stable than the reactants.

If we know the standard heats of formation of various substances, we can calculate heat of reactions under standard conditions

Thus,

$$\Delta H^\circ \text{ of a reaction} = \begin{bmatrix}\text{sum of the standard heats}\\ \text{of formation of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard heats}\\ \text{of formation of reactants}\end{bmatrix}$$

i.e., $$\Delta H^\circ = \sum \Delta H_f^\circ(\text{Products}) \sum \Delta H_f^\circ(\text{reactants})$$

The heats of formation of all the elements in their standard states are arbitrarily taken to be zero. For example, at 1 atm and 298 K, the stable state of aggregation of bromine is the liquid state. Hence liquid bromine, gaseous hydrogen, solid zinc, solid (rhombic) sulphur and solid (graphite) carbon, all have $H_{298}^\circ = 0$.

For elementary solids that exists in more than one crystalline form, the modification that is stable at 25°C and 1 atm is assigned $H^\circ = 0$. For example, zero assignment goes to rhombic sulphur rather than to monoclinic sulphur, to graphite rather than diamond. In cases in which more than one molecular species exists (example O_2 and O_3), the zero enthalpy value goes to the most stable form at 25°C and 1 atm pressure i.e., for O_2, $H_{298}^\circ\ (O_2, g) = 0$.

Once, the value of the standard enthalpy of the elements at 298 K has been assigned, the value at any other temperature can be calculated using Kirchhoff's equation.

$$\int_{298}^{T} dH^\circ = \int_{298}^{T} C_p^\circ dT$$

$$H_T^\circ - H_{298}^\circ = \int_{298}^{T} C_p^\circ dT$$

$$H_T^\circ = H_{298}^\circ + \int_{298}^{T} C_p^\circ dT$$

This expression holds good for both elements as well as compounds. For elements, the first term on the right hand side is zero.

T–1

Why do we assign zero value of enthalpy to an element in free state under standard conditions?

Enthalpy or heat of combustion

The amount of heat evolved or decrease in enthalpy when one mole of a substance is completely oxidized. Organic compounds containing only carbon, hydrogen and oxygen are burnt to gaseous carbon dioxide and liquid water. For example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l);\ \Delta H^\circ = -890.36 \text{ kJ/mol}$$

The measurements of the heat of combustion is used to determine the heats of formation of all organic compounds containing C, H, O, N etc.



Worked-out Example

5. $\Delta H^{\circ}_{combustion}(CH_4, g) = -890.36$ kJ/mol; $H^{\circ}_f(CO_2, g) = -393.51$ kJ/mol;

$H^{\circ}_f(H_2O, l) = -285.83$ kJ/mol;

$H^{\circ}_f(CH_4, g) = ?$

Solution $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H^{\circ}_{combustion} = H^{\circ}(CO_2, g) + 2H^{\circ}(H_2O, l) - H^{\circ}(CH_4, g)$

$\therefore \quad H^{\circ}(CH_4, g) = H^{\circ}(CO_2, g) + 2H^{\circ}(H_2O, l) - \Delta H^{\circ}_{combustion}$

$= -393.51 + 2(-285.83) - (-890.36) = -965.17 + 890.36 = -74.81$ kJ/mol

Later in this lesson using Hess's law we shall find heat of reaction as given below Heat of reaction = ∑Heat of combustion of reactants – ∑Heat of combustion of products.

Enthalpy or heat of solution

The amount of heat evolved or absorbed when one mole of solute is dissolved in excess of solvent so that further addition of solvent makes no heat change. For example,

$H_2SO_4(l)$ + aqueous $\rightarrow H_2SO_4(aq)$; $\Delta H = -20.2$ kcal

$KCl(s)$ + aqueous $\rightarrow KCl(aq)$; $\Delta H = 4.4$ kcal

Heat of an ideal solution is taken as zero.

Heat of dilution

The amount of heat evolved or absorbed when solution containing one mole of solute is diluted from one concentration to another. For example,

$HCl(g) + 10H_2O \rightarrow HCl.10H_2O$; $\Delta H_1 = -69.01$ kJ/mol

$HCl(g) + 25H_2O \rightarrow HCl.25H_2O$; $\Delta H_2 = -72.03$ kJ/mol

$HCl(g) + 40H_2O \rightarrow HCl.40H_2O$; $\Delta H_3 = -72.79$ kJ/mol

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$HCl(g) + \infty H_2O \rightarrow HCl.\infty H_2O$; $\Delta H_\infty = -74.85$ kJ/mol

If we subtract first equation from the second in the above set, we ge

$HCl.10H_2O + 15\ H_2O \rightarrow HCl.25H_2O$; $\Delta H = (\Delta H_2 - \Delta H_1) = -3.02$ kJ/mol

This value of ΔH is the heat of dilution. The heat of dilution of a solution is dependent on the original concentration of the solution and on the amount of the solvent added.

Worked-out Example

6. The enthalpies of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4.5H_2O$ are –66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$.

Solution Given that

(i) $CuSO_4(s) + aqueous \rightarrow CuSO_4(aqueous)$; $\Delta H_1 = -66.5$ kJ/mol

(ii) $CuSO_4.5H_2O(s) + aqueous \rightarrow CuSO_4(aqueous)$; $\Delta H_2 = 11.7$ kJ/mol

$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$; $\Delta H = ?$

$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - 11.7 = -78.2$ kJ

Enthalpy or heat of neutralization

The amount of heat evolved when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base in dilute solution is called heat of neutrlization. For example,

$$HNO_3(aqueous) + NaOH(aqueous) \rightarrow NaNO_3(aqueous) + H_2O(l) \; ; \; \Delta H = -13.7 \text{ kcal}$$

Heat of neutralization of a strong acid and a strong base is 13.7 kcal, or 57 kJ. The constant value is due to the fact that heat of neutralization of strong acid and strong base is merely the heat of formation of H_2O from H^+ of an acid and OH^- of a base.

$$H^+(aqueous) + OH^-(aqueous) \rightarrow H_2O(l); \; \Delta H = -13.7 \text{ kcal}$$

Enthalpies of Phase Transition

(i) Enthalpy of Fusion

It is the enthalpy change involved in the conversion of one mole of a substance from solid state to liquid state at its melting point. This equals latent heat of fusion per gram multiplied by the molar mass. For example,

$$H_2O(s) \rightarrow H_2O(l); \; \Delta H = 1.44 \text{ kcal/mol}$$

(ii) Enthalpy of Vaporization

It is the enthalpy change involved in converting one mole of the substance from liquid state to gaseous state at its boiling point. For example,

$$H_2O(l) \rightarrow H_2O(g) \; ; \; \Delta H = 10.5 \text{ kcal/mol}$$

(iii) Enthalpy of Sublimation

It is the enthalpy change involved in the conversion of one mole of a solid directly into its vapour at a given temperature below its melting point.

For example,

$$I_2(s) \rightarrow I_2(g) \; ; \; \Delta H = 14.9 \text{ kcal/mol}$$

$$\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vapourization}$$

(iv) Heat of Atomisation

The amount of heat required for the formation of one mole of atoms in gaseous state from its elements is known as heat of atomization of that element.

$C(s) \rightarrow C(g)$; $\Delta H = 171.7$ kcal/mol

$H_2(g) \rightarrow 2H(g)$; $\Delta H = 104$ kcal

In this case, heat of atomization of hydrogen is 52 kcal/mol



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

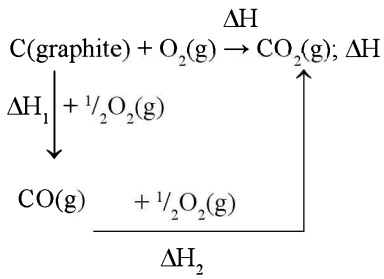
Hess's law of constant heat summation

The change in state of a system produced by a specified chemical reaction is definite. The corresponding enthalpy change is definite, since the enthalpy is a state function

Thus, **"If a specified set of reactants is transformed to a specified set of products by more than one sequence of reactions, the total enthalpy change must be the same for every sequence."**

This rule, which is a consequence of the first law of thermodynamics, is known as **Hess's law.** More precisely, "**the enthalpy change in a chemical or physical process is the same whether the process is carried out in one step or in several steps".**

For example,



$\therefore \quad \Delta H = \Delta H_1 + \Delta H_2$

This property is due to the fact that the enthalpy change in a system is independent of the path followed.

Applications of Hess's law

(i) Using Hess's law, enthalpy changes for the reactions, which are experimentally not possible, can be calculated.

Example for compounds such as C_2H_6, C_6H_6 etc. whose direct synthesis from their constituent elements is not possible, the enthalpy of formation of such compounds can be calculated.

(ii) Calculation of heat of Reaction

$\Delta H_{reaction}$ = ∑Heat of formation of products – ∑Heat of formation of reactants

$\Delta H_{reaction}$ = ∑Heat of combustion of reactants – ∑Heat of combustion of products

Bond Energies

The amount of energy required to break one mole of a particular type of bond between the atoms in the gaseous state i.e., to separate the atoms in the gaseous state under one atmospheric pressure and the specified temperature is called bond dissociation ene gy

Example $H–H(g) \rightarrow 2H(g)$; $\Delta H = 433$ kJ mol^{-1}

$H–I(g) \rightarrow H(g) + I(g)$; $\Delta H = 299$ kJ mol^{-1}

The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends on the nature of bonds and also the molecule in which the bond is present. When a molecule o a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. This average bond dissociation energy required to break

each bond in a compound is called bond energy which is also the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.

Consider the dissociation of water molecule,

$$H_2O\ (g) \rightarrow H(g) + O\text{–}H(g);\ \Delta H = 497.8\ kJ\ mol^{-1}$$

$$O\text{–}H(g) \rightarrow H(g) + O(g)\ ;\ \Delta H = 428.5\ kJ\ mol^{-1}$$

The average of these two bond dissociation energies gives he value of bond energy of O–H bond.

$$\therefore \quad \text{B.E. of O–H bond} = \frac{497.8 + 428.5}{2} = 463.15\ kJ\ mol^{-1}$$

Bond energies can be obtained from the data of heats of combustion and heats of dissociation.



Worked-out Examples

7. Calculate bond energy of C–H bond from the following data.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ ;\ \Delta H = -890.36\ kJ$$

$$CO_2(g) \rightarrow C(\text{graphite}) + O_2(g)\ ;\ \Delta H = 393.51\ kJ$$

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)\ ;\ \Delta H = 571.70\ kJ$$

$$2H_2(g) \rightarrow 4H(g)\ ;\ \Delta H = 871.86\ kJ$$

$$C(\text{graphite}) \rightarrow C(g)\ ;\ \Delta H = 716.68\ kJ$$

Solution Adding all the equations, we get

$$CH_4(g) \rightarrow C(g) + 4H(g)\ ;\ \Delta H = 1663.39\ kJ$$

$$\therefore \quad \text{B.E of C–H bond} = \frac{1663.39}{4} = 415.85\ kJ\ mol^{-1}$$

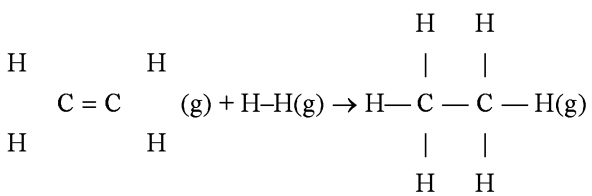
Applications of bond energies

Determination of heat of reactons

$\Delta H_{reaction}$ = Sum of bond energies of reactants – Sum of bond energies of products.

8. Given that the average bond energies of C–C=, C=C, C–H and H–H bonds are 80.5, 145, 98.2 and 103 kcal mol^{-1} respectively, calculate the enthalpy of the reaction per mole.

Solution



$$\Delta H_{reaction} = (\varepsilon_{H-H} + \varepsilon_{C-H}) - (2\varepsilon_{C-H} + \varepsilon_{C-C})$$

$$\Delta H_{reaction} = (103 + 145) - (196.4 + 80.5) = 248 - 276.9$$

$$\Delta H_{reaction} = -28.9\ \text{kcal/mol.}$$

Determination of Resonance Energy

Resonance Energy = (Experimental or actual heat of formation) – (Calculated heat of formation).

9. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are – 156 and 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is – 119 kJ mol^{-1}. Use these data o estimate the magnitude of resonance energy of benzene.

Solution $C_6H_{10}(l) + H_2(g) \rightarrow C_6H_{12}(l)$; $\Delta H = -119$ kJ

(This involves breaking up of one double bond and addition of one H_2 molecule).

$\therefore$ $C_6H_6(l) + 3H_2(g) \rightarrow C_6H_{12}(l)$; $\Delta H = (3 \times -119) = -357$ kJ …… (i)

(This involves breaking up of three double bonds and addition of three H_2 molecules).

Enthalpy change of equation (i) can be given as

$$\Delta H = -357 = \Delta H_f(C_6H_{12}, l) - \Delta H_f(C_6H_6, l)$$

$$\Delta H_f(C_6H_6, l) = -156 + 357 = 201 \text{ kJ}$$

$\therefore$ Resonance energy = Observed ΔH_f – calculated ΔH_f of C_6H_6

$= 49 - 201 = -152$ kJ

KIRCHHOFF'S EQUATION



This is an expression that describes the variation of ΔH of a reaction with temperature. Earlier, we have defined heat capacity of a substance at constant pressure as

$C_p = \left(\frac{\partial H}{\partial T}\right)_P$ or $\partial H = C_p.dT$ (at constant pressure). This expression shows that the enthalpy of substance (H) varies with temperature and this is so, for every reactant and product. ΔH of a reaction (= enthalpy of product minus enthalpy of reactants) also changes with temperature. Thus,

$$\partial(\Delta H) = \Delta C_p.\partial T \text{ or } \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_P$$

This is Kirchhoff's equation. The change in ΔH of a reaction depends on (a) change in temperature (b) the difference between the heat capacities of products and reactants i.e., ΔC_P = (C_p of products – C_p of reactants). If C_p of each substance is assumed to be independent temperature over short temperature ranges (appx), then

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p.dT$$

$$= \Delta C_p(T_2 - T_1).$$

If C_p varies with temperature and it is expressed as a power series in T, such as

$C_p = \alpha + \beta T + \gamma T^2 + \ldots\ldots$ Then ΔC_p can be put in the form,

$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \ldots\ldots\ldots$, so that

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_p dT = \int_{T_1}^{T_2} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + ...)dT$$

$$= \Delta\alpha\,(T_2 - T_1) + \frac{\Delta\beta}{2}\,(T_2^2 - T_1^2) + \frac{\Delta\gamma}{3}\,(T_2^3 - T_1^3) + \ldots\ldots$$

Note: For an isochoric process (constant volume), Kirchhof's equation assumes the form,

$$\Delta E_{T_2} - \Delta E_{T_1} = \int_{T_1}^{T_2} \Delta C_v \; dT$$

Problem: ΔH of formation of $H_2O(l)$ is –68 kcal at 25°C. Calculate ΔH at 100°C, assuming the color heat capacities of $H_2(g)$, $O_2(g)$ and $H_2O(l)$ to be 7.0, 7.0 and 18.0 cal K^{-1} respectively.

Method: $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$; $\Delta H = -68{,}000$ cal

$$\Delta C_p = 18 - (7 + 7 \times 0.5) = 7.5 \text{ cal } K^{-1}$$

$$\Delta H_{373K} = \Delta H_{298K} + 7.5\,(373–298)$$

$$= (-68000 + 7.5 \times 75) \text{ cal} = -67437 \text{ cal} = -67.4 \text{ kcal.}$$

Problem: Calculate ΔH at 127°C for the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, assuming ΔH at 27°C to be –92.4 kJ.

$C_p(N_2 \text{ gas}) = 27.26 + 5.23 \times 10^{-3}\,T$,

$C_p(H_2 \text{ gas}) \; 29.02 - 8.35 \times 10^{-4}\,T$ and

$C_p(NH_3 \text{ gas}) = 25.86 + 32.94 \times 10^{-3}\,T$

(C_p is expressed in $JK^{-1}\,mole^{-1}$)

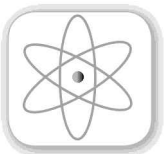
Method: $\Delta C_p = 2[25.86 + 32.94 \times 10^{-3}\,T] - [27.26 + 5.23 \times 10^{-3}\,T] - 3[29.02 - 8.35 \times 10^{-4}]$

$$= -62.60 + 63.16 \times 10^{-3}\,T$$

$$\Delta H_{400K} = -92{,}400 + \int_{300}^{400} [-62.60 + 63.16 \times 10^{-3}\,T]dT \text{ joules}$$

$$= -92.400 - 62.60\,(400–300) + 63.16 \times 10^{-3} \times \frac{1}{2}\,(400^2–300^2) \text{ joules}$$

SECOND LAW OF THERMODYNAMICS



The first law of thermodynamics just deals with the equivalence between two different forms of energy involved in an interconversion, whereas the second law stipulates the conditions for such an interconversion. With reference to chemical process, the second law predicts whether a reaction is feasible or not under a given set of conditions. The second law is variedly stated thus.

1. It is impossible for a self-acting machine, unaided by any external agency to convey heat from a lower to a higher temperature (Clausius). This statement means that only if work is done on the machine, heat can flow up the temperature gradient.

2. Heat cannot be completely converted to an equivalent amount of work without causing other changes in the system. (In an isothermal, reversible expansion, heat is completely converted to mechanical work, but there is a change in the state of the system, namely a volume exchange).
3. It is impossible to construct a machine, operating in cycles, which will produce no effect other than the absorption of heat from a reservoir at constant temperature and its conversion into an equivalent tamount of work (Kelvin). (There are two important aspects of the statement to be understood. It is not enough if we just have a reservoir of heat; we must have a sink at a lowest temperature so that heat is allowed to flow; Also entire heat cannot be completely converted into work i.e., it is impossible to have 100% efficiency for a heat engine operating in cycles.
4. It is impossible to construct a perpetual motion machine of the second kind. It is important to recognize that work has a natural tendency to get converted into heat, but the reverse process is not natural. In the conversion of heat to work, heat must be made to flow (directing influence). Also mechanical and other forms of energy can, in principle, be converted to heat energy with 100% efficiency. But it is not so, for the reverse process. It should be noted that the second law of thermodynamics is statistical in nature, applicable to macroscopic systems, which are the basis of human observation and experience.

Heat Engines: The Carnot Cycle

The conversion of heat into work required an energy. Any device that can convert heat into mechanical work is called a heat engine. S. Carnot (1824) devised a heat engine consisting of one mole of an ideal gas enclosed in a cylinder fitted with a weightless, frictionless piston, and determined its efficienc , that is, the ratio of work done to heat absorbed in the following way.

Carnot completed a cycle consisting of four reversible operations such that after the fourth operation the system reverts back unchanged to its initial starting position. The operations are (I) reversible isothermal expansion, (II) reversible adiabatic expansion, (III) reversible isothermal compression, and (IV) reversible adiabatic compression.

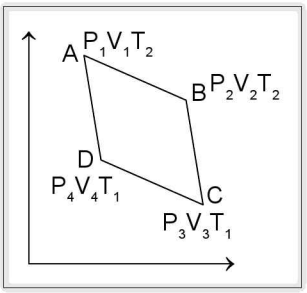


Fig. 5.10

The temperatures in (I) and (III) are T_2 and T_1 respectively and $T_2 > T_1$ because after the second operation the temperature must fall. The parameters at different points of operation are shown in the indicator diagram (Fig. 5.10). The adiabatic curves are steeper because during these operations PV^γ = constant, and not PV = constant.

Two large reservoirs containing liquids at temperatures T_2 and T_1 respectively are necessary for performing the isothermal processes. The first one is called the source as it supplies heat to the system necessary for doing the expansion work and the other is called a sink as it takes up some heat, given up by the system, as a result of compression.

Heat is taken up by the system only during the first operation and let this heat be Q_2. The work done by the system at this stage is then equal to Q_2. The work in different stages are given as,

$$W_I = RT_2 \ln \frac{V_2}{V_1} = Q_2$$

$$W_{II} = C_V (T_1 - T_2)$$

$$W_{III} = RT_1 \ln \frac{V_4}{V_3}$$

and $$W_{IV} = -C_V (T_2 - T_1)$$

W_{II} and W_{IV} are equal and opposite, and hence the total work done by the engine in the complete cyclic operation is,

$$W = W_I + W_{III} \ (W_{II} \text{ and } W_{IV} \text{ cancel out})$$

$$= RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_5} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

As the operations II and IV are adiabatic,

$$T_1 V_3^{\gamma-1} = T_2 V_2^{\gamma-1} \quad \text{or} \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

and $$T_1 V_4^{\gamma-1} = T_2 V_1^{\gamma-1} \quad \text{or} \quad \frac{T_1}{T} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$$

Therefore, $$\frac{V_2}{V_3} = \frac{V_1}{V_4} \text{ or } \frac{V_4}{V_3} = \frac{V_1}{V_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

For (1), and (2)

$$W = RT_2 \ln V_2/V_1 + RT_1 \ln V_1/V_2$$

$$= RT_2 \ln V_2/V_1 - RT_1 \ln V_2/V_1$$

$$= R(T_2 - T_1) \ln V_2/V_1$$

The efficiency γ, of the engine is given by

$$\eta = \frac{W}{Q_2} = \frac{R(T_2 - T_1) \ln V_2/V_1}{RT_2 \ln V_2/V_1}$$

$$\eta = \frac{T_2 - T_1}{T_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The efficiency of a Carnot engine thus depends only on the temperature of the source and the sink, and not on any other factor example, say the nature of, or the amount of the working substance.

Since, $(T_2 - T_1) < T_2$ therefore the efficiency is always less than unity, i.e., an engine operating in cycles cannot convert heat completely into work. Only if $T_1 = 0$ K, then and then only $\eta = 1$ and consequently $W = Q_2$. So complete conversion of heat into work can be effected only if the sink can be placed at 0 K. The temperature of 0 K cannot be achieved and hence in practice we cannot have any heat engine of unit efficienc .

If Q_1 is the amount of heat given up by the engine to the sink then the amount of heat converted into work is $Q_2 - Q_1$ and hence,

$$\eta = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Carnot engine is a hypothetical one with all the stages of the cycle performed reversibly, and since reversible processes yield maximum work, therefore this engine has maximum efficienc . The engine being reversible can also be made to operate in the opposite direction example, in refrigeration.



Worked-out Example

10. A refrigeration engine operates between 0 and 25°C heat being withdrawn from the lower temperature and given up at higher temperature. What would be the work done in freezing 1 g of water the latent heat of fusion of water being 80 kcal/kg?

Calculate also the amount of heat given up to the surroundings.

Solution Here $T_2 = 0°C = 273$ K and $T_1 = 273 + 25 = 298$ K

$Q_2 = 80$ kcal/kg = 80 cal/g. Therefore,

$$W = Q_2\left(\frac{T_2 - T_1}{T_2}\right) = 80 \text{ cal} \times \frac{(273 - 298)\text{K}}{273\text{K}}$$

$= -7.324$ cal

$= -7.324 \times 4.2$ J $= -30.76$ J

Heat given up to the surroundings = Heat taken up by the engine – work done = $Q_2 - W$

$= 80 + 7.324$

$= 87.324$ cal

$= 366.7$ J

Carnot's theorem: This is a consequence of the second law of thermodynamics. It is usually stated in two parts: (a) Of all the cyclic heat engines operating between the same two temperatures (temperatures of source and sink), it is the reversible engine that has the maximum efficienc . (b) All cyclic reversible engines operating between the same two temperatures have the same efficienc .

Entropy Changes for an Ideal Gas

From Eq. (4.14.5), we get

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]dV$$

Now for one mole of an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \text{(Joule's law)}$$

and $$\frac{P}{T} = \frac{R}{V}$$

With these, the previous expression becomes

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{R}{V}\,dV$$

or $$dS = \frac{C_{V,m}}{T}dT + \frac{R}{V}dV$$

For a finite change, we hav

$$dS = \int_{T_1}^{T_2}\frac{C_{V,m}}{T}dT + \int_{V_1}^{V_2}\frac{R}{V}dV$$

Considering $C_{V,m}$ to be independent of temperature, we have

$$\Delta S = C_{V,m} \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

For the amount n of an ideal gas, the expression will be

$$\Delta S = n \left[C_{V,m} \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

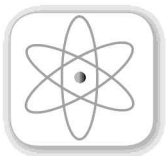
This is the expression when both the volume and temperature of an ideal gas are changed. For an isothermal change in volume, the entropy change is given by the reaction

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and for the change of temperature at constant volume, the expression is

$$\Delta S = n\, C_{V,m} \ln \frac{T_2}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

TEMPERATURE AND PRESSURE VARIATIONS



For an ideal gas, we have

$$\frac{V_2}{V_1} = \frac{p_1 T_2}{p_2 T_1}$$

Substituting this in Eq. (4.16.2), we get

$$\Delta S = n \left[C_{V,m} \ln \frac{T_2}{T_1} + R \ln \frac{p_1 T_2}{p_2 T_1} \right]$$

or $$\Delta S = n \left[(C_{V,m} + R) \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2} \right]$$

or $$\Delta S = n \left[C_{p,m} \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2} \right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

This is the expression for the change of entropy of an ideal gas when both its pressure and temperature are changed. However, if the temperature is varied at constant pressure, then

$$\Delta S = n\, C_{p,m} \ln \frac{T_2}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

and for the isothermal change in pressure, we have

$$\Delta S = nR \ln \frac{p_1}{p_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$



Worked-out Examples

11. For an ideal gas $C_{p,m} = (5/2)R$. Calculate the change in entropy suffered by 3 moles of the gas on being heated from 300 K to 600 K at (a) constant pressure, and (b) constant volume.

Solution (a) The change of entropy as a result of variation in temperature at constant pressure is given by

$$\Delta S_p = nC_{p,m} \ln \frac{T_2}{T_1}$$

Substituting the given values, we get

$$\Delta S_p = (3 \text{ mol}) \left(\frac{5}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right) \times 2.303 \log \left(\frac{600\text{K}}{300\text{K}}\right) = 43.22 \text{ J K}^{-1}$$

(b) The corresponding expression at constant volume is

$$\Delta S_V = nC_{v,m} \ln \frac{T_2}{T_1}$$

which on substituting the given values gives

$$\Delta S_V = (3 \text{ mol}) \left(\frac{3}{2} \times 8.314 \text{ JK}^{-1}\text{mol}^{-1}\right) \times 2.303 \log \left(\frac{600\text{K}}{300\text{K}}\right) = 25.93 \text{ J K}^{-1}$$

12. Calculate ΔS for 3 moles of diatomic ideal gas which is heated and compressed from 298 K and 101.135 kPa to 398 K and 506.625 kPa, Given: $C_{p,m} = (7.2)\ R$.

Solution The entropy change as a result of variation in both temperature and pressure is given by

$$\Delta S = n\left[C_{p,m} \ln + \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2}\right]$$

Substituting the given values, we get

$\Delta S = (3 \text{ mol})$

$$\left[\left(\frac{7}{2} \times 8.314 \text{JK}^{-1}\text{mol}^{-1}\right) \times 2.303 \log \left(\frac{398\text{K}}{298\text{K}}\right) + (8.314 \text{J K}^{-1}\text{mol}^{-1}) \times 2.303 \log \left(\frac{101.325\text{kPa}}{506.625\text{kPa}}\right)\right]$$

$= 3(8.422 \text{ J K}^{-1} - 13.383 \text{ J K}^{-1})$

$= -14.883 \text{ J K}^{-1}$

Standard State for Entropy of an Ideal Gas

The molar entropy change due to the isothermal change in pressure of an ideal gas is given by

$$\Delta S_m = R \ln \frac{p_1}{p_2} = -R \ln \frac{p_2}{p_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The above equation may be written as

$$S_{2,m} - S_{1,m} = -[R \ln p_2 - R \ln p_1] \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where $S_{2,m}$ and $S_{1,m}$ are the molar entropies of an ideal gas at pressures p_2 and p_1, respectively.

The standard molar entropy of an ideal gas at given temperature is defined as the entropy of one mole of the gas at pressure equal to 101.325 kPa (= 1 atm). It is represented s S°. Substituting $p_1 = 101.325$ kPa and replacing p_2 by the general term p in EQ. (4.17.1), we get

$$S_m - S^\circ_m = -R \ln (p/101.325 \text{ kPa}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Equation (4.17.2) gives molar entropy of an ideal gas at pressure p relative to that at 101.325 kPa pressure.

Entropy and Disorderliness

Equation (1) to (7) on page 5.36 describe the characteristics of entropy change for an ideal gas. These characteristics, in turn, reflect the basic nature of the entropy function. According to Eq. (4), we see that on increasing temperature of the gas at constant volume, there occurs an increase in the entropy of the system. The increase in temperature of the gas causes increase in the average kinetic energy of the molecules and thus the latter possess more energy and hence their motions become more random or disordered. Consequently, the increase in entropy of the system may be correlated with the increase in its disorderliness. The same conclusion will be drawn from other equations. For example, according to Eq. (3), the entropy of the gas increases on increasing the volume of the system at a constant temperature. This increase in volume allows the molecules to move in a large space and consequently their motions become more random or disordered. Hence, the entropymay be considered to represent the disorderliness of the system – larger the disorderliness, larger is the entropy of the system.

Take, for example, the three states of a substance, namely, the solid, liquid and gaseous states. In general, the molecules in the gaseous state are more disordered than those in the liquid state. Thus, the entropy of the substance in these three states of matter follows the order.

$$S \text{ (gaseous state)} > S(\text{liquid state}) > S(\text{solid state})$$

The following reactions

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(1)$$

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$$

will be attended to by the decrease of entropy since in converting reactants into products, the number of gaseous species decreases and thus the products are more ordered than the reactants. In the reaction

$$H_2(g) + Br_2(1) \rightarrow 2HBr(g)$$

Entropy of the system increases as products contain larger number of gaseous molecules than the reactants and are thus are more disordered than the latter.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Change in Total Entropy for Different Types of Expansions or Compressions of an ideal Gas. In this section, we derive expressions for the change in total entropy (system + surroundings) when an ideal gas undergoes the following types of expansion or compression processes.

Isothermal Changes

The change of entropy of one mole of an ideal gas is

$$\Delta S_{sys} = R \ln \frac{V_2}{V_1}$$

where V_2 is the final volume and V_1 is the initial volume.

Next we proceed to calculate the change in total entropy for the following categories.

(a) Reversible Change: If the expansion or compression is carried out reversibly, then

$$q_{rev} = -w = RT \ln \frac{V_2}{V_1}$$

and

$$\Delta S_{sys} = \frac{q_{rev}}{T} = R \ln \frac{V_2}{V_1}$$

If it be assumed that the heat q_{rev} is exchanged reversibly between the system and the surroundings at temperature T, it is obvious that

$$\Delta S_{surr} = -\frac{q_{rev}}{T}$$

Thus

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

(b) Irreversible Change: Two cases of expansion process may be considered:

(i) Free expansion: The gas expands into a vacuum. For this process, we have

$$w = 0$$

$$q = 0$$

Since entropy is a state function, the entropy change of a system in going from volume V_1 to V_2 by any path will be same as that of a reversible change; therefore,

$$\Delta S_{sys} = R \ln \frac{V_2}{V_1}$$

Since no heat is supplied by the surroundings the entropy change of the latter would be zero, i.e.,

$$\Delta S_{surr} = 0$$

Thus $$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = R \ln \frac{V_2}{V_1} + 0$$

$$= R \ln \frac{V_2}{V_1} = \text{positive} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

(ii) Intermediate expansion: Since ΔS_{sys} is the same as that of reversible change, therefore,

$$\Delta S_{sys} = R \ln \frac{V_2}{V_1} = \frac{q_{rev}}{T}$$

where q_{rev} is the amount of heat that the system would have absorbed had the process been carried out reversibly. In the present case, the expansion is done against a constant pressure, thus

$$q_{trr} = -w = p_{opp} (V_2 - V_1)$$

The change of entropy of the surroundings will be given by

$$\Delta S_{surr} = -\frac{q_{trr}}{T} = -\frac{p_{opp}(V_2 - V_1)}{T}$$

Since the magnitude of the amount of work involved in the intermediate expansion is smaller than that involved in reversible expansion, it is obvious that $q_{trr} < q_{rev}$. With this, ΔS_{total} becomes

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = \frac{q_{rev}}{T} - \frac{q_{trr}}{T} = \text{positive} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$



Worked-out Examples

13. 1 mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of ΔS_{gas} and ΔS_{total} under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly where 836.8 J of heat is less absorbed than in (i).

(iii) Expansion is free.

Solution The entropy change of the system ΔS_{sys} will be same in all the three processes as it is a state function. The expression of the change of entropy due to volume change at constant temperature is

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

Substituting the given values, we get

$$\Delta S_{sys} = (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303 \log \left(\frac{3}{1}\right) = 9.134 \text{ J K}^{-1}$$

The change of entropy of the surroundings ΔS_{surr} will, however, depend upon the process. We calculate below this change as well as the total change of entropy ($\Delta S_{sys} + \Delta S_{surr}$) for each of the three given processes.

(i) Reversible expansion:

$$\Delta S_{gas} = -\Delta S_{surr}$$

$$\Delta S_{total} = 0$$

(ii) Irreversible expansion: For the irreversible expansion, the quantity of heat absorbed by the system from surroundings would be

$$q_{irr} = q_{rev} - 836.8 \text{ J}$$

The quantity q_{irr} of heat will be supplied reversibly by the surroundings at 298 K and hence

$$\Delta S_{surr} = -\frac{q_{irr}}{298K} = -\left(\frac{q_{rev}}{298K} - \frac{836.8J}{298K}\right)$$

$$= -\left(\Delta S_{sys} - \frac{836.8J}{398K}\right)$$

and

$$S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= \Delta S_{sys} - \Delta S_{sys} + \left(\frac{836.8J}{298K}\right)$$

$$= 2.808 \text{ J K}^{-1}$$

(iii) Free expansion: For this expansion, the system does not absorb any heat, thus q = 0. Hence

$$\Delta S_{sur} = 0$$

and

$$\Delta S_{total} = \Delta S_{sys} = 9.134 \text{ J K}^{-1}$$

14. By how much does the entropy of 3 moles of an ideal gas change in going from a pressure of 202.65 kPa to a pressure of 101.325 kPa at 300 K, without any change in temperature? If the surroundings too are at 101.325 kPa pressure and 300 K, and the expansion is against the constant external pressure of the surroundings, show that the process of expansion is irreversible.

Solution Entropy change of the gas

$$\Delta S_{gas} = nR \ln \frac{p_1}{p_2}$$

$$= (3 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303 \log \left(\frac{200.65kPa}{101.325kPa}\right)$$

$$= 17.29 \text{ J K}^{-1}$$

Entropy change of the surroundings

Since $\Delta T = 0$, therefore, $\Delta U = 0$ and according to the first law of thermodynamics

$$q = -w = p_{opp}(\Delta V) = p_{opp}(V_2 - V_1)$$

$$= p_{opp}\left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right) = nRT\left(1 - \frac{p_{opp}}{p_1}\right) \qquad (\text{since } p_{opp} = p_2)$$

Substituting the values, we get

$$q = (3 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (T)\left(1 - \frac{101.325kPa}{202.65kPa}\right)$$

$$= (12.47 \text{ J K}^{-1})T$$

$$\Delta S_{surr} = -\frac{q}{T} = -12.47 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= (17.29 - 12.47) \text{ J K}^{-1}, \text{ which is positive.}$$

Since ΔS_{total} is positive, the process is irreversible.

Adiabatic Changes

Since in adiabatic processes

$$q = 0$$

therefore $\Delta S_{surr} = 0$

Since in an adiabatic process, both temperature and volume (or pressure) change, the expressions for the molar entropy change as given by Eq. (2) and (5) on page 5.36

$$\Delta S_{sys} = C_{V,m} \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$\Delta S_{sys} = C_{p,m} \ln \frac{T_2}{T_1} + R \ln \frac{p_1}{p_2}$$

Now, we proceed to evaluate the change in total entropy for the following categories,

(a) Reversible change: In this case

$$\Delta S_{sys} = 0$$

since for the adiabatic reversible process, we have

$$C_{V,m} \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and $C_{p,m} \ln \frac{T_2}{T_1} = -R \ln \frac{p_1}{p_2}$ $\ldots\ldots\ldots\ldots\ldots\ldots (2)$

Thus $\Delta S_{total} = \Delta sys + \Delta S_{surr}$

$$= 0 + 0 = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

In the present case of expansion (or compression), the increase (or decrease) in entropy due to the volume change just compensate the decrease (or increase) in entropy due to the fall (or rise) in temperature.

(b) Irreversible change: In this case,

$$\Delta S_{sys} = R \ln \frac{V_2}{V_1} + C_{V,m} \ln \frac{T_2'}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where T_2' is the temperature of the system in the final state. Making use of Eq. (1), we hav

$$\Delta S_{sys} = -C_{V,m} \ln \frac{T_2}{T_1} + C_{V,m} \ln \frac{T_2'}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where T_2 is the temperature, if the process was reversible.
Since we know that

Irreversible Adiabatic Expansion

Hence ΔS of the system is not zero and it can be shown that it is greater than zero. Suppose (P_A, V_A) and (P_B, V_B) correspond respectively to the initial (A) and final (B) states in an irreversible adiabatic expansion. ΔS of the system for the transition fro A to B can be calculated by assuming the path to be reversible. But starting from the same initial state (P_A, V_A), the same final state (P_B,V_B) cannot be attained by a reversible adiabatic process. However, the transition canbe effected by a reversible isothermal path followed by a reversible adiabatic path.

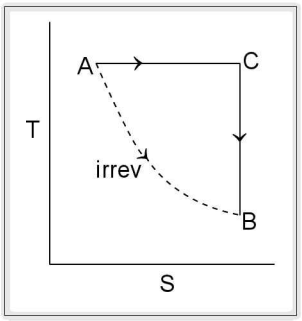


Fig. 5.11

Thus for the system, $\Delta S_{A\to B} = \Delta S_{A\to C} + \Delta S_{C\to B} = R.\ ln\ \frac{V_C}{V_A} + \text{zero} = R\ ln\ \frac{V_C}{V_A}$, since A→C represents a reversible isothermal path and C→B a reversible adiabatic path. Since $V_C > V_A$ for the expansion, ΔS of the system is positive for the transition, A→B. Since the surroundings have neither lost nor gained heat, ΔS of surroundings is zero.

$\therefore$ ΔS of isolated system is > 0.

Entropy change during phase change

Heat absorbed by the thermostat = 18(373–298) cal. Assuming the temperature of the thermostat to be constant (298 K), ΔS of thermostat = $\Sigma\frac{q}{T} = \frac{18\times 75}{298} = 4.53$ cal $K^{-1}mole^{-1}$. Thus the entropy of the system decreases, while that of the surroundings increases.

ΔS of the isolated system = –4.04 + 4.53 = 0.49 cal K^{-1} $mole^{-1}$

Entropy change during phase change

When a solid melts, $\Delta S = \frac{\Delta H_{fusion}}{\text{melting temp.}}$. It is called entropy of fusion. Similarly, ΔS of vaporization

$$= \frac{\Delta H_{vaporization}}{\text{temperature of vaporization}}$$

In general, ΔS of any phase transition = $\frac{\Delta H_{transition}}{\text{transition temperature}}$



Worked-out Example

15. Calculate molar entropy of vaporization of water at 100°C, assuming the latent heat of vaporization to be 540 cal gm^{-1}

Solution $\Delta S = \frac{\Delta H_{vap}}{T} = \frac{540\times 18}{373} = 26.1$ cal K^{-1} $mole^{-1}$

Trouton's rule

For several liquids,

$$\Delta S_{\text{vporisation}} = \frac{\Delta H_{\text{vaporisation}}}{\text{boiling point}} = 21 \text{ cal } K^{-1} \text{ mol}^{-1}$$

Exceptions to the rule are (1) associated liquids like H_2O and C_2H_5OH, which have high boiling points and (2) liquids like H_2 and He, which have low boiling points. In the former case, the Trouton value is much greater than 21, while in the latter it is much less. Hildebrand's rule is a modification of the above rule and it states that $\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = 27$, where T represents the temperature at which the vapour of a liquid has a fixed concentration, arbitrarily taken as 0,005 mole litr $^{-1}$.

Worked-out Example

16. 2 moles of a monatomic gas at 300 K and 10 atm undergoes adiabatic expansion against a pressure of 1 atm. Calculate the entropy change for the process. What would be the entropy change if the gas undergoes reversible adiabatic expansion to 1 atm? (Express the result in eu)

Solution (a) Irreversible adiabatic expansion: As already pointed out, ΔS of the system is calculated on the assumption that the transition from the initial state to the final state is reversible. But for an adiabatic change, starting from a given initial state, the final state attained by an irreversible path (adiabatic) cannot be obtained by a reversible path (also adiabatic). However, the same final state can be attained by a combination of two different reversible paths say reversible isobaric process followed by reversible isochoric process.

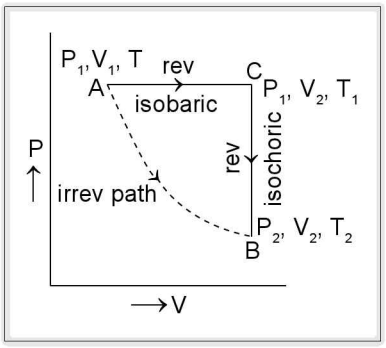


Fig. 5.12

A represents the initial state (P_1, V_1, T_1), and B, the final state (P_2,V_2,T_2).C represents the intermediate state (P_1,V_2, T_i).

For the transition A to C: (isobaric process)

$$\Delta S_{I} = n.C_p \ln \frac{T_i}{T_1}. \text{ But } \frac{T_i}{T_1} = \frac{P_1V_2 / nR}{P_1V_1 / nR} = \frac{V_2}{V_1} \text{ (gas assumed to be ideal)}$$

$$\therefore \quad \Delta S_{I} = n.C_p \ln \frac{V_2}{V_1}$$

Here $V_1 = \dfrac{2\text{mol} \times 0.0821\text{lit atm K}^{-1}\text{mol}^{-1} \times 300\text{K}}{10\text{atm}} = 4.926$ lit. V_2 in this case can be calculated from the irreversible adiabatic transition from A to B. As discussed earlier $C_v(T_1 - T_2) = P_{ext}(\Delta V)$ i.e., $n.C_v(T_1 - T_2) = P_2(V_2 - V_1)$. Here $T_1 = 300$ K; to eliminate T_2. we use the ideal gas equation .

$$\text{Thus } 2 \text{ mol} \times 2.981 \text{ cal K}^{-1} \text{ mol}^{-1} \left(300\text{K} - \frac{1\text{atm} \times V_2\text{lit}}{2\text{mol} \times 0.0821\text{lit atmK}^{-1}\text{mol}^{-1}} \right)$$

$$= 1 \text{ atm } (V_2 - 4.926) \text{ lit} \times 24.2 \text{ cal/lit atm}$$

$$5.962 \left(300 - \frac{V_2}{0.1642} \right) = (V_2 = 4.926)24.2$$

$$1788.6 - 36.31_{\ 2} = 24.2V_2 - 119.21$$

$$60.51\ V_2 = 1907.81;\ V_2 = 31.53 \text{ li}$$

$$\therefore \qquad \Delta S_{I} = nC_p \ln \frac{V_2}{V_1} = 2 \text{ mol} \times 4.968 \text{ cal K}^{-1} \text{ mol}^{-1} \times 2.303 \log \frac{31.53}{4.926}$$

$$= 2 \times 4.968 \times 2.303 \times 0.80623 \text{ cal K}^{-1} = 18.45 \text{ cal K}^{-1} \text{ or } 18.45 \text{ eu}$$

For the transition C to B (Isochoric process)

$$\Delta S_{II} = nC_v \ln \frac{T_2}{T_i} = nC_v \ln \left(\frac{P_2V_2 / nR}{P_1V_2 / nR} \right) = nC_v \ln \frac{P_2}{P_1}$$

$$= 2 \text{ mol} \times 2.981 \text{ cal K}^{-1} \text{ mol}^{-1} \times 2.303 \times \log \frac{1}{10} = (2 \times 2.981 \times 2.303 \ (-1) \text{ cal K}^{-1}$$

$$= -13.73 \text{ cal K}^{-1} \text{ or } -13.73 \text{ eu}$$

ΔS for the entire adiabatic process = $\Delta S_{I} + \Delta S_{II} = 18.45 - 13.73 = 4.72$ eu

Reversible adiabatic expansion

For this process, $\Delta S = 0$. A reversible adiabatic process is isentropic (already seen). This can also be verified through the reversible adiabatic relations.

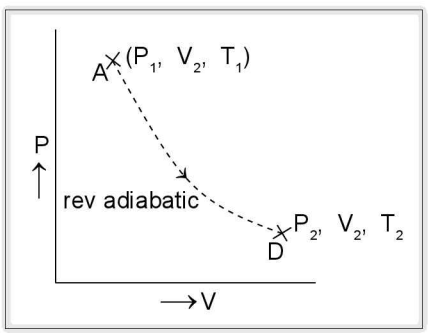


Fig. 5.13

In the present case, the initial state (P_1, V_1, T_1) is the same as in the previous case irreversible process). But the final states are different. The final pressure is the same (P_2) in the two cases, but the final temperatures are different and so too the final volumes. ΔS for the reversible process = $C_v \ln\frac{T_2'}{T_1} + R \ln\frac{V_2'}{V_1}$.

But for reversible adiabatic change, $T_1 V_1^{\gamma-1} = T_2' V_2'^{\gamma-1} \therefore \frac{T_2'}{T_1} = \left(\frac{V_1}{V_2'}\right)^{\gamma-1}$

$$\text{Thus } \Delta S = C_v \ln\left(\frac{V_1}{V_2'}\right)^{\gamma-1} + R\ln\left(\frac{V_2'}{V_1}\right) = C_v \ln\left(\frac{V_1}{V_2'}\right)^{\gamma-1} - R\ln\left(\frac{V_1}{V_2'}\right)$$

$$= \ln\frac{V_1}{V_2'}[C_v(\gamma-1) - R] = \ln\frac{V_1}{V_2'}\left[C_v\left(\frac{C_p}{C_v} - 1\right) - R\right]$$

$$= \ln\frac{V_1}{V_2'}[C_p - C_v - R] = 0, \text{ since for an ideal gas, } C_p - C_v = R.$$

Entropy Change with Two solids at Different Temperatures are Brought Together

Consider two solid bodies of the same material each containing one mole of a substance. Let one be at higher temperature T_h and the other at lower temperature T_c. Let both of them be brought together. Heat will flow from the hotter body to the colder till the temperatures of both of them are the same. Let the equilibrium temperature be T, the value of which can be calculated as follows:

Heat lost by hot body = Heat gained by cold body

$$C_{p,m}(T_h - T) = C_{p,m}(T - T_c)$$

or
$$T = \frac{T_h + T_c}{2}$$

Consequently, entropy changes of two bodies are

The total change of entropy is

$$\Delta S_{total} = \Delta S_h + \Delta S_c$$

$$= \int_{T_h}^{T} \frac{C_{p,m}}{T} dT + \int_{T_c}^{T} \frac{C_{p,m}}{T} dT$$

$$= C_{p,m}\left(\ln\frac{T}{T_h} + \ln\frac{T}{T_c}\right) = C_{p,m}\ln\left(\frac{T^2}{T_h T_c}\right)$$

$$= C_{p,m}\ln\left\{\frac{(T_h + T_c)^2}{4T_h T_c}\right\}$$

$$= C_{p,m}\ln\left(\frac{(T_h - T_c)^2}{4T_h T_c} + 1\right)$$

The quantity within brackets will always be greater than one. Hence, the logarithm of this quantity will always be greater than zero. Thus ΔS_{total} of this process is positive, indicating that it is an irreversible process.

Note that when $T_h = T_c$, ΔS_{total} is zero indicating the system is at equilibrium Thus, the essential condition for a system to be at thermal equilibrium is that the temperature of the system should be same throught.



Worked-out Example

17. A 50 g mass of Cu at a temperature of 393 K is placed in contact with a 100 g mass of copper at a temperature of 303 K in a thermally insulated container. Calculate q and ΔS_{total} for the reversible process. Use a value of 0.418 4 J g^{-1} K^{-1} for the specific heat capacity of Cu.

Solution We have 50 g copper at 393 K and 100 g copper at 303 K. The temperature of the two bodies when they have come to thermal equilibrium can be calculated as follows.

Heat gain = Heat loss

$$m_1C_p(\Delta T_1) = m_2C_p(\Delta T_2)$$

or $m_1(\Delta T_1) = m_2(\Delta T_2)$

Therefore

$$(100\text{ g})(T - 303\text{ K}) = (50\text{ g})(393\text{ K} - T)$$

$$2T - 606\text{ K} = 393\text{ K} - T$$

$$T = 333\text{ K}$$

Thus

$$\Delta Sh = nC_{p,m} \ln \frac{T}{T_h}$$

$$= \left(\frac{50\text{g}}{63\text{g mol}^{-1}}\right)(0.418\ 4\text{ J g}^{-1}\text{ K}^{-1})(63\text{ g mol}^{-1}) \times 2.303 \log \left(\frac{333\text{K}}{393\text{K}}\right)$$

$$= -3.466\text{ J K}^{-1}$$

$$\Delta S_c = nC_{p,m} \ln \frac{T}{T_c}$$

$$= \left(\frac{100\text{g}}{63\text{g mol}^{-1}}\right)(0.418\ 4\text{ J g}^{-1}\text{ K}^{-1})(63\text{ g mol}^{-1}) \times 2.303 \times \log \left(\frac{333\text{K}}{303\text{K}}\right)$$

$$= 3.951\text{ J K}^{-1}$$

and

$$\Delta S_{ttotal} = \Delta S_c + \Delta S_h = (3.951 - 3.466)\text{ J K}^{-1} = 0.485\text{ J K}^{-1}$$

Entropy and probability

The molecules of a macrosystem are distributed over a large number of microstats corresponding to a given property of the system. Statistically speaking, a system at equilibrium attains a constant value of a macroscopic property when the maximum number out of several microstates are very similar and are centred around a microscopic state known as predominant state. In classical thermodynamics, the system at equilibrium attains a maximum value of entropy function. Consequently, it is logical to think that a relation may exist between the maximum value of entropy (S) and the maximum number of microstates (W). This relation is expressed as

$$S \propto f(W)$$

The axact form of the function f can be derived on the basis thai entropy is an additive property whereas W is the multiplicative property, i.e.,

$$S_{AB} = S_A + S_B$$

$$W_{AB} = W_A W_B$$

Where AB is a system obtained by the union of the two distinct identical systems A and B. For S_{AB} and W_{AB}, Eq. becomes

$$S_{AB} \propto f(W_{AB})$$

or $$S_A + S_B \propto f(W_A W_B)$$

Obviously, Eq. is satisfied if the function is a logarithmic function.
Hence

$$S \propto \ln W$$

or $$S = k \ln W$$

To quote Planck, "The logarithmic connection between entropy and probability was first stated by L. Boltzmann in his kinetic theory of gases"where $k = 1.3806505(24) \times 10^{-23}$ J K^{-1} is Boltzmann's constant, and the logarithm is taken to the natural base *e*. *W* is the *Wahrscheinlichkeit*, the frequency of occurrence of a macrostate or, more precisely, the number of possible microstates corresponding to the macroscopic state of a system — number of (unobservable) "ways" in the (observable) thermodynamic state of a system can be realized by assigning different positions and momenta to the various molecules

The third law of thermydynamics can be explained on the basis of Eq. For a crystalline substance 0 K, there is only one way to distribute all the identical atoms or molecules over all the identical lattice sites and hence W = 1 and thus S = 0. Some substances such as carbon monoxide, nitric oxide, ice, etc., do not satisfy the third law of thermodynamics and thus have residual entropy. For such crystals, there is no perfect arrangement of molecules in the crystal lattice. For example, in carbon monoxide, the lattice sites are occupied either as CO or as OC.

Entropy and temperature

Let a solid at a constant pressure be heated from 0 K to some temperature T below its melting point, i.e.,

Solid (0 K, p) $\rightarrow$ Solid (T, p)

According to eq. (6) on page 5.36 the entropy change in the above process is given by

$$\Delta S = S_T - S_{0\,K}$$

$$= \int_{0K}^{T} \frac{C_p}{T} dT$$

or $$S_T = S_0 K + \int_{0K}^{T} \frac{C_p}{T} dT$$

Now since the entropy function increases with temperature, it may be expected that it has a minimum value at 0 K. In 1913, Max Planck suggested that this minium entropy may be assigned a zero value for a pure perfectly crystalline substance. This suggestion is known as the third law of thermodynamics. With this, Eq. reduces to

$$S_T = \int_{0K}^{T} \frac{C_p}{T} dT$$

Where S_T is called the third law entropy or simply the entropy at temperature T and pressure p. If the latter has a value of 101.325 kPa (=1 atm), then S_T becomes the standard entropy S_T^0.

The third law entropy for a liquid at temperature T can be determined following the steps given below.

(1) Heat the solid substance from 0 K to its melting point T_m.
(2) Transform the substance from solid to liquid at its melting point T_m.
(3) Heat the liquid from T_m to the required temperature T.

The addition of entropy changes in the above here processes gives the third law entropy of the liquid at temperature T. Thus

$$S_T = \int_{0K}^{T_m} \frac{C_{p,m}(s)}{T} dT + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T} \frac{C_{p,m}(l)}{T} dT$$

Similarly, for a gas above its boiling point, the third law entropy is given as

$$S_T = \int_{0K}^{T_m} \frac{C_{p,m}(s)}{T} dT + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_b} \frac{C_{p,m(l)}}{T} dT + \frac{\Delta H_{vap}}{T_b} + \int_{0K}^{T} \frac{C_{p,m}(g)}{T} dT$$

If the solid under study undergoes any transition from one crystalline form to another, the entropy of transition should also be added in the above entropy expressions.

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T}$$



Worked-out Example

18. 10 g of ice are heated to become vapour at 373 K and 101.35 kPa. Calculate ΔS for the system. Given that

ΔH_{fus} of ice at 273 K = 334.72 J g^{-1}

ΔH_{vap} of water at 373 K = 2 259.36 J g^{-1}

Average specific heat capacity of liquid water = 4.184 J $^{-1}$

The given transformation can be done following the reversible paths given below.

10 g water (s, 273 K, 101.325 kPa) → 10 g water (1, 273 K, 101.325 kPa)

10 g water (1, 273 K, 101.325 kPa) → 10 g water (1, 373 K, 101.325 kPa)

10 g water (1, 373 K, 101.325 kPa) → 10 g water (g, 373 K, 101.325 kPa)

The entropy changes per g of water in these processes are

$$\Delta S_1 = \frac{334.72 \text{ J g}^{-1}}{273 \text{ K}} = 1.226 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\Delta S_2 = \int_{273K}^{373K} \frac{C_p(l)}{T} dT = C_p(l) \ln\left(\frac{373 \text{ K}}{273 \text{ K}}\right) = 1.3058 \text{ J K}^{-1} \text{ g}^{-1}$$

$$\Delta S_3 = \frac{2259.35 \text{ J g}^{-1}}{373 \text{ K}} = 6.057 \text{ J g}^{-1} \text{ K}^{-1}$$

Thus

ΔS_{total}/g of water = $\Delta S_1 + \Delta S_2 + \Delta S_3$ = 8.588 8 J K^{-1}

ΔS for 10 g = 10 × 8.588 8 J K^{-1} = 85.888 J K^{-1}



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

A **spontaneous process** is the time-evolution of a system in which it releases free energy (most often as heat) and moves to a lower, more thermodynamically stable, energy state. The sign convention of changes in free energy follows the general convention for thermodynamic measurements, in which a release of free energy from the system corresponds to a negative change in free energy, but a positive change for the surroundings.

The gibbs energy (G)

The total entropy change that accompanies a process is

$$\Delta S_{Total} = \Delta S_{system} + \Delta_{Surr}$$

under constant temperature and pressure,

$$\Delta S_{surr} = -\frac{\Delta H_{system}}{T}$$

Hence, $\Delta S_{Total} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$

or, $T\,\Delta S_{Total} = T\,\Delta_{System} - \Delta H_{system}$

or $-T\,\Delta S_{Total} = TG$(change in Gibbs energy) $= \Delta H_{system} - T\,\Delta S_{system}$

For spontaneous process, $\Delta S_{Total} > 0 \quad \Rightarrow \Delta G_{T,P} < 0$

For non spontaneous process $\Delta G_{T,P} > 0$ (or $\Delta S_{Total} < 0$)

At equilibrium $\Delta G_{T,P} = 0$

This Gibb's energy 'G' is a state function and extensive property and it's given as

$$G = H - TS$$

$\Rightarrow \quad \Delta G_{T,P} = \Delta H - T\,\Delta S$ and $\Delta G = w'$ (maximum)

where w' represents maximum non expansion work.

The standard reaction Gibb's energy $\Delta G°$, is the difference in standard molar Gibb's energies of products and reactants

$$\Delta G° = \sum_{product\,tan\,ts} nG_m^\circ - \sum_{reac\,tan\,t} nG_m^\circ$$

and $\Delta G° = -RT \ln K$

where K is the equilibrium constant.

Relation between ΔG and ΔG°

$\Delta G°$ is the standard Gibb's energy change (when the pure reactants change into products, with each species in its standard state.)

ΔG is the change in Gibb's energy when reaction occurs under the condition of constant composition

$$\Delta G = \Delta G° + RT \ln Q$$

where Q is the reaction quotient.

At equilibrium $\Delta G = 0$ and $Q = K_{eq}$

So, $\Delta G° = -RT \ln K_{eq}$

Thermodynamic Criterion of equilibrium under different conditions

$$\Delta E = q - w = q - \Delta V$$

We know, or $dE = dq - p\,dv$

Again, $\frac{dq_{rev}}{T} = dS$, Therefore

$$dE = TdS - P\,dv$$

$\Rightarrow \quad dE_{S,V} = 0$ .... (1)

we know,

$$H = E + PV$$

$$dH = dE + PdV + VdP$$

$$= (TdS - PdV) + PdV + VdP$$

$$= TdS + VdP \Rightarrow dH_{S,P} = 0 \quad \ldots\ldots (2)$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= TdS + VdP - TdS - SdT$$

$$= VdP - SdT \Rightarrow dG_{T,P} = 0 \quad \ldots\ldots (3)$$

All these equations represent the condition of equilibrium under different condition. Equation (3) finds maximum use as most of the processes occur under constant temperature and pressure.

A spontaneous process is capable of proceeding in a given direction, as written or described, without needing to be driven by an outside source of energy. The term is used to refer to macro processes in which entropy increases; such as a smell diffusing in a room, ice melting in lukewarm water, salt dissolving in water, and iron rusting.

The laws of thermodynamics govern the direction of a spontaneous process, ensuring that if a sufficiently large number of individual interactions (like atoms colliding) are involved then the direction will always be in the direction of increased entropy (since entropy increase is a statistical phenomenon).

For a reaction at constant temperature and pressure, the change ΔG in the Gibbs free energy is:

$$\Delta G = \Delta H - T\Delta S$$

The sign of ΔG depends on the signs of the changes in enthalpy (ΔH) and entropy (ΔS), as well as on the absolute temperature (T, in kelvins). Notice that changes in the sign of ΔG cannot occur solely as a result of changes in temperature alone, because the absolute temperature can never be less than zero.

When ΔG is negative, a process or chemical reaction proceeds spontaneously in the forward direction.

When ΔG is positive, the process proceeds spontaneously in reverse.

When ΔG is zero, the process is already in equilibrium, with no net change taking place over time.

We can further distinguish four cases within the above rule just by examining the signs of the two terms on the right side of the equation.

*When ΔS is positive and ΔH is negative, a process is spontaneous

*When ΔS is positive and ΔH is positive, a process is spontaneous at high temperatures, where exothermicity plays a small role in the balance.

*When ΔS is negative and ΔH is negative, a process is spontaneous at low temperatures, where exothermicity *is* important.

*When ΔS is negative and ΔH is positive, a process is not spontaneous at any temperature, but the reverse process is spontaneous.

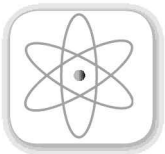
The second law of thermodynamics states that for any spontaneous process the overall change ΔS in the entropy of the system must be greater than or equal to zero, yet a spontaneous chemical reaction can result in a negative change in entropy. This does not contradict the second law, however, since such a reaction must have a sufficiently large negative change in enthalpy (heat energy) that the increase in temperature of the reaction surroundings (considered to be part of the system in thermodynamic terms) results in a sufficiently large increase in entropy that overall the change in entropy is positive. That is, the ΔS of the *surroundings* increases enough because of the exothermicity of the reaction that it overcompensates for the negative ΔS of the system, and since the overall $\Delta S = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}}$, the overall change in entropy is still positive.

Another way to view the fact that some spontaneous chemical reactions can lead to products with lower entropy is to realize that the second law states that entropy of a **closed** system must increase (or remain constant). Since a positive enthalpy means that energy is being released to the surroundings, then the 'closed' system includes the chemical reaction plus its surroundings. This means that the heat release of the chemical reaction sufficiently increases the entropy of the surroundings such that the overall entropy of the closed system increases in accordance with the second law of thermodynamics.

Just because a chemist calls a reaction "spontaneous" does not mean the reaction happens with great speed. For example, the decay of diamonds into graphite is a spontaneous process, but this decay is ex-

tremely slow and takes millions of years. The *rate* of a reaction is independent of its spontaneity, and instead depends on the chemical kinetics of the reaction. Every reactant in a spontaneous process has a tendency to form the corresponding product. This tendency is related to stability. Stability is gained by a substance if it is in a minimum energy state or is in maximum randomness. Only one of these can be applied at a time. Example, Water converting to ice is a spontaneous process because ice is more stable since it is of lower energy. However, the formation of water is also a spontaneous process as water is the more random state.

WHAT IS THE THIRD LAW OF THERMODYNAMICS?



The Third Law of Thermodynamics is the lesser known of the three major thermodynamic laws. Together, these laws help form the foundations of modern science. The laws of thermodynamics are absolute physical laws-everything in the observable universe is subject to them. Like time or gravity, nothing in the universe is exempt from these laws. In its simplest form, the Third Law of Thermodynamics relates the entropy (randomness) of matter to its absolute temperature.

The Third Law of Thermodynamics refers to a state known as "absolute zero." This is the bottom point on the Kelvin temperature scale. The Kelvin scale is absolute, meaning 0° Kelvin is mathematically the lowest possible temperature in the universe. This corresponds to about –273.15° Celsius, or –459.7 Fahrenheit.

In actuality, no object or system can have a temperature of zero Kelvin, because of the Second Law of Thermodynamics. The Second Law, in part, implies that heat can never spontaneously move from a colder body to a hotter body. So, as a system approaches absolute zero, it will eventually have to draw energy from whatever systems are nearby. If it draws energy, it can never obtain absolute zero. So, this state is not physically possible, but is a mathematical limit of the universe.

In its shortest form, the Third Law of Thermodynamics says: **"If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances."** Entropy is a property of matter and energy discussed by the Second Law of Thermodynamics. The Third Law of Thermodynamics means that as the temperature of a system approaches absolute zero, its entropy approaches a constant (for pure perfect crystals, this constant is zero). A pure perfect crystal is one in which every molecule is identical, and the molecular alignment is perfectly even throughout the substance. For non-pure crystals, or those with less-than perfect alignment, there will be some energy associated with the imperfections, so the entropy cannot become zero.

The Third Law of Thermodynamics can be visualized by thinking about water. Water in gas form has molecules that can move around very freely. Water vapour has very high entropy (randomness). As the gas cools, it becomes liquid. The liquid water molecules can still move around, but not as freely. They have lost some entropy. When the water cools further, it becomes solid ice. The solid water molecules can no longer move freely, but can only vibrate within the ice crystals. The entropy is now very low. As the water is cooled more, closer and closer to absolute zero, the vibration of the molecules diminishes. If the solid water reached absolute zero, all molecular motion would stop completely. At this point, the water would have no entropy (randomness) at all.

Most of the direct use of the Third Law of Thermodynamics occurs in ultra-low temperature chemistry and physics. The applications of this law have been used to predict the response of various materials to temperature changes. These relationships have become core to many science disciplines, even though the Third Law of Thermodynamics is not used directly nearly as much as the other two.

Study of the Third Law of Thermodynamics mainly supports the implications of the first two laws. However, some questions do arise. The Third Law of Thermodynamics demonstrates another detectable, absolute, all-encompassing, important natural law. The Laws of Thermodynamics demonstrate very ordered rules of energy interactions, which the entire universe must obey. Why is the Third Law of Thermodynamics true? Why are there no exceptions in the entire universe? This law cannot be an accident, since none of the thermodynamic laws are random. Organization implies an Organizer. Design implies a Designer. If the laws are not random, then who created them?

ONE CORRECT OPTION TYPE QUESTIONS

1. Ionization energy of Al = 5137 kJ mole^{-1} (ΔH) hydration of Al^{3+} = – 4665 kJ mole^{-1}. $(\Delta H)_{hydration}$ for Cl^- = – 381 kJ mole^{-1}. Which of the following statement is correct

(a) $AlCl_3$ would remain covalent in aqueous solution
(b) Only at infinite dilution $AlCl_3$ undergoes ionisation
(c) In aqueous solution $AlCl_3$ becomes ionic
(d) None of these

2. What is value of ΔE (heat change at constant volume) for reversible isothermal evaporation of 90g water at 100°C? Assuming water vapour behaves as an ideal gas and $(\Delta H_{vap})_{water}$ = 540 cals g^{-1}

(a) 9×10^3 cals (b) 6×10^3 cals
(c) 4.49 cals (d) none of these

3. Which of the statement is correct?

(a) Slope of adiabatic P – V curve will be same as that of isothermal one.
(b) Slope of adiabatic P – V curve is smaller than that in isothermal one.
(c) Slope of adiabatic P – V curve is larger than that in isothermal one.
(d) Slope of adiabatic P – V curve may be smaller or larger depending on the value V.

4. The specific heats of iodine vapour and solid are 0.031 and 0.055 cals/g respectively. If heat of sublimation iodine is 24 cals/g at 200°C, its value at 250°C is

(a) 5.7 cals gm^{-1} (b) 11.4 cal g^{-1}
(c) 22.8 cal g^{-1} (d) 45,6 cal g^{-1}

5. The enthalpies of neutralization of $HClO_4$ and Cl_3C – COOH are

– 13.5 kcal/g – equivalent and
– 13.5 kcal/g – equivalent respectively

when 40 g of solid NaOH is added to a mix of 1 g mol. $HclO_4$ and 1 g mol. Cl_3C – COOH, sodium perchlorate and sodium trichloroacetate are formed in molar ratio of 3:1. Then

(a) ΔH for the reaction of NaOH with the mix. Is 6.45 kcal.
(b) ΔH for the reaction of NaOH with the mix. Is 13.8 kcal.
(c) After reaction the total number of moles of acid remained are 0.5 ($HClO_4$ and Cl_3C – COOH)
(d) After reaction the total wt. of acid remained is 147.75 gm. ($HClO_4$ + Cl_3Cl – COOH) and ΔH for the reaction of NaOH with mix. is –13.8 kcal.

6. At 298 k in a constant volume calorimeter, 0.01 mole of TNT was detonated when 8180 cals of heat was released. Each mole of TNT gives 6 moles of gaseous products on detonation. What is ΔH/mole of TNT exploded?

(a) –714 kcals mole^{-1}
(b) –814 kcals mole^{-1}
(c) –914 kcals mole^{-1}
(d) none of these

7. A person requires 2870 kcal of energy to lead normal daily life. If heat of combustion of cane sugar is – 1349 kcal, then his daily consumption of sugar is

(a) 728 g (b) 0.728 g
(c) 342g (d) 0.342 g

8. Isothermally at 27°C, 1 mole of Van der Waals' gas expands reversibly from 2 lits to 20 lits. The work done if a = 1.42×10^{12} dynes cm^4/mole and b = 30 cc/mole

(a) 5.677×10^3kJ (b) 2.3×10^3 kJ
(c) 9.2×10^3 kJ (d) 7.689×10^3kJ

9. At 298°K in a constant volume calorimeter, 0.01 mole of TNT detonates when 8180 cals of heat was released. Each mole of TNT gives 6 moles of gaseous proudcts on detonation. What is ΔH/moles of TNT exploder?

(a) – 714 kcals/mole
(b) – 814 kcals/mole
(c) – 914 kcals/mole
(d) none of these

10. What is the amount of heat to be supplied to prepare 128 g of CaC_2 by using $CaCO_3$ and followed by reduction with carbon? Reactions are

$CaCO_3(s) = CaO(s) + CO_2(g)$ ΔH^0 = 42.8 kcals

$CaO(s) + 3C(s) = CaC_2 + CO(g)$ ΔH^0= 111 kcals

(a) 102.6 kcals (b) 221.78 kcals
(c) 307.6 kcals (d) 453.46 kcals

11. Ionization energy of Al = 5137 kJ mole^{-1} (ΔH) hydration of Al^{3+} = – 4665 kJ mole^{-1}. $(\Delta H)_{hydration}$ for Cl^- = – 381 kJ mole^{-1}. Which of the following statement is correct?

(a) $AlCl_3$ would remain covalent in aqueous solution
(b) Only at infinite dilution $AlCl_3$ undergoes ionisation
(c) In aqueous solution $AlCl_3$ becomes ionic
(d) None of these

12. At 0°C, ice and water are in equilibrium and ΔS and ΔG for the conversion of ice to liquid water is
(a) 0, 21.98 JK^{-1} $mole^{-1}$
(b) –ve, zero
(c) +ve, 21.98 JK^{-1} $mole^{-1}$
(d) Zero, zero

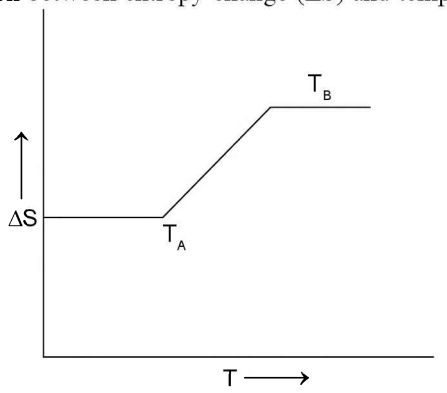
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– 13.5 kcal/g – equivalent and
– 13.5 kcal/g – equivalent respectively
when 40 g of solid NaOH is added to a mix of 1 g mol. $HClO_4$ and 1 g mol. Cl_3C – COOH, sodium perchlorate and sodium trichloroacetate are formed in molar ratio of 3:1. Then.
(a) ΔH for the reaction of NaOH with the mix. Is 6.45 kcal.
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(c) After reaction the total number of moles of acid remained are 0.5 ($HClO_4$ and Cl_3C – COOH)
(d) After reaction the total wt. of acid remained is 147.75 gm. ($HClO_4$ + Cl_3Cl – COOH) and ΔH for the reaction of NaOH with mix. is –13.8 kcal.

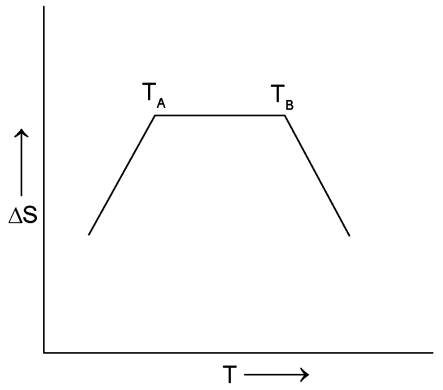
14. The standard heats of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are –76.2, –394.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning $1m^3$ methane measured under normal conditions.
(a) 162897.3 kJ (b) 64078.2 kJ
(c) 35182k! (d) None.

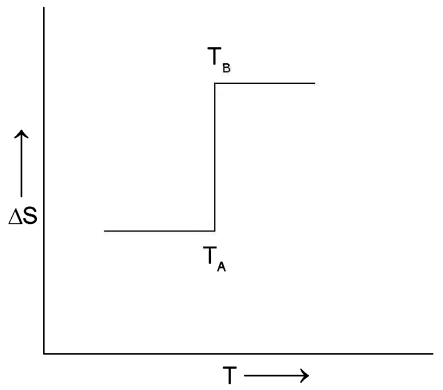
15. Calculate the resonance energy of N_2O from the following data ; ΔH_f of N_2O = 82 kJ mol^{-1}. Bond energies of Ms N, N ≡ N, O = O and N = O bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively.
(a) –88 kJ mol-1 (b) –170 kJ mol^{-1}
(c) –82 kJ mol-1 (d) –258 kJ mol^{-1}

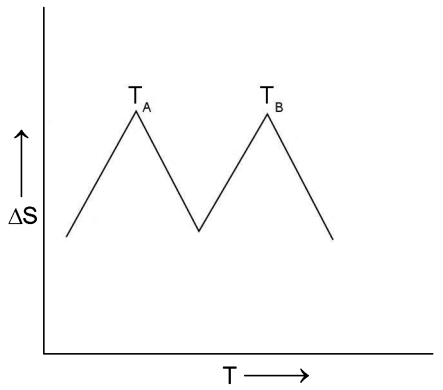
16. Molar heat capacity of water in equilibrium with ice at constant pressure is
(a) zero
(b) infinity (∞)
(c) 40.45 J K^{-1} mol^{-1}
(d) 75.48 J K^{-1} mol^{-1}

17. If for a given substance, T_B is the m.pt. and T_A is the freezing point, then correct variation of entropy by graph between entropy change (ΔS) and temp. is

(a)


(b)


(c)


(d)


18. A cylinder of gas contains 11.6 kg of butane, if a normal family needs 2.0×10^4 kJ of energy per day for cooking, how long will the cylinder last ($\Delta H_{\text{combustion of butane}} = -2600$kJ/mol).
(a) 52 days (b) 26 days
(c) 116 days (d) none

19. Calculate the mass of mercury which can be liberated from HgO at 25°C by the treatment of excess HgO with 10 kcal of heat. Standard enthalpy of formation of HgO is 21.7 kcal/mole.
(a) 92.4 g (b) 9.24 g
(c) 924 g (d) 200 g

20. A person inhales 650 g of oxygen per day. If all the oxygen is used for converting sugar into CO_2 and H_2O, how much heat is evolved in one day?
$\Delta H_{\text{combustion of sucrose}} = -5645$ kJ/mol.
(a) 9408 kJ (b) 570 kJ
(c) 5645 kJ (d) None

21. The combustion of 2.650 g of indium raised the temperature of a calorimeter 1.055 C. The energy equivalent of the calorimeter was 2412.81 cal/°C. Calculate the molar enthalpy combustion of indium (Molar mass of indium 114.8)
(a) 2412.81 cal/mole
(b) 119683.8 cal/mole
(c) 110,273.6 cal/mole
(d) None

22. When 0.2 g of butanol was burnt in a suitable apparatus, the heat evolved was sufficient to raise the temperature of 200 g of water by 5K. The heat of combustion of butanol in k cal/mole will be
(a) 0.37 (c) 37
(b) 307 (d) 370

23. When a certain amount of ethylene was combusted 6226 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ. The volume of O_2 (at NTP) that entered into the reaction is
(a) 296.5 ml (b) 296.5 L
(c) 6226 × 22.4 L (d) 22.4 L.

24. Calculate die endialpy of vaporization of SO_2 at –25 C. If die same at its b. pt. (–10° C) be 5950 cal/mol. Given the molar heat capacity, $C_{p(l)} = 20.6$ cal/mol and $C_{p(g)} = 9.3$ cal/mol
(a) 6119.5 cal/mol (b) 5780.5 cal/mol
(c) 5950 cal/mol (d) None

25. 2.1 g of Fe combines with S evolving 3.77 kJ. The heat of formation of FeS in Id/mol is
(a) –3.77 (b) –1.79
(c) –100.5 (d) None

26. Carnot's cycle operates between T and 300 K (T > 300K). It is 25% efficient when temperature of die source (T) is
(a) 350 K (b) 400 K
(c) 450 K (d) 375 K

27. The specific heats of iodine vapour and solid are 0-031 and 0.055 cal/g respectively. If heat of sublimation of iodine is 24 cal/g at 200° C, then what is its value at 250° C?
(a) 0.024 cal/g (b) 22.8 cal/g
(c) 25.2 cal/g (d) None

28. The heat capacity of air at room temperature and 1 atm. is 210 JK^{-1} mol^{-1}. How much heat is required to heat a room through 1° C at room temperature? (Assuming air present in the room = 290 kg)
(a) 210 kJ (b) 2100 kJ
(c) 214 kJ (d) 420 kJ

29. P-V diagram of a cyclic process ABCA is as shown in figure. Choose the wrong statement.
(a) QA $\longrightarrow$ B = (–) ve
(b) $\Delta U_B \longrightarrow$ C = (+) ve
(c) $\Delta U_C \longrightarrow$ A = (–) ve
(d) W_{CAB} = (–) ve

30. Two moles of an ideal monoatomic gases are allowed to expand adiabatically and reversibly from 300 K and 200 K. The work done in the system is ($C_V = 12.5$ J/K/mole).
(a) –12.5 kJ (b) –2.5 kJ
(c) –625 kJ (d) 500 kJ

31. An athlete is given 100 g of glucose of energy equivalent to 1560 kJ. He utilizes 50% of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. Enthalpy of H_2O for evaporation is 44 kJ mol^{-1}.
(a) 346 g (b) 316 g
(c) 323 g (d) 319 g

32. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (ionisation energy of Al = 5137 kJ mol^{-1}, $\Delta H_{\text{hydration}}$ for Al^{+3} = –4665 kJ mol^{-1}, $AH_{\text{hydration}}$ for C^- = –381 kJ mol^{-1})
(a) Ionic (b) Covalent
(c) Both (d) None

33. The enthalpy change involved in the oxidation of glucose is –2880 kJ mol^{-1}. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk eating 120 g of glucose?

(a) 7.9 km (b) 9.7 km

(c) 4.8 km (d) 8.4 km

34. The temperature coefficie t of e.m.f. of a cell can be given by:

(a) $\left(\frac{\delta E}{\delta T}\right)_P = \frac{\Delta S}{nF}$

(b) $\left(\frac{\delta E}{\delta T}\right)_P = \left(\frac{E_2 - E_1}{T_2 - T_1}\right)_P$

(c) $\left(\frac{\delta E}{\delta T}\right)_P = \left[\frac{\Delta H}{nF} + E\right].\frac{1}{T}$

(d) All of these

35. Molar heat capacity at constant P for a substance is equal to:

(a) $(\delta E/\delta T)_v$ (b) $(\delta H/\delta T)_v$

(c) $(\delta E/\delta T)_P$ (d) $(\delta H/\delta T)_p$

36 For the adiabatic expansion of an ideal gas:

(a) PV^{γ} = constant (b) $TV^{\gamma-1}$ = constant

(c) $T^{\gamma}P^{1-\gamma}$ = constant (d) All of these

37. Internal energy and pressure of a gas of unit volume are related as:

(a) $P = \frac{2}{3}E$ (b) $P = \frac{3}{2}E$

(c) $P = \frac{E}{2}$ (d) $P = 2E$

38. Which statement(s) is/are correct?

(a) $\left(\frac{\delta H}{\delta T}\right)_p - \left(\frac{\delta E}{\delta T}\right)_v = R$

(b) $\left(\frac{\delta H}{\delta T}\right)_p > \left(\frac{\delta E}{\delta T}\right)_v$

(c) $\left(\frac{\delta E}{\delta V}\right)_T$ for ideal gas is zero

(d) All of the above

39. Which statements are correct?

(a) $2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_{vap.}}{R}\frac{[T_2 - T_1]}{T_1 T_2}$ is Clausius-Clapeyron equation

(b) $\frac{\Delta H_{vap.}}{\text{Boiling point}}$ = 88 J mol^{-1} K^{-1} is called Trouton's rule

(c) Entropy is a measure of unavailable energy, i.e., unavailable energy = entropy x temperature

(d) All of the above

40. The molar heat capacity of oxygen gas is given by the expression $C_v = a + bT + cT^2$ where a, b and c are constants. What will be change in internal energy of 8 g of oxygen if it is heated from 200 K to 300 K at constant volume? Assume oxygen as an ideal gas. Given a = 1.2 JK^{-1} mol^{-1}, b = 12.8 × 10^{-2} JK^{-2} mol^{-1}, b = 12.8 × 10^{-2} JK^{-2} mol^{-1}, c = 3.3 × 10^{-7} JK^{-3} mol^{-1}.

(a) 1000 J

(b) 950.15 J

(c) 830.5 J

(d) 315.5 J

41. A balloon filled with helium gas having pressure 2 atm was kept at room temperature at 27°C. What will be resulting temperature if it bursts?

(a) –60°C

(b) –45.65°C

(c) –30.15°C

(d) –10.5°C

ANSWER KEYS

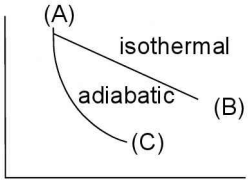
1. (c)	**2.** (d)	**3.** (c)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (a)	**8.** (a)	**9.** (b)	**10.** (c)
11. (c)	**12.** (a)	**13.** (d)	**14.** (c)	**15.** (a)	**16.** (b)	**17.** (a)	**18.** (b)	**19.** (a)	**20.** (a)
21. (c)	**22.** (d)	**23.** (b)	**24.** (a)	**25.** (c)	**26.** (b)	**27.** (b)	**28.** (a)	**29.** (c)	**30.** (b)
31. (a)	**32.** (c)	**33.** (c)	**34.** (b)	**35.** (d)	**36.** (d)	**37.** (a)	**38.** (d)	**39.** (d)	**40.** (c)
41. (b)									

[redacted]TS AND EXPLANATIONS

1. (c) If $AlCl_3$ is present in ionic state in aqueous solution, therefore it has Al^{3+} and $3Cl^-$ ions
Standard heat of hydration of Al^{3+} and $3Cl^-$ ions
$= -4665 + 3 \times (-381)$ kJ mole^{-1}
$= -5808$ kJ/mole
Required energy of ionization of Al = 5137 kJ mole^{-1}
$\therefore$ Hydration energy overcomes ionization energy
$\therefore$ $AlCl_3$ would be ionic in aqueous solution

2. (d) Heat of system $(\Delta H)_v = m \times Lv$
$= 90 \times 540 = 486000$ cal
$\Delta H = \Delta E + P(V_V - V_L) = \Delta E + nRT$
or, $48600 = \Delta E + \frac{90}{18} \times 2 \times 373$
or, $\Delta E = 48600 - 3730 = 44870$ cals

3. (c)



Slope of PV curve, for isothermal process
$\frac{dP}{dV} = -\frac{P}{V}$
Slope of PV curve for adiabatic process
$\frac{dP}{dV} = -\gamma\frac{P}{V}$

As $\gamma > 1$ $\left(\frac{dP}{dV}\right)_{adiabatic} > \left(\frac{dp}{dv}\right)_{isothermal}$

4. (c) Solid I_2 is converted in I_2 vapour
$I_2(s) = I_2(g)$ $\Delta H = 24$ cal/g at 200°C
$\Delta C_p = (CP)_2(g) = (Cp)I_2(s)$
$= 0.031 - 0.055 = -0.24$ cal g^{-1}
From Kirchoff's equation
$\Delta H_{250^\circ C} - \Delta H_{200^\circ C} = \Delta C_p (T_{250^\circ C} - T_{200^\circ C})$
$\Delta H_{250^\circ C} = 24 - 0.024\,(523 - 473)$
$= 24 - 1.2 = 22.8$ cals g^{-1}

5. (d) $HClO_4 + NaOH \longrightarrow NaClO_4 + H_2O$
$Cl_3C - COOH + NaOH \longrightarrow Cl_3C - COONa + H_2O$
Let x mol of NaOH are used in 1st reaction and (1 – x) mol of NaOH are used in 2nd reaction.
Given $\frac{x}{1-x} = 3 \Rightarrow x = \frac{3}{4}$
$\Delta H = -13.5 \times \frac{3}{4} + (-14.7) \times \frac{1}{4}$
$= \frac{-40.5 + 14.7}{4} = -13.8$ kcal
Weak acids $= \frac{1}{4}(1 + 35.5 + 64) + 3$
$\frac{3}{4}(35.5 \times 3 + 24 + 32 + 1)$
$= 147.75$ gm

10. (c) $CaCO_3(s) = CaO(s) + CO_2(g)$ $\Delta H^0 = 42.8$ kcals
$CaO(s) + 3C(s) = CaC_2(s) + CO(g)$ $\Delta H^0 = 111$ kcals

$CaCO_3(s) + 3C(s) = CaC_2(s) + CO(g) + CO_2(g)$
$\Delta H = 153.8$ kcals
Thus heat required to prepare 1 mole of CaC_2 from $CaCO_3$ = 153.8 kcals
Molecular weight of CaC_2 $= 40 + 24 = 64$
64 g of CaC_2 requires 153.8 kcals of heat
128 g of CaC_2 requires 307.6 kcals of heat

11. (c) If $AlCl_3$ is present in ionic state in aqueous solution, therefore it has Al^{3+} and $3Cl^-$ ions
Standard heat of hydration of Al^{3+} and $3Cl^-$ ions
$= -4665 + 3 \times (-381)$ kJ mole^{-1}
$= -5808$ kJ/mole
Required energy of ionization of Al = 5137 kJ mole^{-1}
$\therefore$ Hydration energy overcomes ionization energy
$\therefore$ $AlCl_3$ would be ionic in aqueous solution

12. (a) Since the given process is in equilibrium i.e.,
$\Delta G = 0$
$\Delta G = \Delta H - T\Delta S$

or, $O = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$ or, $\Delta S = \frac{\Delta H}{T}$

$= \frac{6}{273} \times 10^3 \text{ JK}^{-1} \text{ mole}^{-1}$

$= 21.98 \text{ JK}^{-1}\text{mole}^{-1}$

13. (d) $HclO_4 + NaOH \longrightarrow NaClO_4 + H_2O$

$Cl_3C - COOH + NaOH \longrightarrow Cl_3C - COONa + H_2O$

Let x mol of NaOH are used in 1st reaction and (1 – x) mol of NaOH are used in 2nd reaction.

Given $\frac{x}{1-x} = 3 \Rightarrow x = \frac{3}{4}$

$\Delta H = -13.5 \times \frac{3}{4} + (-14.7) \times \frac{1}{4}$

$= \frac{-40.5 + 14.7}{4} = -13.8 \text{ kcal}$

Weak acids $= \frac{3}{4}(1 + 35.5 + 64) + 3$

$\frac{3}{4}(35.5 \times 3 + 24 + 32 + 1)$

$= 147.75 \text{ gm}$

14. (c) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ $\Delta H = \Sigma\Delta H_f^\circ$ (products) – $\Sigma \Delta H_f^\circ$ (reactants)

$= [\Delta H_f(CO_2) + 2\Delta H_f(H_2O)] - [\Delta H_f(CH_4) + 2\Delta H_f(CO_2)]$

$= [-394.8 + 2 \times -241.6] - [-76.2 + 0]$

$= -878.0 + 76.2 = 802.2 \text{ kJ mol}^{-1}$

Now 22.4 L (or 22.4×10^{-3} m^3) of CH_4 on combustion give heat = 802.2 kJ mol^{-1}

$\therefore$ $1 \text{ m}^3 = \frac{802.2}{22.4 \times 10^{-3}} = 35812 \text{ kJ mol}^{-1}$

15. (a) $N \equiv N + 1/2\ O = O \longrightarrow N = N = O$

$\Delta N_f^\circ = \Sigma$BE of reactants – ΣBE of products

$= [BE(N \equiv N) + \frac{1}{2} BE (O = O) - [BE(N = N) + BE (N = O)]$

$= \left(946 + \frac{1}{2} \times 498\right) - (418 + 607) = 170 \text{ kJ}$

Resonance energy $= \Delta H_f^\circ$ (observed) – ΔH_f° (cal.) = 82 – 170 = –88 kJ mol^{-1}

16. (b) Infinit

17. (a) For dissolution of gases in water ΔS = –ve (Non favourbale factor). Since this process is spontaneous i.e., ΔG = –ve so ΔU has to be –ve (favourable factor) and proces is exothermic.

18. (b) $\because$ 2600 kJ energy is liberated by 58 g butane

$\therefore$ 20,000 kJ energy is liberated by $\frac{58 \times 20000}{2600}$

$= 446.15 \text{ g}$

Number of days $= \frac{11600}{446.15} = 26$

19. (a) $2HgO \longrightarrow 2Hg + O_2$

$2 \times 216.6 \quad 2 \times 200.6$

$= 433.2 \quad = 401.2 \text{ g}$

$0 \quad 0$

$\Delta H_f^\circ = 2 \times 21.7$

$\Delta H = \Sigma\Delta H_f^\circ (p) - \Sigma\Delta H_f^\circ (r)$

$= 0 + 0 - (-2 \times 21.7)$

$= 43.4 \text{ kcal/mol.}$

Thus by supplying 43.4 kcal of heat, the mass of mercury liberated = 401.2 g

$\therefore$ 10 kcal of heat, mass of mercury liberated

$= \frac{401.2 \times 10}{43.4} = 92.44 \text{ g}$

20. (a) $C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O$

$\Delta H = -5645 \text{ kJ}$

Moles of oxygen used per day $= \frac{640}{32} = 20$

$\therefore$ Moles of sucrose used per day

$= \frac{20}{12}$ mole of sucrose $= \frac{20 \times 342}{12} = 570 \text{ g}$

21. (c) Molar enthalpy of combustion.

Molar enthalpy of combustion $= \frac{C \times dT \times M_m}{w}$

22. (d) Heat evolve from 0.2 g = 200 × 5 = 1000 cal or 1 k cal

Heat evolve from one mole i.e., 74 g

$= \frac{1}{0.2} \times 74 = 370 \text{ k cal}$

23. (b) $\because C_2H_4 + 3O_2(g) \longrightarrow 2CO_2 + 2H_2O(l)$

$\because$ moles of O_2 reacted $= \frac{6226}{1411}$

$\therefore$ moles of O_2 reacted $= \frac{6226}{1411} \times 3$

$\therefore$ volume of O_2 entered at STP

$= \frac{6226}{1411} \times 3 \times 224 \text{ L} = 296.5 \text{ L}$

24. (a) $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$

$T_1 = -25 + 273 = 248 \text{ K}$

$T_2 = -10 + 273 = 263 \text{ K}$

$\Delta H_1 = 5950 \text{ cal/mol}, \Delta H_2 = ?$

$\Delta C_P = 20.6 - 9.3 = 11.3 \text{ cal/mole}$

$\Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1)$

$\Delta H_2 = 6119.5 \text{ cal/mole}$

25. (c) $Fe + S \longrightarrow FeS$

When 2.1 g iron combines S heat evolved = 3.77 kJ when 56 g (atomic mass) combines with S, heat evolved $= \frac{3.77}{2.1} \times 56 = 100.5$ kJ/mole

Thus heat of formation of FeS = –100.5 kJ/mole

26. (b) $T_2 = TK? \; T_1 = 300 \text{ K}$

$\eta = 25\% = \frac{25}{100} = 0.25$

$\eta = 1 \frac{T_1}{T_2}$

or $\frac{T_1}{T_2} = 1 - \eta = 1 - 0.25 = 0.75$

$T_2 = \frac{300}{0.75} = 400 \text{ K}$

27. (b) Since $I_2(s) \longrightarrow I_2(g)$

$\Delta H_{(\text{heat of sublimation})} = 24$ cal/g at 200°C

Also $\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$

$\therefore \quad \Delta C_P = C_P \text{ of } ½ \text{ (g)} - C_P \text{ of } I_2(s)$

$= 0.031 - 0.055 = -0.024 \text{ cal/g}$

$\Delta H_2 - 24 = 0.024 \times (523 - 473)$

$= 22.8 \text{ cal/gm}$

28. (a) $\because \quad \Delta H = q_p = msdT = C_p dT$

$= 210 \times 1 = 210$

29. (c) C $\longrightarrow$ A is isochoric process

V $\longrightarrow$ constant

or $P \propto T$

Now, $P_A > P_C$

Also $T_A > T_C$ or $\Delta U_C - A$ is positive.

30. (b) $\gamma = \frac{C_P}{C_V} = \frac{12.5 + 8.314}{12.5} = 1.665$

$W = \frac{nR(T_1 - T_2)}{\gamma - 1} = -2.5 \text{ kJ}$

31. Amount of energy left unused $= \frac{1560}{2} = 780$ kJ

Amount of water perspired

$= \frac{\text{Energy left unused}}{\text{Enthalpy of evaporation of water}}$

$= \frac{780 \text{kJ}}{44 \text{kJ mol}^{-1}} = \frac{780}{44} \text{ mole}$

$= \frac{780 \times 18}{44} = 319.14 \text{ g}$

32. If $AlCl_3$ is present in ionic state in aqueous solution (Al^{+3} and three Cl^- ions), then standard heat of hydration of Al^{+3} and three Cl^- ions

$= -4665 + (3 \times -381)$

$= -5808 \text{ kJ mol}^{-1}$

This hydration energy is greater than ionisation energy of Al, hence $AlCl_3$ would be ionic in solution.

33. Energy available for muscular work

$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$

$\therefore$ Energy available for muscular work for 120 g of glucose $= 720 \times \frac{120}{180} = 480$ kJ

$\because$ 100 kJ is used for walking = 1 km

$\therefore$ 480 kJ is used for walking

$= 1 \times \frac{480}{100} = 4.8 \text{ km}$

34. (b) $\Delta G = \Delta H + T\left[\frac{\delta \Delta G}{\delta T}\right]_P$ (Gibbs Helmholtz equation)

Also, $\Delta G = \Delta H - T\Delta S$; and $-\Delta G = nF.E$

$\therefore \quad \Delta G - \Delta H = T\Delta S$

or $-T\Delta S = T\left[\frac{\delta \Delta G}{\delta T}\right]_P = T\left(\frac{-nF.E}{\delta T}\right)_P$

or $\left[\frac{\delta E}{\delta T}\right]_p = \frac{\delta S}{nF}$;

similarly derive for other values.

35. (d) $C_p = \frac{Q_b}{\Delta T} = \frac{\Delta T}{\Delta T}$ or $\left(\frac{\delta H}{\delta T}\right)_p$.

36. (d) For adiabatic expansion q = 0 ; thus, from first law $-\Delta E = -W$ or $-W = -C_v n.dT$. The expression on integration leads to $W_{max} = \frac{nR}{r-1}[T_2 - T_1]$ having the relation PV^r = constt. as an intermediate setp., TV^{r-1} = constt. and $T^r \cdot P^{1-r}$ = constant can be obtained by PV^r = constt.

37. (a) P x 1 = RT

Also internal energy $E = \frac{3}{2}RT$

$\therefore$ $E = \frac{3}{2}P$

or $P = \frac{2}{3}E$.

38. (d) $\left(\frac{\delta H}{\delta T}\right)_P = C_P$, $\left(\frac{\delta E}{\delta T}\right)_v = C_v$.

Also, $(\delta E/\delta V)T$ for ideal gas = 0.

39. (d) These all are facts.

40. (c) $C_v = a + bT + cT^2$

$dE = nC_v\,dT$

Change in internal energy

$$= \int_{E_1}^{E_2} dE = n\int_{T_1}^{T_2}(a + bT + cT^2)dT$$

$$\Delta E = E_2 - E_1 = n\left[aT + \frac{bT^2}{2} + \frac{cT^3}{3}\right]_{200}^{300}$$

$$= n\left[a(300-200) + \frac{b}{2}[(300)^2 - (200)^2] + \frac{c}{3}[(300)^3 - (200)^3]\right]$$

$$= \frac{8}{32}[100a + 2.5 \times 10^4 b + 6.3 \times 10^6 C]$$

$$= \frac{1}{4}[1.2 \times 100 + 2.5 \times 10^4 \times 12.8 \times 10^{-2} + 6.3 \times 10^6 \times 3.3 \times 10^{-7}]$$

$$= 830.5 \text{ J.}$$

41. (b) Bursting of the balloon is adiabatic process for which

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}} \text{ or } \left(\frac{P_1}{P_2}\right)^{\gamma-1} = \left(\frac{T_1}{T_2}\right)^{\gamma}$$

Helium is mono atomic gas for which $\gamma = 5/3$. After bursting the pressure of gas enclosed will be lowered to 1 atm.

$\therefore$ $\left(\frac{2}{1}\right)^{\frac{5}{3}-1} = \left(\frac{300}{T}\right)^{\frac{5}{3}}$

Taking log to both sides

$$\frac{5}{3}\log\frac{300}{T} = \frac{2}{3}\log 2$$

on solving

T = 227.35 K

= –45.65°C

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. Which of the following statements is/are correct?
(a) Absolute value of enthalpy cannot be determined
(b) Absolute value of internal energy cannot be determined
(c) Absolute value of entropy can be determined
(d) Internal energy, enthalpy and entropy are intensive properties.

2. Identify the intensive properties among the following:
(a) Enthalpy (b) Temperature
(c) Volume (d) Refractive index

3. Which of the following is/are endothermic process?
(a) Combustion of glucose
(b) Decomposition of water
(c) Dehydrogenation of ethane to ethane
(d) Conversion of graphite to diamond

4. For an ideal gas undergoing isothermal irreversible expansion?
(a) $\Delta U = 0$ (b) $\Delta H = 0$
(c) $\Delta S = 0$ (d) $w = 0$

5. In which of the reaction, $\Delta H > \Delta U$?
(a) $H_2 + I_2 \rightarrow 2HI$
(b) $PCl_5 \rightarrow PCl_3 + Cl_2$
(c) $2H_2O_2 \rightarrow 2H_2o + O_2$
(d) $C + O_2 \rightarrow CO_2$

6. The correct expression(s) for an adiabatic process is/ are
(a) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ (b) $\frac{P_2}{P_1} = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma-1}{\gamma}}$
(c) $P_1V_1^{\gamma} = P_2V_2^{\gamma}$ (d) $P_1V_2^{\gamma-1} = P_2V_2^{\gamma-1}$

7. During an adiabatic reversible expansion of an ideal gas
(a) internal energy of the system decreases.
(b) temperature of the system decreases.
(c) the value of γ changes
(d) pressure increases

8. One mole of an ideal monoatomic gas at 27°C expands adiabatically against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3.
(a) $w = 1013$ J
(b) $\Delta U = -1013$ J
(c) $\Delta H = -1688$ J
(d) The final temperature achieved is = 29.18 K

9. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is
(a) 11.4 kJ (b) –11.4 kJ
(c) 0 kJ (d) 4.8 kJ

10. On mole of an ideal gas at 300 K is expanded Isothermally from an initial volume of 1 litre to 10 litres. The ΔE for this process is ($R = 2$ cal mol^{-1} K^{-1})
(a) 163.7 cal (b) zero
(c) 1381.1 cal (d) 9 lit atm

11. Which is true about the efficiency of carnot cycle?
(a) efficiency is always less than one
(b) efficiency is independent of the substance consider
(c) For all reversible carnot cycle operating between the same initial and final temp.
(d) Efficiency is one only when $T_1 = 0$; $T_2 = \infty$

12. If x and y are arbitrary extensive variable, then
(a) (x + y) is an extensive variable
(b) x/y is intensive variable
(c) dx/dy is intensive variable
(d) Both 'b' and 'c'

13. If x and y are arbitrary intensive variable, then
(a) xy is intensive variable
(b) x/y is intensive variable
(c) x +y is extensive variable
(d) $\frac{dx}{dy}$ is intensive properly.

14. Which is correct statement?
(a) The entropy of the universe increases and tends towards the max. value
(b) All natural processes are irreversible
(c) For reversible isolated processes, change of entropy is zero
(d) For irreversible isolated processes, entropy change > 0.

ANSWER KEYS

1. (a,b,c) **2.** (b,d) **3.** (b,c,d) **4.** (a,b) **5.** (b,c) **6.** (a,c) **7.** (a,b)
8. (a,b,c,d) **9.** (a,b) **10.** (a,c,d) **11.** (a,b,c,d) **12.** (a,b,c,d) **13.** (a,b,c) **14.** (a,d)

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

In thermodynamics, for each thermodynamic process there will be an equation which defined the process, this is known as thermodynamic process equation. For all thermodynamic process we can use ideal gas equation with thermodynamic process equation. For work done and change in internal energy in all the thermodynamic process we can use $w = \int_{v_i}^{v_f} pdv$ and $\Delta U = \frac{nR}{\gamma - 1}\int_{T_i}^{T_f} dT$ dT (all the symbols have their usual meaning. To get specific heat for a thermodynamic process use first law of thermodynamics.

Assume one mole of ideal gas $\left(\gamma = \frac{C_P}{C_V}\right)$ expanded according to the law $p = \alpha V$, where α is constant. Initial volume of the gas is V_0 and it is expanded to the volume nV_0.

1. The thermodynamic process is
(a) isothermal (b) adibatic
(c) isochoric (d) none of these

2. The work done by the gas is
(a) $\frac{\alpha V_0^2}{2}(n^2 - 1)$ (b) $\alpha V_0^2 (n^2 - 1)$
(c) $\alpha V_0^2 (1 - n^2)$ (d) $\frac{\alpha V_0^2}{2}(1 - n^2)$.

3. Change in internal energy of gas is
(a) $\frac{\alpha R}{(1-\gamma)} V_0^2 (n^2 - 1)$
(b) $\frac{\alpha R}{(\gamma - 1)} V_0^2 (n^2 - 1)$
(c) $\frac{\alpha R}{2(1-\gamma)} V_0^2 (n^2 - 1)$
(d) $\frac{\alpha R}{2(\gamma - 1)} V_0^2 (n^2 - 1)$

4. The specific heat for the process i
(a) $\frac{(\gamma + 1)R}{2(\gamma - 1)}$ (b) $\frac{(\gamma - 1)R}{2(\gamma + 1)}$
(c) $\frac{(\gamma - 1)R}{(\gamma - 1)}$ (d) $\frac{(\gamma - 1)R}{(\gamma + 1)}$

COMPREHENSION-II

An ideal gas, having ratio of specific heat γ undergoes a process in which its internal energy relates to the volume as $U = \alpha\sqrt{V}$, where α is a constant. If the gas is expanded from volume V_1 to V_2

Given that $U = \frac{RT}{\gamma - 1}$

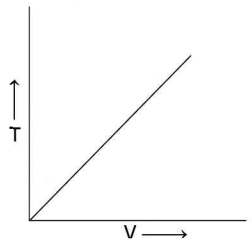
5. The work performed by gas is
(a) $2\alpha(\gamma - 1)[\sqrt{V_2} - \sqrt{V_1}]$
(b) $\alpha(\gamma - 1)[\sqrt{V_2} - \sqrt{V_1}]$
(c) $2\alpha(\gamma - 1)[V_2 - V_1]$
(d) $\alpha(\gamma - 1)[V_2 - V_1]$

6. If the ideal gas is diatomic and its increase in internal energy is 100 J then the work performed by gas is
(a) 80 J (b) 180 J
(c) 100 J (d) 20 J

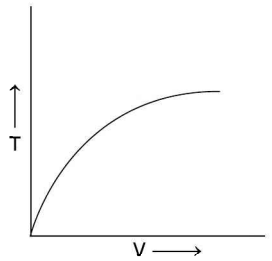
7. The above question, the heat supplied to gas is
(a) 80 J (b) 180 J
(c) 100 J (d) 20 J

8. Which of the following graph shows variation in temperature with volume for the process?

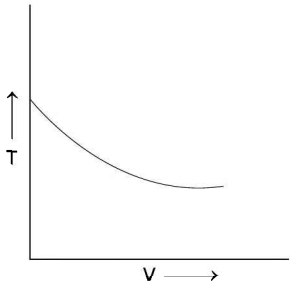
(a)



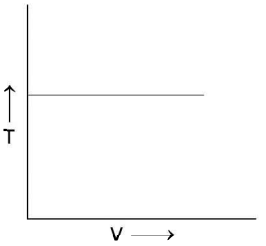
(b)



(c)



(d)



ANSWER KEYS

1. (d) **2.** (a) **3.** (b) **4.** (a) **5.** (a) **6.** (a) **7.** (b) **8.** (b)

HINTS AND EXPLANATIONS

2. $W = \int p.dV = \alpha \int_{V_0}^{nV_0} VdV$

$= \frac{\alpha V_0^2}{2} = \frac{\alpha V_0^2}{2}(n^2 - 1)$

3. $\because \quad \Delta U = \frac{R}{(\gamma - 1)} \int dT$

Here $pV = RT = \alpha V^2$

$\Rightarrow RdT = 2\alpha 2VdV$

So, $\Delta U = \frac{2\alpha R}{(\gamma - 1)} \int_{V_0}^{nV_0} V.dV$

$= \frac{\alpha R}{\gamma - 1} V_0^2 (n^2 - 1)$

4. Using $\Delta Q = \Delta U + \Delta w$ we'll get $C = \frac{(\gamma + 1)R}{2(\gamma - 1)}$

5. Given $U = \frac{RT}{(\gamma - 1)} = \frac{pV}{(\gamma - 1)}$

$\therefore \quad W = \int p.dv = \int \frac{U(\gamma - 1)}{V} dV$

$= \alpha(\gamma - 1) \int V^{-1/2}.dV$

$\Rightarrow \quad W = 2\alpha(\gamma - 1)\left[\sqrt{V_2} - \sqrt{V_1}\right]$

6. Since $\Delta U = \alpha\left[\sqrt{V_2} - \sqrt{V_1}\right]$

$\Rightarrow \quad W = 2(\gamma - 1)\Delta U$

Here $\gamma = 1.4$, $\Delta U = 100$ J

So $\Delta W = 80$ J.

MATCH THE COLUMN TYPE QUESTIONS

1. Match list I (Partial derivatives) with list II (Thermodynamic quantity) and select the correct answer using the codes given below the lists:

List I	List II
(a) $(\partial E/\partial T)_V$	1. V
(b) $(\partial H/\partial T)_P$	2. –S
(c) $(\partial G/\partial P)_T$	3. T
(d) $(\partial E/\partial T)_P$	4. C_P
	5. C_V

Code:

	A	B	C	D
(a)	5	4	1	2
(b)	2	3	5	1
(c)	5	3	1	2
(d)	2	4	5	1

2. Match list I with list II and select the correct answer using the codes given below the lists:

List I	List II
(a) Arrhenius law of dissociation	1. $\alpha = \Lambda/\Lambda_\infty$
(b) Gibbs phase rule	2. $\Lambda_\infty = \lambda_+^\infty + \lambda_-^\infty$
(c) Kirchhoff relation	3. $dH = C_p dT$
(d) Kohlrausch's law	4. $P = C + 2 - F$

Code:

	A	B	C	D
(a)	1	2	3	4
(b)	2	1	4	3
(c)	3	4	1	2
(d)	1	4	3	2

3.

List I	List II
(i) Isothermal process	(a) $\Delta P = 0$
(ii) Adiabatic process	(b) $\Delta V = 0$
(iii) Isochoric process	(c) $\Delta T = 0$
(iv) Isobaric process	(d) $\Delta Q = 0$

ANSWER KEYS

1. (a) **2.** (d) **3.** (c); (i) (d); (ii) (b); (iii) (a); (iv)

TRUE/FALSE TYPE QUESTIONS

1. First law of thermodynamics is not adequate in predicting the direction of a process.

2. Heat capacity of a diatomic gas is higher than that of a monoatomic gas.

3. All ideal gases have the same value for the ratio C_P/C_V.

4. The heat of reaction does not depend upon the physical state of reactants and products but depends upon the manner how the change has been brought.

5. The heat of combustion as determined from bomb calorimeter gives the value of heat evolved at constant pressure.

6. The heat absorbed during the isothermal expansion of an ideal gas against vaccum is zero.

ANSWER KEYS

1. T **2.** F **3.** F **4.** F **5.** F **6.** T

ASSERTION/REASON TYPE QUESTIONS

INSTRUCTIONS: In the following questions, an Assertion(A) is given followed by a Reason (R). Mark your responses from the following options.

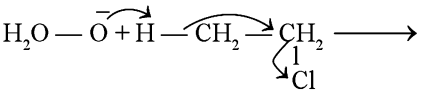
(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'
(b) Both Assertion and Reason are true and Reason is not the correct explanation of 'Assertion'
(c) Assertion is true but Reason is false
(d) Assertion is false but Reason is true

1. **Assertion:** The slope of adiabatic process is lesser than that isothermal process, while P and V is drawn in Y–axis and X–axis respectively.
   Reason: The slope of adiabatic process is γ times of isothermal process.
   (a) If both assertion and reason are correct and reason is the correct explanation of the assertion
   (b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion
   (c) If assertion is correct, but reason is incorrect
   (d) If assertion is incorrect, but reason is correct.

2. **Assertion:** Even for the constant volume condition, the work done in isothermal expansion condition is higher than that of adiabatic expansion conditions is graph is drawn, P and Y-axis and V on X-axis.
   Reason: Because the area under the curve in isothermal expansion process is higher than that of adiabatic expansion process.
   (a) If both assertion and reason are correct and reason is the correct explanation of the assertion
   (b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion
   (c) If assertion is correct, but reason is incorrect
   (d) If assertion is incorrect, but reason is correct.

3. **Assertion:** The enthalpy of neutralization of equivalent of HF and 1 equivalent NaOH is 14 kcal/mol, which is higher than HCl and NaOH.
   Reason: This is because the enthalpy of hydration of F^- is higher that of its heat enthalpy of dissociation.
   (a) If both assertion and reason are correct and reason is the correct explanation of the assertion
   (b) If both assertion and reason are correct, but reason is not the correct explanation of the assertion
   (c) If assertion is correct, but reason is incorrect
   (d) If assertion is incorrect, but reason is correct.

4. **Reason:** The entropy chang ein the reaction.



$$H_2O + \bar{Cl} + CH_2 = CH_23$$

   is positive.
   Reason: Entropy increases when number of particles or (i.e., molecules or ions) of the product or, in the product directions increases.

5. **Assertion:** The slope of adiabatic process is lesser than that isothermal process, while P and V is drawn in Y–axis and X–axis respectively.
   Reason: The slope of adiabatic process is γ times of isothermal process.

6. **Assertion:** The enthalpy of neutralisation of equivalent of HF and 1 equivalent NaOH is 14 kcal/mol, which is higher than HCl and NaOH.
   Reason: This is because the enthalpy of hydration of F^- is higher that of its heat enthalpy of dissociation.

ANSWER KEYS

1. (a) 2. (a) 3. (a) 4. (a) 5. (d) 6. (a)

SUBJECTIVE QUESTIONS

1. Isothermally at 27°C, one mole of a vander waal's gas expands reversibly from 2 litres to 20 litres. Calculate the work done if a $=1.42 \times 10^{12}$ dynes cm^4 per mole and b = 30 c.c.

2. Calculate the lattice energy of $AlI_3(s)$ from the following data:

   $(\Delta H_f^0)_{AlI3} = -52$ kcals $mole^{-1}$

   $(\Delta Hv^0)_I = 6$Kcals $mole^{-1}$

   $(\Delta H_s^0)_{Al} = 15$ Kcals $mole^{-1}$

   $(\Delta H_b^0)_{I2} = 5$kcals $mole^{-1}$

   $(\Delta H_f^0)_{I2} = 10$ kcals $mole^{-1}$

   $(\Delta H^0_{EA})_{I2}(g) = -28.67$ Kcals $mole^{-1}$

   The sum of 1st two ionization energies and 3 times the third is 74 kcals $mole^{-1}$. The sum of 1st and 3rd ionization energies along with the two times 2nd ionization energy is 54 kcals $mole^{-1}$ while 3 times the 1st ionization enerty added to 5 times the 3rd ionization energy subtracted by 2nd ionization energy gives 98 kcals $mole^{-1}$.

3. In order to get maximum calorific output a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6 x litre/hour of O_2) is to be readjusted for butane C_4H_{10}. In order to get same calorific output, what should be the rate of supply of butane and oxygen. Assume that losses due to incomplete combustion etc., are the same for both fuels and that gases behave ideally. Heats of combustion: CH_4 = 809 kJ/mol; C_4H_{10} = 2878 kJ/mol.

4. An intimate mixture of Fe_2O_3 and Al is used in solid fuel rocket. Calculate the fuel value/g and per ml of mixture. $(\Delta H)_{Al2O3} = 399$ kcals.

   $(\Delta H)_{Fe2O3} = 199$ kcals. Density of Fe_2O_3 and Al are 5.2 g//ml and 2.7 g/ml respectively.

5. 0.50 g of benzoic acid was subjected to combustion in a bomb calorimeter at 15°C when the temperature of the calorimeter system (including water) was found to rise by 0.55°C. Calculate the heat of combustion of benzoic acid: (i) at constant volume, (ii) at constant pressure. The thermal capacity of the calorimeter system including water was found to be 23.85 kJ.

6. The heat of reaction (ΔH) for the formation of NH_3 according to the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 27°C was found to be –91.94 kJ kJ. What will be the heat of reaction ΔH at 50°C. R [= 8.31 J/mol – ^{0}k].

7. A reversible carnot engine produces 3.36×10^4 J. ,of work by taking up 10 Kcal heat. If the temperature of the source is 527°C. at what temperature the sink be placed?

8. The temperature and pressure of one mole of an ideal monoatomic gas are changes from 25°C and 1 atm pressure to 250°C and 25 atm. Calculate the change of entropy for the process.

9. A natural gas may be assumed to be a mixture of CH_4 and C_2H_6 only. On complete combustion of 10 L of the gas at STP, the heat evolved was 474.6 kJ. Assuming $\Delta H_c(CH_{4(g)}) = -894$ kJ/mol and $\Delta H_C(C_2H_{6(g)}) = -1560$ kJ/mole. Calculate the % of volume of each gas in the mixture.

10. The heat of formation of one mole of HI from hydrogen and iodine vapour at 25°C is 8000 cal.

    $$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \longrightarrow HI(g),\ \Delta H = -8000 \text{ cal}$$

    Calculate the heat of formation at 10°C and also the total change in the heat capacity at constant pressure. It is given that the molar heat capacities of hydrogen, iodine and HI vapours are given by the equations.

    $C_P = 6.5 + 0.0017\ T$ for Hydrogen (g)
    $C_P = 6.5 + 0.0013\ T$ for Iodine (g)
    $C_p = 6.5 + 0.0016\ T$ for HI (g)

    Where T is the absolute temperature.

11. Calculate the boiling point benzene under a pressure of 80 cm of Hg. The normal boiling point is 80°C. Latent heat of vaporization is 380 Joule/g density of vapour at the boiling point is 4 gm/litre and that of the liquid 0.9 gm/ml.

12. 12.5 g of ice at – 24°C is converted into steam at 100°C. Calculate the change in entropy. It is given

that latent heat of steam = 536 cal/g, latent heat of ice = 80 cal/gm. Specific heat of ice = 0.5 cal/g K.

13. An aero plane weighing 70,000 Kg files up from sea level to a height of 7000 meter, Its engine run with pure normal octane [C_8H_{18}] has 30% efficienc . Calculate the fuel cost of the flight, if octane sells at Rs 5/-per litre.
Given density of octane = 0.705 gm/ml, heat of combustion of octane=1300 Kcal/mol (g=981 cm/sec^2)

14. 5 mole of ice at 0°C and 7.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find ΔH and ΔE if the latent heat of fusion of ice is 80 cal/g and latent heat of vaporization of liquid water at 0°C is 596 cal/g and the volume of ice in comparison to that of water(vapour) is neglected.

15. H_2 gas is mixed with air at 25°C under a pressure of 1 atmosphere and exploded in a closed vessel. The heat of the reaction.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\ (g)$$

At constant volume, $\Delta E_{298} = -240.60$ kJ mol^{-1} and C_p values for H_2O vapour and N_2 in the temperature range 298 K and 3,200 K are 39.06 JK^{-1} mol^{-1} and 26.40 JK^{-1} mol^{-1} respectively. Calculate the explosion temperature under adiabatic conditions.

16. Compute the heat of reaction at 1000^0 C for

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$$

$\Delta H^0_{298K} = 92.236$ kJ mol^{-1}

C^0_P (H_2, g = 29.0284 – 0.8355 × 10^{-3}T + 2.0097 × 10^{-6} T^2

C^0_P (Cl_2, g) = 31.6555 + 1.0134 × 10^{-2} T – 4.0337 × 10^{-6} T^2

C^0_P (HCl, g) = 28.1359 + 1.8078 × 10^{-3} T + 1.5453 × 10^{-6} T^2

17. An intimate mixture of Fe_2O_3 and Al is used in solid fuel rocket. Calculate the fuel value per gram and per ml of mixture. $\Delta H_{Al_2O_3}$ = 399.0 Kcal. $\Delta H_{Fe_2O_3}$ = 199.0 kcal density of Fe_2O_3 and Al are 5.2 g/ml and 2.7 g/ml respectively.

[redacted]TS AND EXPLANATIONS

1. $$W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2}\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)dV$$

$$= \left[RT\ln(V-b) + \frac{a}{V}\right]_{V_1}^{V_2}$$

$$= RT\ln\frac{V_2-b}{V_1-b} + a\left[\frac{1}{V_2} - \frac{1}{V_1}\right]$$

$$= 2.303 \times 8.31\times10^7 \times 300 \log \frac{20-0.03}{2-0.03} + 1.42 \times 10^{12}\left[\frac{2000-2000}{2000\times2000}\right]$$

$$= 5778 \times 10^7 \text{ erg}$$

$$= 5778 \text{ joules}$$

2. Let 1st, 2nd and 3rd ionization energies of Al be x, y and z kcals/mole respectively.

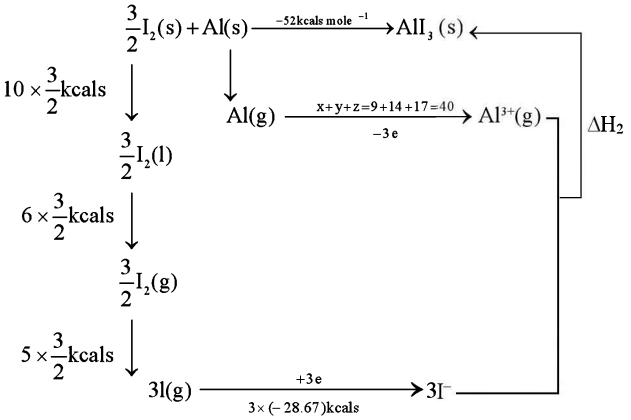
$x + y + 3z = 74$ ... (1)

$x + 2y + z = 54$ ... (2)

$3x - y + 5z = 98$ ... (3)

Solving we get x = 9 kcals mole^{-1}

Y = 14 kcals mole^{-1} z = 17 kcals mole^{-1}



$$-52 = 15 + 40 + \frac{3}{2} \times 10 + 6 \times \frac{3}{2} + 5 \times \frac{3}{2} + 3 \times (-28.67) + \Delta H_2$$

$$\Delta H_2 = -52 - 65 - 15 - 9 - 7.3 + 85.01$$

$$= -148.5 + 85 = -63.5 \text{ kcals mole}^{-1}$$

3. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$;

$\Delta H = -809$ kJ mol^{-1}

Initial volume/h x 6x x 6x
(in litre)

Let the temperature be T and assume volume of 1 mole of a gas is V litre at this condition

$\therefore$ V litre or 1 mole CH_4 gives energy on combustion = 809 kJ

x litre of CH_4 gives energy on combustion = $\frac{809(x)}{V}$ kJ

$\because$ 2878 kJ energy is obtained by 1 mole or V litre C_4H_{10}

$\therefore$ $\frac{809(x)}{V}$ kJ energy is obtained by = $\frac{809(x) \times V}{V \times 2878}$ litre C_4H_{10} = 0.281 (x) litre C_4H_{10}

Thus butane supplied for same calorific output = 0.281 x litre

$\because$ $C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$;

$\Delta H = -2878$ kJ/mole.

Volume of O_2 required = 3 × Volume of O_2 for combustion of C_4H_{10}
= $3 \times \frac{13}{2} \times$ volume of $C_4H_{10} = 3 \times \frac{13}{2} \times 0.281$ (x) =

5.48(x) litre O_2

4. $2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$

Given $2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3$ $\Delta H = -399$ kcals ... (1)

and $Fe + \frac{3}{2}O_2 \longrightarrow Fe_2o_3$ $\Delta H = -199$ kcals ... (2)

(1) – (2) gives.

$2Al + Fe_2O_3 \longrightarrow 2Fe + Al_2O_3$ $\Delta H = -200$ kcals

Molecular weight of fuel mixture = 2 × 27 + 2 × 56 + 48 = 214g

214g mixture produces = 200 kcals heat

1g mixture produces = $\frac{200}{214} = 0.9346$ kcals/g

Also volume of fusion mixture = volume of Al + volume of Fe_2O_3

$= \frac{54}{2.7} + \frac{160}{5.2} = 20 + 30.76 = 50.76$ ml

50.76 ml mixture produces 200 kcals

1 ml mixture produces = $\frac{200}{50.76} = 3.94$ kcals/ml

5. (i) Heat of combustion at Constant Volume (ΔE):

Weight of benzoic acid m = 0.50 g

Rise in temperature, $\theta = 0.55°C$

Molecular weight of benzoic acid, M = 122

Thermal capacity of the calorimeter system, z = 23.85 kJ

$\therefore$ Heat of combustion at constant volume, ΔE

$= z \times \theta \times \frac{M}{m}$

$= -23.85 \times 0.55 \times \frac{122}{0.50}$

$= -3200.7$ kJ $= -3200.7$ kJ

(ii) Heat of combustion at constant pressure (ΔH):

The combustion of benzoic acid at 25°C involves the following reaction:

$C_6H_5COOH(s) + 7.5O_2(g) \longrightarrow$

$7CO_2(g) + 3H_2O(l)$

$\Delta H = \Delta E + \Delta nRT$

In the present case:

$\Delta E = -3200.7$ kJ $\Delta n = 7 - 7.5 = -2.5$

$R = 8.314 \times 10^{-3}$ kJ

$T = 273 + 25 = 298°K$

$\therefore$ $\Delta H = -3200.7 + (-0.5) \times 8.314 \times 10^{-3} \times 298$

$= -3201.9$ kJ

$\therefore$ Heat of combustion at constant pressure, $\Delta H = -3201.9$ kJ

6. $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$

(We know C_p (diatomic gas)

$= \frac{7}{2}R$, C_p (polyatomic gas = 4R)

$\therefore$ $\frac{\Delta H_{50°C} - \Delta H_{27°C}}{(50+273)-(27+273)} = \left\{2 \times 4R - \left(\frac{7}{2}R + 3 \times \frac{7}{2}R\right)\right\}$

$\Delta H_{50°C} = 91.94 + 23 \times \{-6R\} = -93.087$kJ

7. $W = -3.36 \times 10^3$ J

$Q = 10$ Kcal $= 4.18 \times 10^4$ J.

$\eta = \frac{T_{source} - T_{sink}}{T_{source}} = \frac{W}{Q} = \frac{3.36 \times 10^4}{4.18 \times 10^4}$

$$\eta = \frac{800 - T_s}{800} = \frac{3.36}{4.18}$$

$$3344 — 4.18\ T_s = 2688$$

$$T_s = \frac{656}{4.18} K$$

$$= 156.93\ K \approx 157\ K$$

8. Change in entropy

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

as for monoatomic gas $\Rightarrow \gamma = \frac{C_P}{C_v} = \frac{5}{3}$

$$C_v = \frac{3}{5} C_p$$

$$C_p - C_v = 2 \Rightarrow C_p — \frac{3}{5} C_p = 2$$

$$\Rightarrow \frac{2}{5} C_p = 2 \Rightarrow C_p = 5\ cal/kg\ K$$

$$\Delta S = 2.303 \times \left[5 \log \frac{523}{298} - 2 \times \log \frac{25}{1} \right]$$

$$= 2.303 \times (5 \times 0.2442 — 2 \times 1.397)$$

$$\Delta S = —3.6226\ cal$$

9. Let V be the volume of CH_4 in 10 L mixture. We have

Amount of methane = $\frac{V}{22.4}$

Amount of ethane = $\frac{10 - V}{22.4}$

The expression of heat evolved, we will get

$$\frac{V}{22.4} \times 894 + \frac{10 - V}{22.4} \times 1560 = 474.6$$

$$V = 7.45 \text{ litre}$$

% of $CH_4 = 74.5\%$

% of $C_2H_6 = 25.5\%$

10. $\Delta C_p = C_{P(HI)} - \frac{1}{2} [C_{p(HI)} + C_{p(I_2)}]$

$$= 6.5 + 0.0016T - \frac{1}{2}$$

$$[6.5 + 0.0017T + 6.5 + 0.0038T]$$

$$= -0.00115T \text{ cal. deg}^{-1}$$

Here $\Delta H_{298} = \Delta H_{283} + \int_{283}^{298} \Delta C_p dT$

Where $T_1 = 273 + 10 = 283K$, $T_2 = 273 + 25$

$= 298\ K$

Also, $\Delta H_{293} K = -8000$ cal.

$$-8000 = \Delta H_{283} + \int_{283}^{298} (-0.00115) T dT$$

or $$\Delta H_{283} = -8000 + \frac{0.00115}{2} [T^2]_{283}^{298}$$

$$= -8000 + \frac{0.00115}{2} [(298)^2 - (283)^2]$$

$$= -7995 \text{ cal (nearly)}$$

11. $\Delta P = 80 - 76$

$= 4$ cm of Hg

$= 4 \times 13.6 \times 980$ dyne/cm^2

$T = 80°C = 80 + 273 = 353\ K$

$L = 380$ joule/gm

$= 380 \times 10^7$ ergs/gm

$$V_1 = \frac{1}{0.9} = 1.11\ cm^3$$

$$\frac{\Delta P}{\Delta T} = \frac{L}{T(V_2 - V_1)}$$

$$\Delta T = \frac{\Delta P \times T \times (V_2 - V_1)}{L}$$

$$= \frac{4 \times 13.6 \times 980 \times 353 (250 - 1.11)}{380 \times 10^7} = 1.233\ K$$

$= 1.233°C$

$\therefore$ The boiling point of benzene at a pressure of 80 cm of Hg

Boiling point = 80 + 1.233 = 81.233°C

12. $m = 12.5\ g = 12.5 \times 10^{-3}$ kg

latent heat of ice = 80 cal/g = $80 \times 10^3 \times 4.2$ J/kg = 3.36×10^5 J/kg

latent heat of steam = 536 cal/g = $536 \times 10^3 \times 4.2 = 2.25 \times 10^6$ J/kg

specific heat of ice = 0.5 cal/gm–K

$= 0.5 \times 10^3 \times 4.2 = 2.1 \times 10^3$ J/kg–K

specific heat of water = 1 cal/gram–K

$= 1 \times 10^3 \times 4.2$ J/Kg–K

(i) Increase in entropy when temperature of 12.5×10^{-3}kg of ice is increased from –24°C to 0°C (249 to 273 K)

$$ds_1 = \int_{T_1}^{T_2} \frac{\Delta H}{T} = ms\int_{T_1}^{T_2} \frac{dT}{T} = ms\log_e \frac{T_2}{T_1}$$

$$= 12.5 \times 10^{-3} \times 2.1 \times 10^3 \log_e \left(\frac{273}{249}\right)$$

$$= 12.5 \times 2.1 \times 2.303 \times \log_{10} \frac{273}{249}$$

$$s_1 = 2.42 \text{ J/K}$$

(ii) Increase in entropy when 12.5×10^{-3} kg of ice at 0°C is converted into water at 0°C

$$ds_2 = \frac{\Delta H}{T} = \frac{mL}{T} = \frac{12.5 \times 10^{-3} \times 3.36 \times 10^5}{273}$$

$$= 15.38 \text{ J/K}$$

(iii) increase in entropy when the temperature of 12.5×10^{-3} kg of water is raised from 0°C to 100°C (273 K to 373 K)

$$ds_3 = \int_{T_1}^{T_2} \frac{\Delta H}{T}$$

$$= ms \times 2.303 \times \log_{10} \left(\frac{T_2}{T_1}\right)$$

$$= 12.5 \times 10^{-3} \times 4.2 \times 10^3 \times 2.303 \times \log_{10} \frac{373}{273}$$

$$s_3 = 16.38 \text{ J/K}$$

(iv) increase in entropy when 12.5×10^3 kg of water at 100°C is converted into steam at 100°C *(373 K)

$$ds_4 = \frac{\Delta H}{T} = \frac{ML}{T}$$

$$= \frac{12.5 \times 10^{-3} \times 2.25 \times 10^6}{373}$$

$$= 75.4 \text{ J/K}$$

total increase in entropy = 2.42 + 14.38 + 16.38 + 75.4

= 109.58 J/K

13. Wt. of plane(m) = 7×10^7 g

Height (h) = 7×10^5 cm

Work required to lift the plane to height h $\Rightarrow$ mgh

$W = 7 \times 10^7 \times 7 \times 10^5 \times 981$

$= 48.069 \times 10^{15}$

$= 48. \times 10^{15}/4.18 \times 10^7$ calories

$= 1.15 \times 10^9$ calories

As the efficiency of fuel is 30% than the

Actual work required = $(1.15 \times 10^9) \times \frac{100}{30}$

$= 3.83 \times 10^6$Kcal

As heat of combustion of C_8H_{18} = 1300 Kcal/mol

so

Number of moles of $C_8H_{18} = \frac{3.83 \times 10^6}{1300}$ moles

$= 2.94 \times 10^3$ moles

wt. of $C_8H_{18} = (2.94 \times 10^3) \times 114 = 3.35 \times 10^5$ g

so volume of the fuel $= \frac{3.35 \times 10^5}{0.705}$ ml

$= 4.7517 \times 10^2$ L

v = 475.17 L

so cost of fuel = 475.17×5 Rs.

= 2375.88 Rs.

14. Latent heat of fusion of ice per mole = 18×5×80 = 7200 cal.

Latent heat of vaporization of liquid water per mole

= 596×18×5

= 53640 cal

So the total heat absorbed by 5 mole of water vapour

= 7200+53640 = 60840 cal

As the conversion took place at constant pressure

so $Q = \Delta H = 60840$ cal

$\Delta E = \Delta H - P\Delta V$

Volume of 5 mole of water at 0°C and 7.6 mm of Hg pressure

$$V_2 = 5 \times 22.4 \times \frac{760}{7.5} \text{ (Boyle's Law)}$$

$= 11200 \text{ L} = 11200 \times 10^{-3} \text{ m}^3$

volume of ice is to be neglected $V_1 = 0$

So $W = P\Delta V$

$$= \frac{7.6}{760} \times 1.013 \times 10^5 (11200 \times 10^{-3} - 0)$$

$W = 11345.6 \text{ J} = 2714.2$ cal .

So ΔE = 60840—2714.2=58125.74 cal

15. For a constant volume process under adiabatic conditions,

$\Delta E = \Delta E_{heating} + \Delta E_{298} = 0$

$\therefore \quad \Delta H_{heating} = -\Delta E_{298}$

$$= -\int_{298}^{T_f} n\sum C_V dT = -240.60 \text{ kJ mol}^{-1}$$

As 2 moles of unreacted N_2 are associated with $\frac{1}{2}$ mole of O_2, we have

$$\Sigma nC_V = C_V(H_2O, g) + 2C_V(N_2, g)$$
$$= (39.06 + 2 \times 26.40)\ JK^{-1}\ mol^{-1}$$
$$= 91.86\ J\ K^{-1}\ mol^{-1}$$

Hence, from equation (1) on integrating, we get $(91.86\ J\ K^{-1}\ mol^{-1})\ (T_f - 298) = 240{,}600\ J\ mol^{-1}$

$$T_f - 298 = \frac{240600\ J\ mol^{-1}}{91.86 JK^{-1}mol^{-1}}$$

$$= 2619\ K,\ T_f = \mathbf{(2619 + 298)K = 2917\ K}$$

16. $\Delta H^0_{1273K} = \Delta H^0_{298\ K} + \int_{298K}^{1273K} (\Delta C_p)dT$

Where

$$\Delta C_p = C_P^0\ (HCl, g) - \frac{1}{2}C_P^0(H_2, g) - \frac{1}{2}\ C_P^0\ (Cl_2, g)$$

$$= (28.1359 - \frac{1}{2} \times 29.0284 - \frac{1}{2} \times 31.6555)$$
$$+ (1.8078 + \frac{1}{2} \times 0.8355 - \frac{1}{2} \times 10.134) \times 10^{-3}\ T$$
$$+ (1.5453 - \frac{1}{2} \times 2.0097 + \frac{1}{2} \times 4.0337) \times 10^{-6}\ T^2$$

Hence,

$$\Delta H^0_{1273K} = \Big[-92.236 \times 10^2 + (-2.2061) - (2.8415 \times 10^{-3})\left(\frac{1273^3}{2} - \frac{298^3}{2}\right) + (2.5573 \times 10^{-6}) \times 10^{-6}\left(\frac{1273^3}{3} - \frac{298^3}{3}\right)\Big]\ J\ mol^{-1}$$

$$= -92236 - 2151.0 + 2176.2 + 1736.0$$

$$= -94827\ J\ mol^{-1}$$

$$= \mathbf{-\ 94.827\ kJ\ mol^{-1}}$$

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

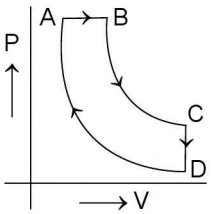
1. Consider the following reaction at 300K

$H_{2(9)} + Cl_{2(9)} \rightarrow 2HCl_{(g)}$, $\Delta H° = —\ 185$ KJ

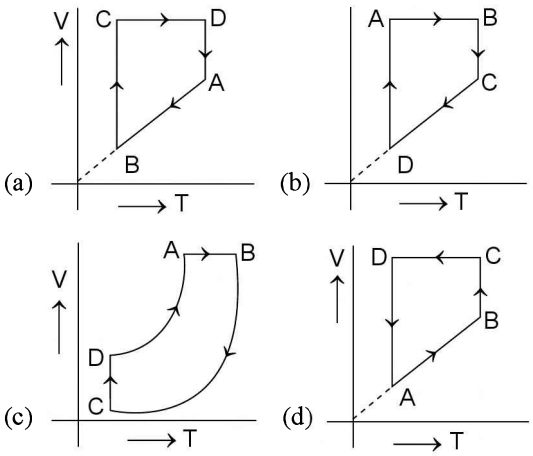
If 3 mole of $\mathbf{H_E}$ completely react with 3 mole of CI_2 to form CI, AU° of the reaction will be

(a) Zero
(b) –185 KJ
(c) 555 KJ
(d) None

2. A cyclic process ABCD is shown in PV diagram for an ideal gas.



Which of the following diagram represents the same process

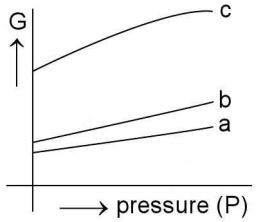


3. The change in free energy accompanied by the isothermal reversible expansion of 1 mole of an ideal gas when it doubles its volume is ΔG_1. The change in free energy accompanied by sudden isothermal irreversible doubling volume of 1 mole of the same gas is ΔG_2 Ratio of ΔG_1 and ΔG_2

(a) 1 (b) $\frac{1}{2}$

(c) –1 (d) $-\frac{1}{2}$

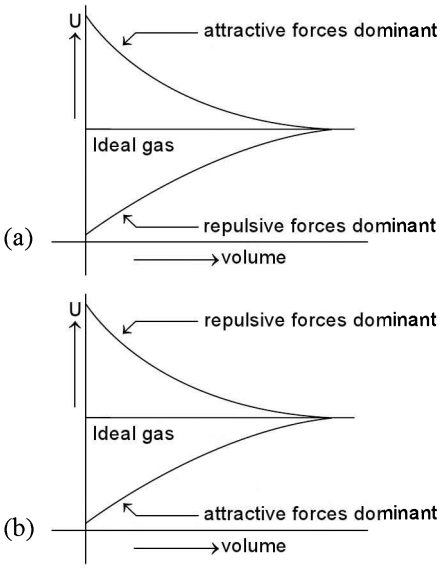
4. The following curve represents the variation of Gibbs function 'G' with pressure at constant temperature.

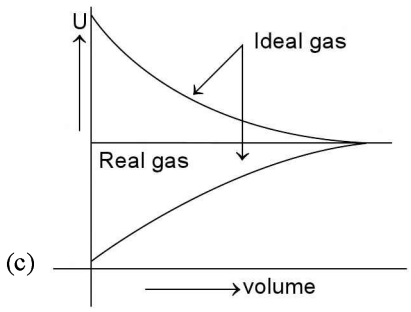


Correct match of given plots with the physical state of a substance is

(a) c – solid, a – gas, b – liquid
(b) c – gas, b liquid, a – solid
(c) a – liquid, b – solid, c – gas
(d) c – gas, b – solid, a – liquid

5. Which of the following diagram correctly represents the variation of internal energy (U) of gas under expansion at constant temperature.

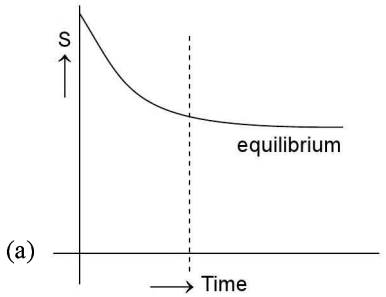




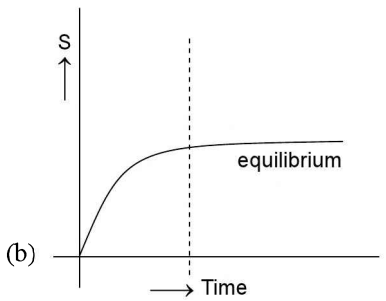
(c)

(d) None of these

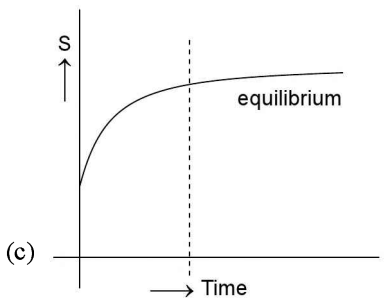
6. Which of the following correctly represents the entropy (s) of an isolated system during a process.



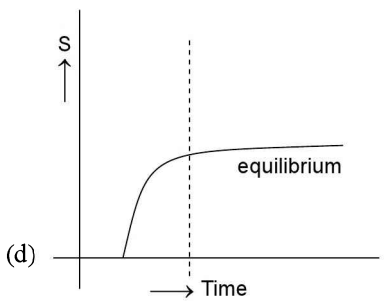
(a)



(b)

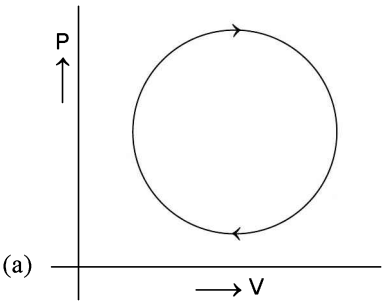


(c)

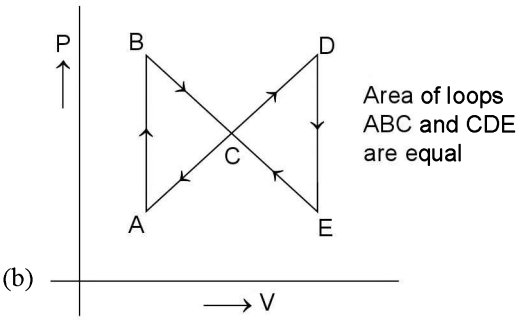


(d)

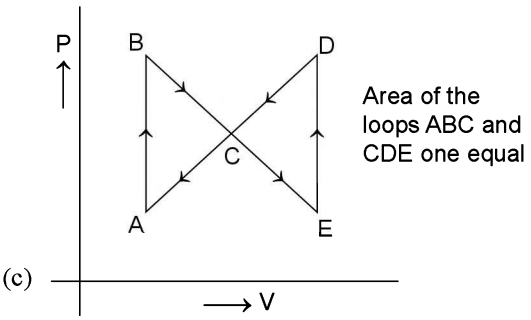
7. Which of the following represents positive work i.e., work of compression



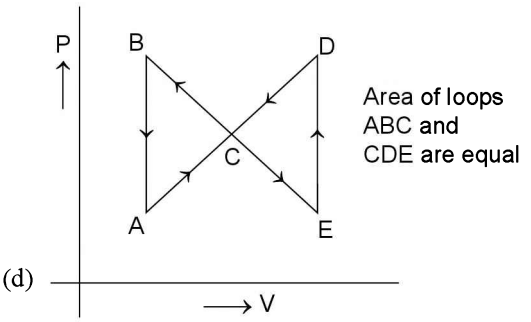
(a)



(b)



(c)



(d)

8. For a perfectly crystalline solid $C_{pm} = aT^3$, where a is constant. If C_{pm} is 0.42 J/K-mol at 10 K, molar entropy at 10 K is

(a) 0.42 J/K-mol

(b) 0.14 J/K-mol

(c) 4.2 J/K-mol

(d) zero

9. At 1000 K water vapour at 1 atm. has been found to be dissociated into H_2 and 0_2 to the extent of 3×10^{-6} %. Calculate the free energy decrease of the system, assuming ideal behaviour.

(a) $-\Delta G = 90{,}060$ cal (b) $-\Delta G = 20$ cal

(c) $-\Delta G = 480$ cal (d) $-\Delta G = -45760$ cal

10. When 1 mole of an ideal gas at 20 atm pressure and 15 L volume expands such that the final pressure becomes 10 atm and the final volume become 60 L. Calculate entropy change for the process ($C_{pm} = 30.96$ J mole^{-1} K^{-1})

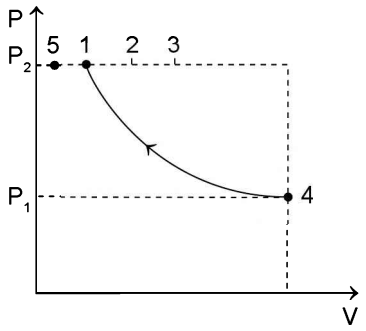
(a) 80.2 J.k^{-}lmo1^{-1}

(b) 62.42 kJ.k^{-1} mol^{-1}

(c) 120×10^2 J1c^{1}mol^{-1}

(d) 27.22 J.k^{-1}mor

11. An ideal gas is taken from the same initial pressure P_1 to the same final pressure P2 by three different processes. If it is known that point 1 corresponds to a reversible adiabatic and point 2 corresponds to a single stage adiabatic then



(a) Point 3 may be a two stage adiabatic.

(b) the average K.E. of the gas is maximum at point 1

(c) Work done by surrounding in reaching point number '3' will be maximum

(d) If point 4 and point 5 lie along a reversible isotherm then $T_5 < T_1$.

12. During winters, moisture condenses in the form of dew and can be seen on plant leaves and grass. The entropy of the system in such cases decreases as liquids possess lesser disorder as compared to gases. With reference to the second law, which statement is correct, for the above process?

(a) The randomness of the universe decreases

(b) The randomness of the surroundings decreases

(c) Increase is randomness of surroundings equals to the decrease in randomness of system

(d) The increase in randomness of the surroundings is greater as compared to the decrease in randomness of the system.

13. For which process will AHD° and AG° be expected to be most similar.

(a) $2AI(s) + Al_2O_3(s) \rightarrow 2Fe(s) + Ai_2O_3(s)$

(b) $2Na(s) + 2H_2O(I) \rightarrow 2NaOH(aq) + H_2(g)$

(c) $2NO_2(g) \rightarrow N_2O_4(9)$

(d) $2H_2(9) + O_2(9) \rightarrow 211_2O(g)$

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

14. One mole of an ideal diatomic gas ($C_V = 5$ cal) was transformed from initial 25°C and 2 litre to the state when temperature is 200°C and volume 10 litre. Then for this process (R = 2 calories/moIN) (take calories as unit of energy and kelvin for temperature)

(a) $\Delta H = 525$

(b) $\Delta S = 5 \text{ In } \frac{373}{298} + 2 \ln 10$

(c) $\Delta E = 525$

(d) ΔG of the process can not be calculated using given information.

15. Which of the following statements) is/are false?

(a) $\Delta_r S$ for $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ is positive.

(b) $\Delta E < 0$ for combustion of $CH_4(g)$ in a sealed container with rigid adiabatic system.

(c) ΔG is always zero for a reversible process in a closed system.

(d) $\Delta G°$ for an ideal gas reaction is a function of pressure.

ASSERTION/REASON TYPE QUESTIONS

16. **Statement-1:** Due to adiabatic free expansion temperature of real gas may increase

Statement-2: In adiabatic free expansion, temperature is always constant irrespective of real or ideal gas

(a) Statement-1 is True, Statement-2 is. True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

17. **Statement-1:** Under free expansion, $\left(\frac{dU}{dV}\right)_T$ is +ve when attractive forces are dominant between gas dB molecules [U, V, T respresent internal energy, volume and temperature of gas respectively]

Statement-2: Internal energy is a state function.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement-1 is True, Statement-2 is False
(d) Statement-1 is False, Statement-2 is True

18. **Statement-1:** Diamond is thermodynamically less stable than its allotrope graphite

Statement-2: Molar entropy of graphite is greater than that of diamond under similar conditions.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

19. **Statement-1:** 'Diamonds are forever' is generally quoted for diamond as rate of conversion of diamond to graphite at room condition is nearly zero.

Statement-2: At room condition, conversion of diamond into graphite is spontaneous.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

20. **Statement-1:** The heat absorbed during isothermal expansion of an ideal gas against vacuum is zero.

Statemept-2: In isothermal process, change in internal energy is always zero, irrespective of ideal or real gas.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

21. **Statement-1:** Heat of neutralization of CI and NaOH is same as that of H_2SO_4 with NaOH.

Statement-2: HCI, H_2SO_4 and NaOH are all strong electrolyte.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

22. **Statement-1:** A reaction which is spontaneous and accompanied by decrease of randomness must exothermic.

Statement-2: All exothermic reactions are accompanied by decrease of randomness.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

TRUE AND FALSE TYPE QUESTIONS

23. Consider the following statements.

S_1: Change in state function between two states is a definite quantity and does not depend on path.

S_2: Intensive properties cannot be algebraically added or subtracted.

S_3: Ratio of two extensive properties result into a parameter that depends on the amount of substance.

S_4: Molar heat capacity is a path function.

The correct order of true/false of the above statements is

(a) FTFT (b) FFFT

(c) TTFT (d) TTTF

24. Consider the following statements

S_1: Unit of molar entropy of a substance is SI system is Joule / Kelvin

S_2: Molar entropy of vapourization of ice is –ve.

S_3: In adiabatic free expansion, heat involved is zero and therefore entropy change mil be zero.

S_4: At absolute zero temperature, entropy of a perfectly crystalize substance is zero.

(a) TFFT (b) TFTT

(c) FFFT (d) FFTT

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

Chemical reactions are invariably associated with transfer of energy miner in form of heat or light. In the laboratory, heat changes in physical and chemical processes are measured with an instrument called calorimeter. Heat change in the process is calculated as:

$q = ms\,\Delta T$ s = specific heat J/K-gm

$= C\,\Delta T$ C = heat capacity J/K

In Bomb calorimeter measurement are taking at constant volume.

So heat of reaction at constant volume:

$q = \Delta U$ (Internal energy change)

Here, heat is released by combustion so sign of AU and heat should be negative. In water colarimeter measurement are taking at constant pressure.

So, $q_p = \Delta H$

$q_p = q_v + P\,\Delta V$

$\Delta H = \Delta U + \Delta n_g RT$

25. Match the list-I and list-II and select the answer:

List-I (Unbalanced reaction)	List-II
(a) $CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O$ *(t)*	(i) $\Delta H = \Delta U$
(b) $C_6H_6(\ell) + O_2(g) \rightarrow 6CO_2(g) + 3H_2O$ *(t)*	(ii) $\Delta H = \Delta U - RT$
(c) $S(\ell) + O_2(g) \rightarrow SO_2(g)$	(iii) $\Delta H = \Delta U - 2RT$
(d) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	(iv) $\Delta H = \Delta U - \frac{3}{2}RT$

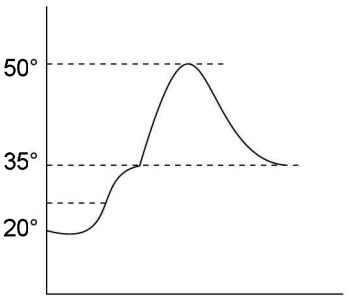
(a) (a) - (iii) (b) - (iv) (c) - (i) (d) - (ii)

(b) (a) - (ii) (b) - (iii) (c) - (i) (d) - (iv)

(c) (a) - (iii) (b) - (iv) (c) - (ii) (d) - (i)

(d) (a) - (ii) (b) - (i) (c) - (iii) (d) - (iv)

26. What volume of AT should be used for the calorimeter experiment when the following graphical results are obtained?



(a) 15° (b) 35°

(c) 50° (d) 30°

27. The heat capacity of a bomb calorimeter is 100 J/K. When 1 gm C_7H_16 *(1)* was burnt in this calorimeter, the temperature increases by 5°C. The value of ΔH in KJ/mole at 300 K temperature will be

(a) –50 (b) –40.03
(c) –59.97 (d) none

COMPREHENSION-2

J.W. Gibbs and H.Von Helmoltz had given two equations and are known as Gibbs-Helmholtz equation. One equation can be expressed in terms of change in free energy (ΔG) and enthalpy (ΔHD) while other can be expressed in terms of change in internal energy (ΔE) and work function (ΔW)

$$\Delta G = \Delta HD + T\, d\left(\frac{\Delta G}{dT}\right)_P \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\Delta W = \Delta E + T.d\left(\frac{\Delta W}{dT}\right)_V \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where T is temperature equation (1) is obtained at constant pressure, while equation (b) is obtained at constant volume system. It is observed that for the reaction.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Free energy change at 25°C is –33 kJ
while at 35°C is –28 kJ which are at a constant pressure.

28. What would be the difference between enthalpy change at 25°C and 35°C for a given reaction:
(a) 4 kJ (b) 5 kJ
(c) 3 kJ (d) zero

29. What would be the free energy change at 30°C
(a) 30.5 kJ (b) 33 kJ
(c) –28 kJ (d) –30.5 kJ

30. Internal energy change at 25°C is E_1, while at 35°C is E_2 then
(a) $E_1 = E_2$ (b) $E_2 > E_1$
(c) $E, > E_2$ (d) None

COMPREHENSION-4

The enthalpy in the process

$$HCl + nH_2O \rightarrow HCl \text{ in n moles of } H_20$$

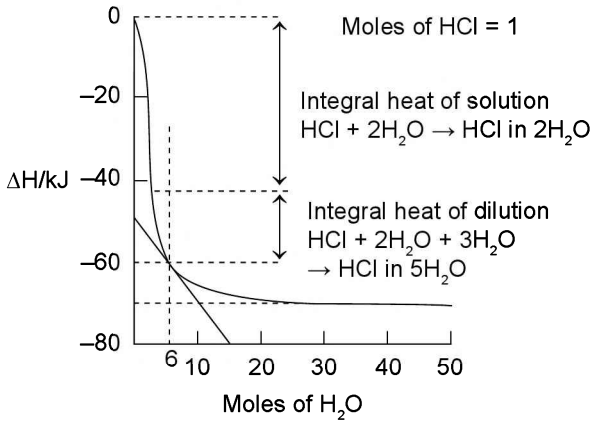
where n is the number of moles of water, is called the **integral heat of solution.** When 'n' is large enough that continous addition of water does not increase the heat of solution, one simply writes

$$HCl + aq \rightarrow HCl\,(aq)$$

The enthalpy for this process is the limiting value for the integral heat of solution. The enthalpy for the process

$$HCl \text{ in n moles of } H_2O + mH_2O \longrightarrow HCl \text{ in } (n+m) \text{ moles of } H_2O$$

is called the **integral heat of dilution.** These quantities are indicated in figure. Another quantity of interest is the **differential heat of solution,** defined as the slope of the enthalpy curve. The heats of solution depend on the composition of the solution as shown in the figure



31. Integral heat of solution for the following step is :
$HCl + 5H_2O \rightarrow HCl\,(5H_2O)$
(a) –12 kJ (b) –44 kJ
(c) + 60 kJ (d) –60 kJ

32. What is the enthalpy change for the reaction
HCl (aq) → HCl (aq)
(a) –80 kJ/mole (b) –60 kJ/mole
(c) –70 kJ/mole (d) –20 kJ/mole

33. Approximate value of differential heat of that solution in which 1 mole of Cl is dissolved in 6 mole of water is:
(a) – 2.4 kJ (b) – 3.33 kJ
(c) – 1.5 kJ (d) + 3.33 kJ

COMPREHENSION-5

A gaseous sample is generally allowed to do only expansion/compression type of work against its surroundings. The work done in case of an irreversible expansion (in the intermediate stages, of expansion/compression the states of gases are not defined). The work done can be calculated using

$$dW = -N_{ext}\, dV$$

while, in case of reversible process the work done can be calculated using

$$dw = -PdV$$

where P is pressure of gas at some intermediate stages. Like for an isothermal reversible process.

$$\text{Since, } P = \frac{nRT}{v} \text{ so}$$

$$W = \int dw = -\int_{V_i}^{V_f} \frac{nRT}{v}.dv = -nrT\ln\left(\frac{V_f}{V_i}\right)$$

Since, dw = – PdV, so magnitude of work done can also be calculated by calculating the area under the PV curve of the reversible process in PV diagram.

34. An ideal gaseous sample at initial state i $(P_0V_0T_0)$ is allowed to expand to volume $2V_0$ using two different processes in the first process the equation of process is $PV^2 = K_1$ and in second process the equation of the process is $PV = K_2$. Then

(a) work done in first process will be greater than the work in second process (magnitude wise)

(b) The order of values of work done can not be compared unless, we know the value of K_1 and K_2.

(c) value of work done (magnitude) in second process is greater in above expansion irrespective of the value of K_1 and K_2.

(d) Ist process is not possible

35. There are two samples of same gas initially under similar initial state. Gases of both the samples are expanded. Ist sample using reversible isothermal process and IInd sample using reversible adiabatic process till final pressures of both the samples becomes half of initial pressure, then

(a) Final volume of Ist sample < final volume of IInd sample

(b) Final volume of IInd sample < final volume of Ist sample

(c) final volumes will be equal

(d) Information is insufficien

36. In the above problem

(a) work done by gas in Ist sample > work done by gas in IInd sample

(b) work done by gas in IInd sample > work done by gas in Ist sample

(c) work done by gas in Ist sample = work done by gas in IInd sample

(d) none of these

37. If four identical samples of an ideal gas initially at similar state (P_0, V_o, T_0) are allowed to expand to double their volumes by four different processes.

I: by isothermal irreversible process

II: by reversible process having equation

$P^2 V$ = constant

III: by reversible adiabatic process

IV: by irreversible adiabatic expansion against constant external pressure.

Then in the graph shown the final state is represented by four different points then, the correct match can be:

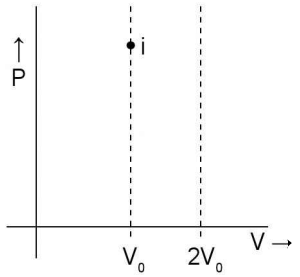
(a) 1 - I , 2 - II, 3 - III, 4 - IV

(b) 1 - II , 2 - I, 3 - IV, 4-III

(c) 2 - III, 3 - II, 4 - I, 1 - IV

(d) 3 - II, I - I, 3 - IV, 4 - III

38. Two samples (initially under same states) of an ideal gas are first allowed to expand to double their volume using irreversible isothermal expansion against constant external pressure, then samples are returned back to their original volume first by reversible adiabatic process and second by reversible process having equation PV^2 = constant then



(a) final temperature of both samples will be equal

(b) final temperature of first sample will be greater than of second sample

(c) final temperature of second sample will be greater than of first sample

(d) none of these

COMPREHENSION-6

Spontaneity of any process can be predicted with the help of ΔS_{total}. But this requires calculation of changes in system as well as surroundings. If some criteria (depending upon the system only) can be developed for checking spontaneity under specific conditions, then that would be a more useful parameter. The criteria can be derived from Clausius inequality.

$T\,dS \geq q$, > sign for reversible process

= sign for reversible process

or $T\,dS > dB - W$ for an irreversible Process

or $T\,dS_{sy}s > dU_{sys} + p\,dV$ [consider no non-PV work]

If U and V are constant,

$T\,dS_{sys} > 0$

or $(dS)_{u\,v} > 0$ for spontaneous process

If V and T are constant

$T\,dS > dU$

or $dB - T\,dS < 0$

As temperature is constant, $dU - d(TS) < 0$

or $d(U - TS) < 0$

Another state function A(Helmholtz's function) = B – TS

A decrease in Helmholtz function (A) under constant volume and temperature is the criteria of spontaneity of a process.

39. For a spontaneous process, if entropy and volume are constant, the internal energy of system must
(a) increase (b) decrease
(c) remain constant (d) be zero

40. If a state function G is defined such as O = H – TS, then dO must decrease for a spontaneous process (involving only PV work) occuring at
(a) Constant volume and temperature
(b) Constant pressure and temperature
(c) Constant volume and pressure
(d) Constant entropy and volume

41. For an irreversible cyclic process $\oint \frac{dq}{T}$ is.
(a) equal to zero
(b) greater than zero
(c) less than zero
(d) equal to chance in Oibb's energy.

COMPREHENSION-8

The contributions of both heat (enthalpy) and randomness (entropy) shall be considered to the overall spontaneity of a process. When deciding about the spontaneity of a chemical reaction or other process, we define a quantity called the Gibb's energy change (ΔG).

$$\Delta G = \Delta H - T\Delta S$$

where, ΔH = Enthalpy change ; ΔS = Entropy change; T = Temperature in kelvin.

If $\Delta G < 0$, Process is spontaneous ; $\Delta G = 0$, Process is at equilibrium, $AG > 0$, Process is non-spontaneous.

42. For the change H_2O (s, 273 K, 2 atm) $\longrightarrow$ H_2O (ℓ, 273K, 2 atom), choose the correct option.
(a) AG = 0 (b) AG < 0
(c) AG > 0 (d) None

43. 5 mole of liquid water is compressed from 1 bar to 10 bar at constant temperature. Change in Gibb's energy (ΔG) in Joule is t [Density of water = 1000 kg/m^3].
(a) 18 (b) 225
(c) 450 (d) 900

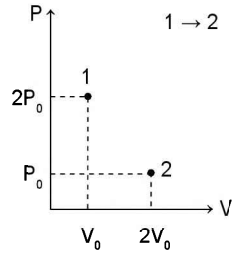
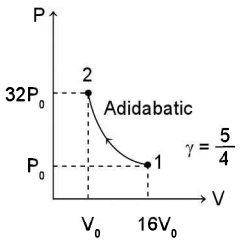
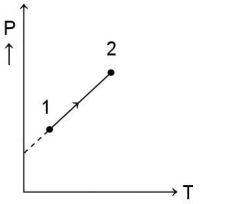
44. Quick lime, CaO is produced by heating limestone, CaCO3 to drive off CO_2 gas.

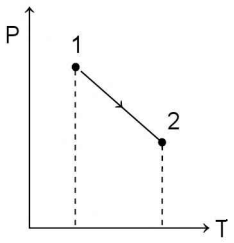
CaCO3 (s) $\rightarrow$ CaO (s) + CO_2 (g), ($\Delta H°$) = 180 KJ, $\Delta S°$ = 150 J/K.

Assuming that variation of enthalpy change and entropy change with temperature to be negligible, choose the correct option :
(a) Decomposition of $CaCO_3$ (s) is never spontaneous.
(b) Decomposition of $CaCO_3$ (s) becomes spontaneous when temperature is less than 900°C.
(c) Decomposition of $CaCO_3$ (s) becomes non-spontaneous when temperature is greater than 1000°C
(d) Decomposition of $CaCO_3$ (s) becomes spontaneous when temperature is greater than 927°C.

MATCH THE COLUMN TYPE QUESTIONS

45.

Column-I **(For a definite amount of an ideal gas)**	**Column-II** **(Enthalpy change I work done)**
W > 0 (s)W < 0	
(a) 	(p) AH >°
(b) 	(q) $\Delta H = 0$
(c) 	(r) W > 0

(d) 

(s) W < O

46. The feasibility of a chemical reaction can be explained based on ΔH, ΔS and ΔG, so answer the following:

Column-I	**Colomn-II**
(a) $20_3(g) \rightarrow 30_2(g)$	(p) ΔH = +ve, ΔS = –ve
(b) $30_2(g) \rightarrow 20_3(g)$	(q) ΔH = –ve, ΔS = +ve
(c) $NH_2COONH_4(s) \xrightarrow{\text{Low temp.}} 2NH_3(g) + CO_2(g)$	(r) ΔG = +ve
(d) Ice $\rightleftharpoons$ $H_2O(\ell)$ at room temperature 25°C	(s) ΔH = –ve (t) ΔG = —ve

47. Match the following:

Column-I	**Column–II**
(c) For spontaneous reaction	(p) $\sum(\text{B.E.})_R - \sum(\text{B.E.})_P$
(b) For endothermic reaction	(q) ΔH = ΔE
(c) Bond dissociation energy	(r) ΔG = –ve
(d) For solids and liquids in a therrnochemical reaction	(s) $\sum H_P > \sum H_R$

48. Match the following:

Column-I	**Column-II**
(a) $\Delta H = q_p$	(p) $\Delta H_f^0 = 0$
(b) Kirchhoff's equation	(q) A definite quardit
(c) H^+(aq.)	(r) Path function
(d) Spontaneous process	(s) ΔG > 0
	(t) $\Delta S^\circ_{\text{Total}} > 0$
	(u) $\Delta H_2 - \Delta H_1 = \Delta C_P(T_2 - T_1)$

49. Match the column.

Column-I	**Column-II**
(a) Perfectly crystalline solid	(p) $\Delta H_{sys} = 0$
(b) Reversible cyclic process	(q) $\lim_{T \to 0} S \to 0$
(c) Irreversible cyclic process	(r) $\Delta S_{surrounding} = 0$
(d) Any adiabatic process	(s) $\Delta U_{sys} = 0$ (t) net heat change is zero

50. Based on data given below, match column-I and column-II

$3X(g) \xrightarrow{250K, 1atm} X_3(g)$, ΔH = – 200 KJ/mol; ΔS = – 300 J/K/mol

$X(t) \xrightarrow{1 atm, 250k} X(g)$, $\Delta H_{vap} = 10$ KJ/mol

$X_3(\ell) \xrightarrow{250K, 1atm} X_3(\ell)$, $\Delta H_{vap} = 80$ KJ/mol

X_3 (g, 250 K, 1 atm) ⟶ X_3 (g, 500 K, 1 atom) ΔH =100 KJ/mol;

ΔS = 100 J/K/mol; ΔG = 60 kJ/ml Normal boiling point of X = 250 K,

Normal boiling point of X_3 = 500 K,

Enthalpy change and entropy change of cooling X. (1) to lower temperature is negligible.

Column-I	**Column-II**
(a) For $3X(\ell) \rightarrow X_3(\ell)$, ΔS in J/K/mol is	(p) 40
(b) For $3X(\ell) \xrightarrow{250K, 1atm} X_3(\ell)$, ΔH in KJ/mol is	(q) –150
(c) For $3X(\ell) \xrightarrow{250K, 1atm} X_3(\ell)$, ΔG in KJ/mol is	(r) –240
(d) For $X(\ell) \xrightarrow{250K, atm} X$ (g), ΔS in J/Klmol is	(s) – 65

SUBJECTIVE TYEP QUESTIONS

SHORT SUBJECTIVE

51. Only $\mathbf{N_2}$, **CO** and CO_2 gases remain after 0.72 gm of carbon is treated with one litre of air at 27°C and 4.92 atm pressure. Assume air composition O_2= 0%, $\mathbf{N_2}$ = 79% and CO_2 = 1% (by volume). The heat evolved (in Kcal) under constant pressure is:

Given : $C + O_2 \longrightarrow CO_2$, $\Delta H = -100$ Kcal/mol

$C + O_2 \longrightarrow CO$, $\Delta H = -25$ Kcal/mol

52. A sample of an ideal gas (Poisson's ratio = $\frac{7}{5}$) in a state X (44.8 litre 1 atm, 273 K) is taken to a state (44.8 litre 2 atm, 546 K). The entropy change (in calories) is [Given In 2 = 0.7 and RT = 22.4 at 0°C temperature]

53. It is known that entropy of neutralization of a strong acid and strong base is –13.68 kcal/mol. If enthalpy of neutralization of N_2H_4 (hydrazine) with strong acid is equal to –11.68 kcal/mol, then enthalpy of the reaction $N_2H_4 + H_2O \longrightarrow N_2H_5$ (aq) + OH^- (aq) in Kcal/mol is:

54. All of HgO (s) is 20 kcal/mol. The mass (in gm) of mercury, which can be liberated if 800 cal of heat is given to excess HgO (s) is:

55. The magnitude of work done (in kcal) when 140 gm of Mg (s) is reacted with excess of hydrochloric acid in an open vessel at 27°C is.

56. Heat supplied to the carnot engine is 37.3 kJ. How much useful work in kJ can be done by engine which works between 10°C and 100°C.

57. For the synthesis of ammonia of 300 K:

$N_2(g) + 3H_{2(g)} \rightarrow 2NH_3(g)$

Calculate the value of $\Delta G°$ in Kcal and give your answer in magnitude by using the following data:

	N_2	H_2	NH_3
$\Delta H°_f$ (Kcallmole)	0	0	–10
S° (Cal/K-mole)	40	30	45

58. If a monatomic ideal gas from state (5 atm, 1 It, 300K) is expanded to 5 L volume by reversible adiabatic process and reversible Isothermal process seperately. What is the value of $2(w_{isothermal} - w_{adiabatic})$ in atm^x L.

(Given: $(1/4)^5 I^3 = 0.1$, In 2 = 0.3).

59. Calculate the pH at which the following conversion (reaction) will be at equilibrium in basic medium

$I_2(s) \rightleftharpoons I^-(aq) + IO_3^-(aq)$

when the equilibrium concentrations at 300 K are $[I^-]$ = 0.10 M and $[IO_3^-]$ = 0.10 M

{Given that $\Delta G_f°(I^-, aq) = -50$ kJlmole, $\Delta G_f°(IO_3^-, aq) = -123.5$ kJlmole,

$\Delta G_f°(H_2O, \ell) = -233$ kJ/mole,

$G_f°(OH^-, aq) = -150$ kJlmole, Ideal gas constant = R

$= \frac{25}{3}$ Jmole^{-1}K^{-1}

ANSWER KEYS

1. (d)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (d)	**8.** (b)	**9.** (d)	**10.** (d)
11. (d)	**12.** (d)	**13.** (a)	**14.** (a, b, d)	**15.** (b, c, d)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (b)	**20.** (c)
21. (a)	**22.** (c)	**23.** (c)	**24.** (c)	**25.** (a)	**26.** (d)	**27.** (c)	**28.** (d)	**29.** (d)	**30.** (c)
31. (d)	**32.** (c)	**33.** (a)	**34.** (c)	**35.** (b)	**36.** (a)	**37.** (b)	**38.** (c)	**39.** (b)	**40.** (b)
41. (c)	**42.** (b)	**43.** (d)	**44.** (d)	**45.** (a – s, q), (b – r, p), (c – s, p), (d – s, p)					

46. (a –q, t), (b – p, r), (c – r), (d – t) **47.** (a – r), (b – s), (c – p) (d – q) **48.** (a – q), (b – u), (c – p), (d – t)

49. (a – q), (b – p, r, s, t), (c – p, s), (d – r, t) **50.** (a – r), (b – q), (c – t), (d – p)

58. $= 2(W_{Isothermal} - W_{adtabatic}) = 2 \times \left(-3 + \frac{9}{2}\right) = 3$

HINTS AND EXPLANATIONS

1. (d) $\Delta ng = 0$, $\Delta H° = \Delta U° = -185$ KJ

For 3 mole, $\Delta U° = 3x(-185) = -555$ KJ

8. (b) $0.42 = a(10)^3$

$\Rightarrow a = 0.42 \times 10^{-3}$

$$S = \int_0^{10} \frac{C_{p.m.}}{T}$$

$$dT = \int_0^{10} aT^2 = \frac{a}{3}[10^3 - 0] = \frac{0.42}{3} = 0.14 J/K\text{-mol}$$

9. (d) $H_2O(g) \rightleftharpoons H_2O + \frac{1}{2} O_2$

$1 - \alpha \qquad \alpha \qquad \alpha/2$

$K_P = \frac{\alpha \times (\alpha/_2)^{1/_2}}{(1-\alpha)} \times \frac{P}{(1+\alpha/_2)} = 11.62 \times 10\text{-}11 \text{ (atm)}^{1/2}$

$\Delta G° = -RT \ln K_p = -45.76 \text{ kcal} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

10. (d) $\frac{T_2}{T_1} = \frac{6}{3}$

$\Delta S = 2.303 \times n \left\{ C_p \log_{10} \frac{T_2}{T_1} + R \log_{10} \frac{P_1}{P_2} \right\}$

$\Delta S = 2.303 \times 1 \left\{ 10.96 \log_{10} \frac{6}{3} + R \log_{10} \frac{20}{10} \right\}$

$\Delta S = 27.22 \text{ J.K}^{-1} \text{ mol}^{-1}$

11. (d) Since work done on the system, is maximum in single stage compression, hence all other adiabatic points will fall between 1 and 2.

12. (d) As dew formation is spontaneous process, therefore entropy or randomness of the universe will increase. As randomeness of system has decreased but randomness of the surrounding will increase larger so that change is positive.

13. (a) All product and reactants are in solid state
So $\Delta S° \approx 0$
$\Delta G° = \Delta H - T\Delta S°$
So $\Delta G° \approx \Delta H°$

14. (a, b, d)

$\Delta S = nC_V \text{ In} \left(\frac{T_f}{T_i} \right) + nR \text{ In} \left(\frac{T_f}{T_i} \right)$

$\Delta H = nC_p \Delta T$

$\Delta E = nC_V \Delta T$

$\Delta G = \Delta H - \Delta(TS)$

25. (a) $\Delta H = \Delta U + \Delta n_g RT$ for (a) $\Delta n_g = -2$
(b) $\Delta n_g = -\frac{3}{2}$
(c) $\Delta n_g = 0$
(d) $\Delta n_g = -1$

26. (d) From combustion of fuel, the temperature of calorimeter raises and reaches to maximum value and then it decreases due to heat loss to the surrounding.
So, $\Delta T = T_{max} - T_{initial} = 50 - 20 = 30°$

27. (c) $C_7H_{16}(\ell) + 110 \longrightarrow 7CO_2(g) + 8H_2O(\ell)$

$q = C\Delta T = 5 \times 100 = 500 \text{ J}$

$\Delta V = \frac{q}{n} = -\frac{500}{\frac{1}{100}} = -50 \text{ KJ/mole (heat release).}$

$\Delta H = \Delta U + \Delta n_g RT = -50 - 4 \times \frac{8.31 \times 300}{1000}$

$(\Delta n_g = -4)$

$= -59.97 \text{ KJ/mole.}$

28. (d) $\Delta G_1 = \Delta H_1 + T_1 \, d \left(\frac{\Delta G}{dt} \right)_P$

$\Delta G_2 \, \Delta H_2 + T_2 \, d \left(\frac{\Delta G}{dt} \right)_P$

$\Delta G_2 \, \Delta G_2 = (\Delta H_2 - \Delta H_1) + (T_2 - T_1) \, d \left(\frac{\Delta G}{dt} \right)_P$

$(\Delta H_2 - \Delta H_1) = (\Delta G_2 - \Delta G_1) - (T_1 - T_2) \left[\frac{\Delta G_2 - \Delta G_1}{T_2 - T_1} \right]$
$= 0$

29. (d) $\Delta S = -d \left(\frac{\Delta G}{dt} \right)_P = -\left[\frac{\Delta G_2 - \Delta G_1}{T_2 - T_1} \right]$

$= -\left[\frac{-28 - (-33)}{308 - 298} \right]$

$= -0.5 \text{ KJ/K}$

$\Delta G_1 = \Delta H_1 + T_1 \, d \left(\frac{\Delta G}{dt} \right)_P$

$-33 = \Delta H_1 + 298 \times 0.5$

$\Delta H_1 = -33 - 149 = -182 \text{ KJ/mole}$

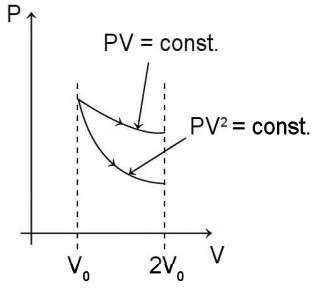
Now, $\Delta G = \Delta H + T.d$

$\Delta G = -182 + 303 \times 0.5 = -30.5 \text{ KJ}$

This is average of ΔG at 25°C of 35°C.

30. (c) $\Delta H_1 = \Delta E_1 + \Delta n_g RT$
$\Delta H_2 = \Delta E_2 + \Delta \, n_g RT_2$
So $\Delta E_1 + \Delta n_g RT_1 = \Delta E_2 + \Delta n_g RT_2$
$(\Delta E_1 - \Delta E_2) = \Delta n_g R(T_2 - T_1)$
But $(\Delta E_1 - \Delta E_2) > 0$
So $(\Delta E_1 > \Delta E_2)$

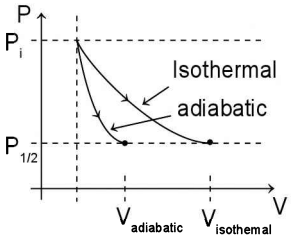
34. (c) Work done in isothermal process will be more than PV^2 = constant process whatever the value of K_1 and K_2 is



$$W_I = -\int_{V_0}^{2V_0} \frac{K_0}{2V_0} dv = -\frac{k_1}{2V_0} = -\frac{1}{2} P_0 V_0$$

$$W_{II} = -K_2 \text{ In } \frac{2V_0}{V_0} = -0.7\, P_0 V_0.$$

$|W_{II}| > |W_I|$

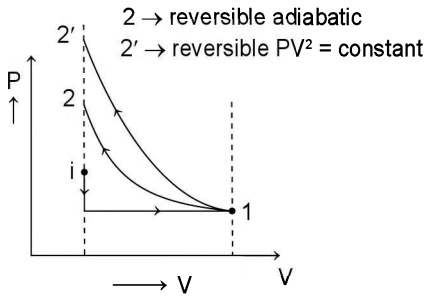


35. (b) Clearly $(V_f)_{isothermal} > (V_f)_{adiabatic}$

36. (a) Magnitude of work done in isothermal expansion process is more than adiabatic expansion process.

37. (b) Work done is least incase of reversible adiabatic process. Work done will be greatest in the process P^2V = Constant

38. (c) Processes may be represented as



If initial temperature is same, then the temperature in 2nd case is more.

42. (b) H_2O (s) → H_2O (ℓ),
As P↑, more H_2O (ℓ) is formed.
At P = 1 atm, ΔG = 0.

43. (d) $\Delta G = V(P_2 - P_1) = 5 \times 18 \times 10^{-6} (101 - 1) \times 10^5$
Joule $= 5 \times 18 \times 10^{-1} \times 10^2 = 900$ Joule.

44. (d) $T = \frac{\Delta H}{\Delta S} = \frac{180 \times 10^3}{150} = 120K.$
Temperature = 1200 – 273 = 927°C
For ΔG < 0, T > 927°C

45. (a – s, q), (b – r, p), (c – s, p), (d – s, p)

46. (a – q, t), (b – p, r), (c – r), (d – t)

47. (a – r), (b – s), (c – p, (d – q)
All the matching is obvious from the fact see the formula.

48. (a – q), (b – u), (c – p), (d – t)

49. (a – q), (b – p, r, s, t), (c – p, s), (d – r, t).
(a) IIIrd law states $\lim_{x \to 0} S \to 0$ for perfect solid.
(b) In reversible cyclic process the every net energy change is zero.
(c) In irrcyclic process $\Delta S_{sys} = 0$ but $\Delta S_{surrounding} > 0$ by IIrd law and all state function are zero.
(d) In adiabatic process net heat change is zero so $\Delta S_{surrounding} = 0$.

50. (a – r), (b – q), (c – t), (d – p).
3X (ℓ, 250K, 1 atm) x_3 (ℓ, 250K, 1 atm)
ΔH = 3 × 10 ΔH = 0

$\Delta G = 0, \quad \Delta S = \frac{3 \times 10 \times 10^3}{250} = 120$ J/K ΔS = 0

3X (g, 250K, 1 atm) X, (ℓ, 500K, 1 atm)
ΔH = – 200 KJ/mol ΔG = 0
ΔS = – 300 JK/mol ΔH = – 80 KJ/mol

$\Delta G = -125$ KJ/mol $\quad \Delta S = \frac{80 \times 10^3}{500} = -160$JK/mol

X_3 (g 250, 1 atm) $\xrightarrow{\Delta H = 100 J/mol/K}$ X3 (g, 500K, 1 atm)
ΔS = + 100 J/mol/K
ΔG = 60 KJ/mol

Overall, ΔH = 3 × 10 – 200 + 100 – 80 + 0 = 30 – 200 + 100 – 80 = –150 KJ/mol.
ΔS = 20 – 300 + 100 –160 + 0 = – 240 J/mol/K.
ΔG = 0 + (– 125) + 0 + 0 = – 65 KJ/mol.

51. $n = \frac{4.92 \times 1}{24.6} = 0.2$ mol.

$n_{O_2} = 0.2 \times 0.2 = 0.4$ mol

$C + \frac{1}{2} O_2 \longrightarrow CO$

0.06 0.04mol, 0.01 0.06

$CO + \frac{1}{2} O_2 \rightarrow CO_2$

0.06 0.01 0.02
0.04

Heat evolved = 0.04 × 25 + 0.02 × 100 = 1 + 2 = **3 Kcal.**

52. $\Delta S_{X-Y} = nC_V \text{In}\ \frac{T_2}{T_1} + nR \text{In}\ \frac{T_2}{T_1}$

$= \frac{44.8 \times 1}{22.4} \times \frac{5}{2} \times R \times \text{In}\ \frac{546}{273} = 2 \times \frac{5}{2} \times 2 \times \text{In}\ 2$

$= 10 \times 0.7 = 7$ cal.

53. $\Delta H_{ion} = 13.68 - 11.68 = 2$, kcal/mol.

54. $HgO\ (s) \rightarrow Hg\ (\ell) + \frac{1}{2}O_2$ 20kcal/mol.

Mol of Hg $(\ell) = \frac{0.8}{20}$ mol $\uparrow$.

Mass of Hg $(\ell) = \frac{0.8}{20} \times 200 = 8$ gm.

55. $Mg\ (s) + 2HCl\ (aq) \rightarrow MgCl2 + x_2$

$W = -P_{ext}\ (V_2 - V_1) = -\Delta nRT = -5 \times \frac{2 \times 300}{1000} = -3$ Kcal.

56. $T_1 = 10 + 273 = 283$ K;

$T_2 = 100 + 273 = 373$ K

Work = heat × efficienc

$= 37.3 \times \left(\frac{T_2 - T_1}{T_2}\right) = 37.3 \times \frac{373 - 283}{373} = 9KJ$

57. $\Delta H°_R = 2 \times \Delta H°\ f(NH_3) - 3 \times \Delta H°\ f(H_2) - \Delta H°f(N_2)$

$= -20$ Kcal

$\Delta S°_R = 2 \times S°\ f(NH_3) - 3 \times S°\ (H_2 - S°N_2 = 2 \times 45 - 3 \times 30 - 40 = -$ Cal/K

$\Delta G° = \Delta H° = -20 - \frac{300 \times (-40)}{1000} = -20 + 12 =$ -8 Kcal

58. Adtabatic process:

$P_2V_2^y = P_1V_1^y$

$P_2 \times (4)^y = 5 \times (1)^y$

$P_2 = 5 \times \left(\frac{1}{4}\right)^y = 0.5$

Isothermal process:

$w_{Isothermal} = -nRT \text{In}\ \frac{V_2}{V_1} = -PV \text{In}\ \frac{V_2}{V_1}$

$= -5 \times 1 \text{In}\ \frac{4}{7} = -5 \times 0.6 = -3$

$= 2(W_{Isothermal} - W_{adtabatic}) = 2 \times \left(-3 + \frac{9}{2}\right) = 3$

59. Balanced equation will be

$3I_2(s) + 6OH^- \rightleftharpoons 5I^-(aq) + IO_3^-(aq) + 3H_2O(\ell)$

$\Delta G° = 5 \times (-50) + (-123.5)$

$+ 3 \times (-233)$

$- 0 - 6 \times (-150)$

$= -172.5$ KJ/mol.

$\Delta G° = -172.5$ KJ mol^{-1}

$= -\frac{25}{3} \times 300 \times 2.3 \times 10^3 \log K$

$\log k = 30$

$10^{30} = \frac{10^{-5} \times 10^{-1}}{[OH^-]^6}$

So $[OH^-]$ 10^{-6}

SUBJECTIVE ANSWER TYEP QUESTIONS

24. Consider the following reactions:

$Au(OH)_3 + 4HCl \rightarrow HAuCl_4 + 3H_2O;$ $\Delta H = -2.8$ kcal

$Au(OH)_3 + 4HBr \rightarrow HAuBr_4 + 3H_2O;$ $\Delta H = +36.8$ kcal

If 1 mole of $HAuBr_4$ was mixed with 4 moles of HCl, 0.44 kcal heat was absorbed, what fraction of $HAuBr_4$ was converted into $HAuCl_4$? Also report the percentage conversion.

Sol. $Au(OH)_3 + 4HCl \rightarrow HAuCl_4 + 3H_2O;$ $\Delta H = -28$ kcal

$HAuBr_4 + 3H_2O \longrightarrow Au(OH)_3 + 4HBr;$ $\Delta H = +36.8$ kcal

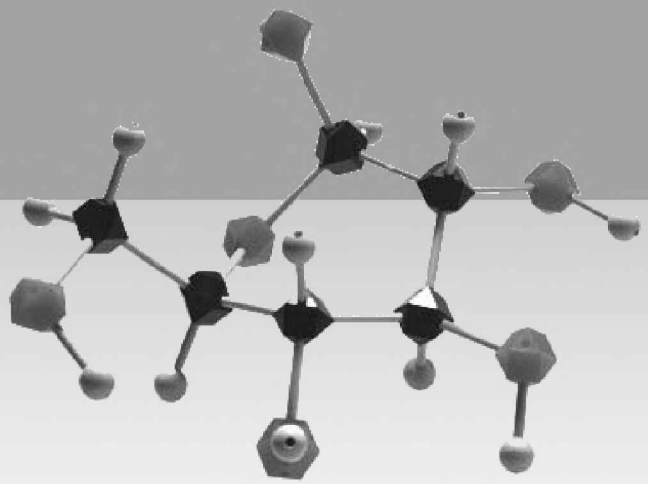
$\therefore$ $HAuBr_4 + 4HCl \longrightarrow HAuCl_4 + 4HBr;$ $\Delta H = 8.8$ kcal

$\therefore$ fraction of $HAuBr_4$ converted to $HAuCl_4$

$= \frac{0.44}{8.8} = 0.05$

$\therefore$ % of $HAuBr_4$ converted $= 0.05 \times 100 = 5\%$

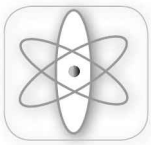
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CHAPTER 6

Chemical Equilibrium

INTRODUCTION



Chemical change occurs when the atoms that make up one or more substances rearrange themselves in such a way that new substances are formed. These substances are the components of the chemical reaction system; those components which decrease in quantity are called reactants, while those that increase are products.

A given chemical reaction system is defined by a balanced net chemical equation which is conventionally written as,

reactants → products

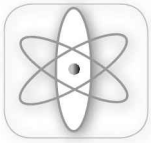
The first thing we need to know about a chemical reaction represented by a balanced equation is whether it can actually take place. If the reactants and products are all substances capable of an independent existence, then the answer is always "yes", at least in principle. This answer must always be qualified, however, by the following two considerations:

- Does the reaction take place to a sufficient extent to produce useful (or even detectable) quantities of products?

  This refers to the thermodynamics (energetics) of the reaction, which controls its tendency to occur. The concept of chemical equilibrium which we treat in this chapter addresses this question directly.

  Kinetics applies to the speed of the reaction, the concentration of product appearing (or of reactant disappearing) per unit time.
- Equilibrium applies to the extent of a reaction, the concentration of product that has appeared given unlimited time, or when no further change occurs.

LAW OF MASS ACTION



According to the law of mass action, the rate of reaction, at given temperature is directly proportional to the product of the active masses of the reacting substances each raised to power equal to corresponding stoichiometric coefficient appearing in balanced chemical equations. Law of mass action is applicable to elementary process (one step reaction).

Active mass of reactant (a) = Concentration × activity coefficien

i.e., a = Molarity × f

for dilute solution f = 1

Applying Law of mass action for general reversible reaction

Consider the following reaction:

- $aA(g) + b(B)(g) \rightleftharpoons cC(g) + dD(g)$

Rate of forward reaction $\propto [A]^a[B]^b$ at constant temperature 'T'

$r_f \propto [A]^a [B]^b$ …… constant T

or,

$r_f = K_f [A]^a[B]^b$ K_f = Rate constant for forward reaction

Similarly for backward reaction,

$r_b \propto [C]^c [D]^d$

$r_b = K_b [C]^c [D]^d$

K_b = Rate constant for backward reaction

The rate constants depends upon temperature and nature of reaction but these are independent of concentration.

Forward reaction will take place at a faster rate initially. At equilibrium, the rates of the two reactions will be equal and concentration of all the reactants and products will be constant.

At equilibrium, $r_f = r_b$

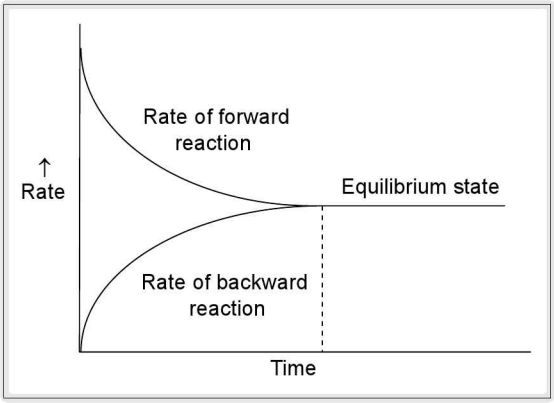


Fig. 6.1

$$K_f [A]^a[B]^b = K_B[C]^C[D]^d \quad K_{eq} = \frac{K_f}{K_B} = \frac{[C]^C[D]^d}{[A]^a[B]^b}$$

The concentration (active mass) of pure solid and pure liquid are constant. Here, 'B' is a pure solid. Hence, [B] is a constant.

$$K_{eq}[B]^b = \frac{[C]^c[D]^d}{[A]^a} = K_C \text{ (a new constant)}$$

$$K_C = \frac{[C]^c[D]^d}{[A]^a}$$

Hence, we see that pure solid and pure liquid cannot appear in the expression of K_C.

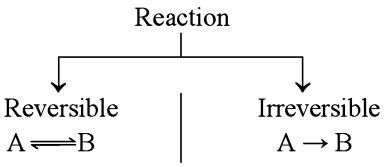
Concept of Reversible and Irreversible Reaction

If the equilibrium state is one in which significant quantities of both reactants and products are their, then the reaction is said to incomplete or ***reversible***.

The latter term is preferable because it avoids confusion with "complete" in its other sense of being finished, implying that the reaction has run its course and is now at equilibrium

- If it is desired to emphasize the reversibility of a reaction, the single arrow in the equation is replaced with a pair of hooked lines pointing in opposite directions, as in $A \rightleftharpoons B$. There is no fundamental difference between the meanings of $A \rightarrow B$ and $A \rightleftharpoons B$

In principle, all chemical reactions are reversible, but this reversibility may not be observable if the fraction of reactants in the equilibrium mixture is very small, or if the reverse reaction is **kinetically inhibited.** Those reactions can be termed irreversible reactions.



In the true sense, all chemical reactions are reversible. There are no irreversible chemical reactions. If this equilibrium constant (K_{eq}) has a very large value we can assume the concentration of 'A' is negligible as compared to concentration of 'B' formed at equilibrium.

So we tend to think 'A' has formed 'B' but the reverse reaction in which 'B' forms 'A' can be neglected. This is why, say that this $A \rightarrow B$ is almost an irreversible reaction.

$$A \rightleftharpoons B \qquad K_{eq} = \frac{[B]}{[A]} \text{ very high (say } 10^{10})$$

Reversible reactions with a very high value of equilibrium constant can be regarded almost as an irreversible reaction.



Worked-out Examples

1. For the reaction equilibrium;

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$; the concentration of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol/L respectively. The value of K_c for the reaction is: **[AIEEE-2003]**

(a) 3×10^{-3} M (b) 3×10^{3} M

(c) 3.3×10^{2} M (d) 3×10^{-1} M

Solution (a) $K_c = \frac{[NO_2]^2}{[N_2O_4]}.K_c = \frac{(1.2\times10^{-2})^2}{4.8\times10^{-2}} = K_c = 3 \times 10^{-3}$ moles lit^{-1}

2. What is the equilibrium constant for the reaction: $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$; **[AIEEE-2004]**

(a) $K_c = \frac{1}{[O_2]^5}$ (b) $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]}$

(c) $K_c = [O_2]^5$ (d) $K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$

Solution (a) (Note that pure solid does not appear in the expression of K_c)

State of Equilibrium

When the equilibrium is reached, neither the forward reaction nor the reverse reaction stops. The rates of the two opposite reactions become equal. This is why the equilibrium is not static equilibrium; it is dynamic equilibrium.

When equilibrium is attained, there is no further change in the concentrations of any component, i.e., Concentration becomes independent of time.

$C \neq f(t)$
(concentration is not a function of time)

K_C depends only on temperature. If we try to change the concentration of any component at the equilibrium, the reactants and products will have to adjust their concentration as to keep the value of K_C constant.

The two diagrams below show how the concentrations of the three components of this chemical reaction change with time (under the conditions in which this particular reaction is usually carried out, the time scale is typically 10 to 100 minutes). Examine the two sets of plots carefully, noting which substances have zero initial concentrations, and are thus "products" of the reaction equations shown. Satisfy yourself that these two sets represent the same chemical reaction system, but with the reactions occurring in opposite directions. Most importantly, note how the final (equilibrium) concentrations of the components are the same in the two cases.

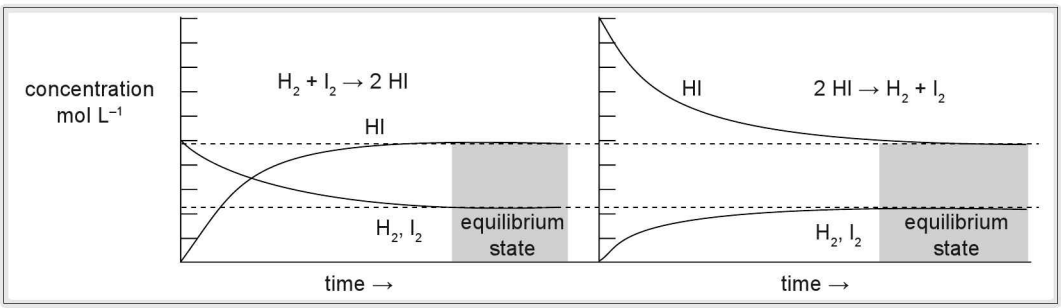


Fig. 6.2

The equilibrium state is independent of the direction from which it is approached. Whether we start with an equimolar mixture of H_2 and I_2 (left) or a pure sample of hydrogen iodide (shown on the right, using twice the initial concentration of HI to keep the number of atoms the same), the composition after equilibrium is attained (shaded regions on the right) will be the same.

Another equilibrium constant: K_p

In terms of partial pressures of gases equilibrium constant is denoted by K_p. Let us consider he following reaction $aA + bB \rightleftharpoons mC + nD$ (where all components are gases.)

The expression of K_p for this reaction is as follows $K_p = \frac{P_C^m \times P_N^n}{P_A^a \times P_B^b}$ ($PV = nRT$; $P = \left(\frac{n}{V}\right) RT$; $P = CRT$, $P \propto C$ at constant temperature)

Where P terms represent partial pressures of gases at equilibrium. Remember K_p does not include the pressure of solid or liquid.

In terms of mole fraction equilibrium constant is denoted by K_X.

$$K_p = \frac{P_C^m \times P_D^n}{P_A^a \times P_B^b}$$

Relation between K_p and K_C

Consider the following equilibrium $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$
For the above equilibrium K_C is given by,

For gas

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT$$

$$P = CRT$$

When temperature is constant

$$P \propto C$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a}$$

or

$$K_C = \frac{C_C^C C_D^d}{C_A^a}$$

Since pressure for the gaseous component is a measure of concentration, the equilibrium constant can be expressed interms of partial pressures of the gaseous exponents.

$$K_P = \frac{P_C^c P_D^d}{P_A^a} = \frac{(C_C RT)^C (C_D RT)^D}{(C_A RT)^a}$$

Pressure equilibrium constant or thermodynamic equilibrium constant.

$$K_P = \left[\frac{C_C^c C_D^d}{C_A^a}\right] RT^{[c+b-a]}$$

Equilibrium constant in terms of pressure depends only on temperature.

$$K_P = K_C(RT)^{\Delta n}$$

Δn_g = [the sum of the stoichiometric coefficient of gaseous product] – [Sum of stoichiometry coefficients of gaseous reactants

Unit of $K_P = (atm)^{\Delta n}$:

Hence, it is constant for a given reaction. This proves that K_P depends only on temperature (and on nature of reaction) and nothing else.



Worked-out Examples

3. The K_p value for an equilibrium is 0.82 atm at 27°C. Calculate the K_C value at the same temperature. ($R = 0.082$ L atm mol^{-1} K^{-1})

(a) $\frac{1}{300}$ (b) $\frac{1}{30}$

(c) 0.082 (d) can't be predicted as equation is not supplied

Solution (b) Note that K_p has unit $(atm)^{\Delta ng}$ = atm (according to equation)

$$\text{Hence, } \Delta ng = 1 \Rightarrow K_C = \frac{K_p}{RT} = \frac{0.82\,\text{atm}}{(0.082\,\text{L atm mol}^{-1}\,\text{K}^{-1})(300)} = \frac{1}{30} \text{ (we keep } K_C \text{ as unit less)}$$

4. For the reaction; $CO_{(g)} + ½O_2(g) \rightleftharpoons CO_{2(g)}$, K_p/K_c is: **[AIEEE-2002]**

(a) RT (b) $(RT)^{-1}$

(c) $(RT)^{-1/2}$ (d) $(RT)^{1/2}$

Solution (c) $K_p/K_c = (RT)^{\Delta n}$; $\Delta n = -\frac{1}{2}$

5. For the reaction $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$, the K_p/K_c is equal to: **[AIEEE-2004]**

(a) 1.0 (b) RT

(c) $\sqrt{RT}$ (d) 1/RT

Solution (d) $\Delta ng = -1 \Rightarrow K_p = K_c(RT)^{-1} \Rightarrow \frac{K_p}{K_c} = (RT)^{-1}$

6. For the reaction; $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$

$K_c = 1.8 \times 10^{-6}$ at 184°C and R = 0.083 JK^{-1} mol^{-1}. When K_p and K_c are compared at 184°C, it is found that: **[AIEEE-2005]**

(a) $K_p > K_c$ (b) $K_p < K_c$

(c) $K_p = K_c$ (d) $K_p \gtrless K_c$ depends upon pressures of gases

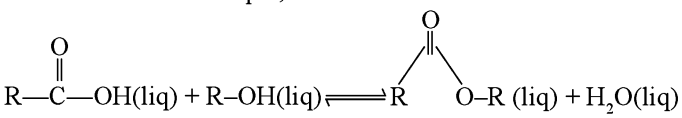
Solution (a) $K_p = K_c(RT)^{\Delta n} \because \Delta n = 3-2 = +ve \therefore K_p > K_c$

Equilibrium constant of a reaction involving condensed phase

The expression for the equilibrium constant of a reaction involving condensed phase (solid or liquid) and gaseous state is obtained by considering the concentrations or partial pressures of only the gaseous species. The concentration of condensed phases being constant are merged with the equilibrium constant.

Reactions for which K_c is only defined

Now consider another example,



$$\text{Acid} + \text{Alcohol} \rightleftharpoons \text{Ester} + H_2O(l)$$

For this reaction, K_p is not defined as there is no gas involved

$$K_C = \frac{[\text{Ester}][H_2O]}{[\text{Acid}][\text{Alcohol}]}$$

If product components are liquid then liquid is not neglected.

Water is taken up in expression of K_C because concentration of water will change with progress of reaction as all other components are liquid.



Worked-out Examples

7. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mole $litre^{-1}$, is **[IIT-2000]**

(a) $\frac{1.44\times10^{-5}}{(0.082\times500)^{-2}}$ (b) $\frac{1.44\times10^{-5}}{(8.314\times773)^{-2}}$

(c) $\frac{1.44\times10^{-5}}{(0.082\times773)^{2}}$ (d) $\frac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$

Solution (b) $K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$, (R in L.atm.$K^{-1}$ $mole^{-1}$).

8. For a given reversible reaction at a fixed temperature, equilibrium constants K_p and K_c are related by..... **[IIT-1994]**

Solution $K_p = K_c (RT)^{\Delta n}$;

Here, Δn = [the sum of the stoichiometric coefficient of gaseous product] – [Sum of stoichiometry coefficients of gaseous reactants]

R = gas constant, and T = absolute temperature.

9. For a gaseous reaction $2B \rightarrow A$, the equilibrium constant K is..... to/than K_c. **[IIT-1997]**

Solution Less; $K_p = K_c (RT)^{\Delta n}$

for $2B \rightarrow A$, $\Delta n = 1 - 2 = -1 \Rightarrow K_p = \dfrac{K_c}{RT}$ or $K_p < K_c$

Some facts about equilibrium constant

(a) The equilibrium constant of a forward reaction and that of its backward reaction are reciprocal of each other.

If $A + B \rightleftharpoons C + D \quad K = x$

Then $C + D \rightleftharpoons A + B \quad K' = \dfrac{1}{x}$

(b) If a chemical equation is multiplied by certain factor, its equilibrium constant must be raised to a power equal to that factor in order to obtain the equilibrium constant for the new reaction.

If, for $NO + \dfrac{1}{2}O_2 \rightleftharpoons NO_2 \quad K = \dfrac{[NO_2]}{[NO][O_2]^{1/2}}$

Then for $2NO + O_2 \rightleftharpoons 2NO_2 \quad K^1 = \dfrac{[NO_2]^2}{[NO]^2[O_2]} = K^2$

(c) If K_1, K_2 and K_3 are step-wise equilibrium constant for

$A \rightleftharpoons B$ (1)

$B \rightleftharpoons C$ (2)

$C \rightleftharpoons D$ (3)

Therefore, the equilibrium constant 'K' for $A \rightarrow D$ is given as follows:

$K = K_1 \times K_2 \times K_3$



Worked-out Examples

10. Write the equilibrium expression for the following equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

If K is calculated to have a value of 2.5 for the reaction above, what is the value of the equilibrium constant for the following reaction?

$$4HI_{(g)} \rightleftharpoons 2H_{2(g)} + 2I_{2(g)}$$

Solution The equilibrium constant expression for the reaction is,

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

The reaction has been doubled and reversed, so the new K is the reciprocal of the old K squared (since the reaction coefficients are doubled):

$$K' = \frac{1}{2.5^2} = 0.16$$

11. The equilibrium constant for the reaction;

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ at temperature T is 4×10^{-4}. The value of K_c for the reaction.

$NO_{(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$ at the same temperature is: **[AIEEE-2004]**

(a) 0.02 (b) 50

(c) 4×10^{-4} (d) 2.5×10^{-2}

Solution (b) $N_2 + O_2 \rightleftharpoons 2NO$

$$K_{c_1} = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$$

$$NO \rightleftharpoons \tfrac{1}{2} N_2 + \tfrac{1}{2} O_2$$

$$K_{c_2} = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]}$$

$$K_{c_2} = \sqrt{\frac{1}{K_{c_1}}} = \sqrt{\frac{1}{4\times10^{-4}}} = 50$$

12. The equilibrium constant for the given reaction:

$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$; $K_c = 4.9 \times 10^{-2}$

The value of K_c for the reaction:

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, will be: **[AIEEE-2006]**

(a) 416 (b) 2.40×10^{-3}

(c) 9.8×10^{-2} (d) 4.9×10^{-2}

Solution (a) $K_{c_1} = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 4.9 \times 10^{-2}$

$$K_{c_2} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \left[\frac{1}{K_{c_1}}\right]^2 = \left[\frac{1}{4.9\times10^{-2}}\right]^2$$

13. For the following three reactions I, II and III, equilibrium constants are given

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; K_1

(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; K_2

(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; K_3

Which of the following relations is correct? **[AIEEE-2008]**

(a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$

(c) $K_3 = K_1K_2$ (d) $K_3K_2^3 = K_1^2$

Solution (c) Reaction (iii) can be obtained by adding reactions (i) and (ii) therefore $K_3 = K_1.K_2$

14. If equilibrium constant for the reaction $A_2 + B_2 \rightleftharpoons 2AB$, is K, then for the backward reaction $AB \rightleftharpoons 1/2A_2 + 1/2\ B_2$, the equilibrium constant is 1/K. **[IIT-1984]**

Solution **False:** K for $A_2 + B_2 \rightleftharpoons 2AB$ is $\frac{[AB]^2}{[A_2][B_2]}$

K′ for $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$ is $\frac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]}$

or $(K')^2 = \frac{[A_2][B_2]}{[AB]^2} = \frac{1}{K}$

$\therefore\ K' = \sqrt{\frac{1}{K}}$

15. $A(s) + B(g) \rightleftharpoons C(g) + D(s)$ …… $K_{P_1} = x$

$2E(s) + 2B(g) \rightleftharpoons 2C(g) + 3F(s)$ …… $K_{P_2} = ?$

The value of K_{P_2} is

(a) x (b) 2x

(c) x^2 (d) can not be calculated

Solution (c) Solution $K_{P_1} = \frac{P_C}{P_B} = x \Rightarrow K_{P_2} = \frac{P_C^{\,2}}{P_B^{\,2}} = x^2$

Reaction Quotient

One use is to determine in advance whether a particular chemical system will be at equilibrium or not. To do this, we must introduce another concept, closely related to the equilibrium constant.

For a chemical system, whether in equilibrium or not, we can calculate the value given by the law of mass action. Only if the system is at equilibrium, will this value be the equilibrium constant. In general, we call this value the reaction quotient Q. Taking again the Haber equilibrium, we can write the reaction quotient for the system at any time.

$$3\ H_2 + N_2 \rightleftharpoons 2\ NH_3$$

$$Q = \frac{[P_{NH_3}]^2}{[P_{NH_3}]^3[P_{N_2}]}$$

In this case, we are not necessarily using equilibrium concentrations and hence, we calculated not the equilibrium constant K but the reaction quotient Q. We can now compare the two values as follows:

- $Q < K$: This implies that the reaction is not at equilibrium and that the reaction must proceed to the right (make more products) to get to equilibrium.
- $Q = K$: at this point the amount of products and reactants is just right to meet equilibrium conditions.
- $Q > K$: implies that there are too many products. The reaction will proceed to the left to produce more reactant (and lower the among of product) until $Q = K$.

Note: If you are not using the relative activities to calculate Q and K, you must compare a Q_c with a K_c, a Q_p with a K_p etc.



Worked-out Examples

16. Consider the Haber equilibrium at 500°C. K = 3.5 * 10^{-7}. Predict which way the equilibrium will shift for each of the following cases.

	$p(NH_3)$	$p(H_2)$	$p(N_2)$
(a)	4.16 kPa	8.3 kPa	403.5 kPa
(b)	0.83 kPa	1470 kPa	6.20 kPa
(c)	0.416 kPa	416 kPa	2.08×10^4 kPa

Solution (a)

$$Q = \frac{[P_{NH_3}]^2}{[P_{H_2}]^3[P_{N_2}]}$$

$$= \frac{(4.16/100)^2}{(8.3/100)^3(403.5/100)}$$

$$= 0.75$$

Since, Q > K the reaction will proceed to the left until equilibrium.

(b) $Q = \frac{(0.83/100)^2}{(1470/100)^3(6.20/100)} = 3.50 \times 10^{-7}$.

Since, Q = K the reaction is at equilibrium.

(c) $Q = \frac{(.416/100)^2}{(416/100)^3(208\times10^4/100)} = 1.1557 \Rightarrow 10^{-13}$

Since, Q < K the reaction will proceed to the right until equilibrium.

17. For the reaction $A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)}$ at 25°C, a 3 litre vessel contains 1, 2, 4 moles A, B and C respectively. Predict the direction of reaction if

(a) K_C for the reaction is 10

(b) K_C for the reaction is 15

(c) K_C for the reaction is 10.66

Solution $A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)}$

$[A] = 1/3\ [B] = 2/3, [C] = 4/3 \Rightarrow Q = \frac{\left(\frac{4}{3}\right)^3}{\left(\frac{1}{3}\right)\left(\frac{2}{3}\right)} = 10.66$

(a) Since, $K_C = 10 \Rightarrow Q > K_C$, thus reaction will occur in backward direction.

(b) Since, $K_C = 10 \Rightarrow K_C > Q$, the reaction will occur in forward direction.

(c) $\because$ $Q = K_C$ reaction is at equilibrium.

$K'' = \sqrt{1.37}$

18. When two reactants, A and B are reacted to give products C and D, the reaction quotient Q, at the initial stages of the reaction

(a) is zero
(b) decreases with time
(c) is independent of time
(d) increases with time

Solution (d) At initial stage of reaction, concentration of each product will increase and hence, Q will increase.

Le Chateliers Principle

Le Chateliers principle states that any change in a system at equilibrium results in a shift of the equilibrium in the direction which minimises the change. The law was originally applied only to pressure and was first published in a note as:

Any system in stable chemical equilibrium, subjected to the influence of an external cause which tends to change either its temperature or its condensation (pressure, concentration, number of molecules in unit volume), either as a whole or in some of its parts, can only undergo such internal modifications as would, if produced alone, bring about a change of temperature or of condensation of opposite sign to that resulting from the external cause.

Qualitative Idea of Le Chateliers Principle

Concentration

Changing the concentration of an ingredient will shift the equilibrium to the side that would reduce that change in concentration. The chemical system will attempt to partially oppose the change affected to the original state of equilibrium. In turn, the rate of reaction, extent and yield of products will be altered corresponding to the impact on the system.

This can be illustrated by the equilibrium of carbon monoxide and hydrogen gas, reacting to form methanol.

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

Suppose, we were to increase the concentration of CO in the system. Using Le Chatelier's principle, we can predict that the amount of methanol will increase, decreasing the total change in CO. If we are to add a species to the overall reaction, the reaction will favour the side opposing the addition of the species. Likewise, the subtraction of a species would cause the reaction to fill the "gap" and favour the side where the species was reduced. This observation is supported by the collision theory. As th the frequency of successful collisions of that reactant would increase also, allowing for an increase in forward reaction, and generation of the product. Even if a desired product is not thermodynamically favoured, the end product can be obtained if it is continuously removed from the solution.Hence, concentration of CO is increased,

How a system would behave if any of the parameter of the system at equilibrium be altered was first enunciated by Le-Chatelier (1885) and Braun (1886). They made a generalization that:

"If a system is in equilibrium, a change in any of the factors that determine the condition of equilibrium will cause the equilibrium to shift in such a way as to minimize the effect of this change."

This is a general statement and qualitatively applicable to all systems to predict their behaviour when parameters are changed. We shall use this principle, which is sometimes called 'the principle of mobile equilibrium'. To express the effects of pressure. temperature and concentration on chemical equilibrium.

Addition or removal of pure solid or pure liquid cannot disturb the equilibrium.

Pressure

Changes in pressure are attributable to changes in volume. The equilibrium concentrations of the products and reactants do not directly depend on the pressure subjected to the system. However, a change in pressure due to a change in volume of the system will shift the equilibrium.

Once again, let us refer to the reaction of nitrogen gas with hydrogen gas to form ammonia:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad \Delta H = -92 kJ\,mol^{-1}$$

$$4 \text{ volumes} \rightleftharpoons 2 \text{ volumes}$$

Note the number of moles of gas on the left hand side, and the number of moles of gas on the right hand side. When the volume of the system is changed, the partial pressures of the gases change. Because there are more moles of gas on the reactant side, this change is more significant in the denominator of the equilibrium constant expression, causing a shift in equilibrium.

Thus, an increase in pressure due to decreasing volume causes the reaction to shift to the side with the fewer moles of gas. A decrease in pressure due to increasing volume causes the reaction to shift to the side with more moles of gas. There is no effect on a reaction where the number of moles of gas is the same on each side of the chemical equation.

An inert gas (or noble gas) such as helium is one that does not react with other elements or compounds. Adding an inert gas into a gas-phase equilibrium at constant volume does not result in a shift. This is because the addition of a non-reactive gas does not change the partial pressures of the other gases in the container. While it is true that the total pressure of the system increases, the total pressure does not have any effect on the equilibrium constant; rather, it is a change in partial pressures that will cause a shift in the equilibrium. If, however, the volume is allowed to increase in the process, the partial pressures of all gases would be decreased resulting in a shift towards the side with the greater number of moles of gas.

When, total pressure is increased the reaction shifts to the side where the sum of stoichiometric co-efficient of the gases is less (to decrease the number of moles of gases) to regain the equilibrium.

When the total pressure is decreased at constant temperature (or the volume is increased), the reaction shifts to the side where the sum of stoichiometric co-efficient of the gaseous component is greater (to increase the number of moles) to regain the equilibrium.

Temperature

The effect of changing the temperature in the equilibrium can be easily viewed by incorporating heat as either a reactant or product. That is, when the reaction is exothermic (negative heat of reaction), we incorporate heat as a product and when the reaction is endothermic (positive heat of reaction), we include it in the reactant side. Hence, we can straightforwardly tell whether increasing or decreasing the temperature would favour the forward or reverse reaction by applying the same notion as in concentration changes.

Let us take for example, the reaction of nitrogen gas with hydrogen gas. This is a reversible reaction, in which the two gases react to form ammonia:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad \Delta H = -92\ kJ\,mol^{-1}$$

One could also write the above formula as follows, if one sees heat as a product:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 + 92kJ$$

This is an exothermic reaction when producing ammonia. If we were to lower the temperature, the equilibrium would shift in such a way as to produce heat. Since this reaction is exothermic to the right, it would favour the production of more ammonia. In practice, in the Haber process the temperature is instead increased to speed the reaction rate at the expense of producing less ammonia.

In exothermic reactions, increase in temperature decreases the equilibrium constant, K. While in endothermic reactions, increase in temperature increases the K value.

Le Chatelier's Principle are shown in the table below.

External Stress	*Predicted Equilibrium Shift*
Change in pressure	Affects gases only
Concentration of reactant(s) increased	Equilibrium shifts toward products (to the right)
Concentration of product(s) increased	Equilibrium shifts toward reactants (to the left)
Temperature increased (exothermic reaction)	Equilibrium shifts towards reactants (to the left)
Temperature increased (entothermic reaction)	Equilibrium shifts toward products (to the right)

To illustrate, the synthesis of ammonia may be taken,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \; ; \qquad \Delta H^\circ = -3000 \text{ J}$$

$$K_P = \frac{P^2_{NH_3}}{P_{N_2} \times P^2_{H_2}} \qquad \text{or} \qquad K_P = \frac{64x^2}{27P^2}$$

Where the extent of reaction is x per mole of nitrogen.

(i) This is an exothermic reaction. If the temperature be raised, according to Le-Chatelier's principle, the system would behave in a way to absorb and utilise the supplied heat. This means that dissociation of ammonia would occur. In fact, less ammonia is produced at equilibrium at highest temperature. It may be stated that,

"When the temperature of a system in equilibrium is increased, the equilibrium is shifted in the direction that absorbs heat."

(ii) If pressure is increased in the system at equilibrium according to Le-Chatelier's principle, the volume would tend to diminish so as to nullify the effect of pressure. In this system, volume would diminish if number of molecules decrease, i.e., if more ammonia is formed. Hence with increased presure equilibrium will shift in a direction to produce more ammonia, which is a well-known fact. We also find that $K_P = \frac{64x^2}{27P^2}$; to keep K_p constant with increase in P, x must increase i.e., more ammonia should be formed. It may be stated that,

"When the pressure of a system in equilibrium is increased, the equilibrium is shifted in the direction that reduced the number of molecules in the system."

(iii) If ammonia or hydrogen is added to this system from external sources, then the partial pressure of the said component would increase. According to Le Chaterlier's principle, the system would attempt to use up the added component. Thus, if hydrogen is added hydrogen as far as possible it is hence stated,

"The addition of a reactant or product to a system in equilibrium causes the equilibrium to shift in the direction that decreases the concentration of the added component."

Effect of Catalyst

A catalyst can change the rate of a reaction by providing an alternative path to the same reaction. Catalyst does not change the initial and final states i.e, the reactant and the product remain the same. Therefore, the thermodynamic state functions such as ΔH, ΔG, ΔS are not changed. Equilibrium is a thermodynamic concept and the equilibrium constant depends on thermodynamic state functions only. Hence, catalyst can not change equilibrium constant and it has no effect on the equilibrium.

A positive catalyst can decrease the activation energies of forward and reverse reactions in such a way that the difference between the activation energies remains the same. So the rate constants of the forward and the reverse reactions are increased in such a way that their ratio, the equilibrium constant remains the same.

If E_f and E_r are the activation energies of the uncatalysed forward and the reverse reactions and E_f' and E_r' are the activation energies of the catalysed forward and the reverse reactions, we can write, $\Delta H_f = (E_f - E_r) = (E_f' - E_r')$

If K_f and K_r are the rate constants of the uncatalysed forward and the reverse reactions and K_f' and K_r' are the rate constants of the catalysed forward and the reverse reactions,applying Arrhenius equation we can write,

$$\frac{K_f}{K_R}=\frac{A_f e^{-\frac{E_F}{RT}}}{A_r e^{-\frac{E_F}{RT}}}=\frac{A_f}{A_r}e^{-\frac{(E_F-E_F)}{RT}}=\frac{A_f}{A_r}e^{-\frac{(E_F'-E_F')}{RT}}=\frac{A_f e^{-\frac{E_F'}{RT}}}{A_r e^{-\frac{E_F'}{RT}}}=\frac{K_f'}{K_R'}=K_{eqm}$$



Worked-out Examples

19. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium? **[AIEEE-2002]**

(a) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$ (b) $C_{(g)} + 1/2O_{2(g)} \rightleftharpoons CO_{(g)}$

(c) $H_{2(g)} + ½O_{2(g)} \rightleftharpoons H_2O_{(g)}$ (d) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Solution (d)

20. Change in volume of the system does not alter the number of moles in which of the following equilibrium: **[AIEEE-2002]**

(a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ (b) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

(c) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ (d) $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$

Solution (a)

21. The conditions favourable for the reaction; $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$; $\Delta H^o = -198$ kJ are: **[AIEEE-2003]**

(a) low temperature, high pressure (b) any value of T and P

(c) low temperature and low pressure (d) high temperature and high pressure

Solution (a) High pressure favour the reaction showing decrease in mole or voluming i.e., forward reaction. Also low temperature favours exothermic reaction i.e., forward reaction.

22. The exothermic formation of ClF_3 is represented by the equation:

$$Cl_{2(g)} + 3F_{2(g)} \rightleftharpoons 2ClF_{3(g)};\ \Delta H = -329 \text{ kJ}$$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3? **[AIEEE-2005]**

(a) Increasing the temperature (b) Removing Cl_2

(c) Increasing the volume of container (d) Adding F_2

Solution (d) Favourable condition for forward reaction according to Le Chetelier principle are:

(i) Decrease in temperature

(ii) Increase in concentration of reactant and

(iii) Increase in pressure

23. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by **[IITJEE-1999]**

(a) temperature and pressure (b) temperature only

(c) pressure only (d) temperature, pressure and catalyst

Solution (a)

24. A ten-fold increase in pressure on the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium results in .... in Kp. **[IITJEE-1996]**

Solution No change; (K of an equilibrium reaction is independent of the pressure of the system.)

25. For the gas phase reaction: **[IITJEE-1984]**

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6(\Delta H = -32.7\text{kcal})$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by :

(a) increasing the temperature
(b) decreasing the pressure
(c) removing some H_2
(d) adding some C_2H_6

Solution (a, b, c, d) The reaction is exothermic, hence increasing temperature will favour backward reaction (i.e., concentration of C_2H_4 increases). Again decreasing pressure, removing H_2 and adding C_2H_6 favours backward reaction.

26. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_3$ is left behind. At equilibrium **[IITJEE-1986]**

(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours reverse reaction

Solution (c, d) $2NaNO_3 \rightleftharpoons 2NaNO_2 + O_2$

According to Le-chatelier principle an increase in pressure always favours the reaction, where volume or moles decrease (i.e., reverse direction). As heat is added, i.e., reaction is endothermic and is supported in forward direction with increase in temperature.

Quantitative Idea of Le-Chatelier's Principle

Effect of change in concentrations of reactants or products at equilibrium

To understand this effect, let us consider the following gaseous equilibrium in a closed container of volume 'V',

$$A_2(g) + B_2(g) \rightleftharpoons 2\,AB(g)$$

We can assume that the system has attained equilibrium and we have two moles of each A_2, B_2 and AB at the equilibrium.

Now, we can change the concentrations of reactants or products by the addition or removal of reactants or, products. Note that temperature remains constant during these changes.

Before we do that we must keep in mind the following points.

(a) **The goal of any reaction is to attain equilibrium.**
Attaining equilibrium means the concentration of reactants and products will correspond to K_C or K_P value.
For example, the K_C value of the equilibrium under consideration will be as follows:

$$[A_2]_e = \text{equilibrium concentrations} = \frac{n_{A_2}}{V(L)} = \left(\frac{2}{V}\right) \text{of } A_2$$

$$[B_2]_e = \text{equilibrium concentrations} = \frac{n_{B_2}}{V(L)} = \left(\frac{2}{V}\right) \text{of } B_2$$

$$[AB]_e = \text{equilibrium concentrations} = \frac{n_{AB}}{V(L)} = \left(\frac{2}{V}\right) \text{of 'AB'}$$

Hence, $$K_C = \frac{[AB]_e^2}{[A_2]_e\,[B_2]_e} = \frac{\left(\frac{2}{V}\right)^2}{\left(\frac{2}{V}\right)\left(\frac{2}{V}\right)} = 1$$

This value of K_C will remain constant as there is no change in temperature.

(b) **When concentration of reactants or products in changed, the system may not be at equilibrium just after the change.**

To understand this clearly we introduce a term 'Reaction quotient' represented by 'Q'

Reaction quotient 'Q' has similar expression to that equilibrium constant but the system may or may not be at equilibrium. So, 'Q' is defined under any condition of the reaction. So 'Q' can have different values for a reaction but equilibrium constant is constant for a given reaction at constant temperature.

So, 'Q' for the reaction under combination is expressed as $Q = \frac{[AB]^2}{[A_2]\,[B_2]}$

- The concentration terms may not correspond to equilibrium concentration if $Q \neq K_C$
  In this case 'Q' might be greater or less than K_C and the system in not at equilibrium.
- If $Q = K_C$, we say that the system is at equilibrium and the concentration terms of reactants and products correspond to equilibrium concentrations.

(c) **When we change the concentration of reactants or products, the system may not be at equilibrium after the change and 'Q' at that instant may not be equal to K_C.**

Since the goal of any equilibrium is to attain equilibrium, the 'Q' value will keep on changing until it become equal to K_C.

For example, $Q > K_C = 1$ [in case of $K_C = 1$ this equilibrium under condition]

$$\Rightarrow Q = \frac{[AB]^2}{[A]\,[B]} > K_C$$

Not 'Q' has to decrease to become equal to K_C.
How does it decrease?

'Q' can decrease if [AB] in the nominator decreases and $[A_2]$ and $[B_2]$ in the di nominator increase. It is possible reverse reaction proceeds to some extent. We say 'the equilibrium will shift to the reactant side or to the left'

$$A_2(g) + B_2(g) \xleftarrow{} 2AB(g)$$

We can also denote the decrease in a quantity by a down heated arrow ↓. If we apply the same notation to 'Q' we get,

$$Q\downarrow = \frac{[AB]^2}{[A_2][B_2]}\downarrow$$

Note that the direction of arrow also represent of chemical change.
Similarly, when $Q < K_C$, Q will increase untill its value becomes equal to K_C.

$$Q\uparrow = \frac{[AB]^2}{[A_2][B_2]}\uparrow$$

Hence, A_2 and B_2 will react to form AB to regain the equilibrium.

$$A_2(g) + B_2(g) \xrightarrow{} 2AB(g)$$

We say 'the equilibrium is shifted to the product side or to the right'

Let us take some numerical calculations based on these concepts.

Case I:

Product taken out suppose one mole of 'AB' is taken out from the equilibrium and we have to find out composition or number of moles of A_2, B_2 and AB in the regained equilibrium.

We can solve this in the following way:

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

Number of moles at equilibrium:	$A_2(g)$ +	$B_2(g)$ $\rightleftharpoons$	$2AB(g)$	
	2	2	2	... equilibrium $K_C = 1$
Number of moles just when:	2	2	1	... $Q = \frac{[AB]^2}{[A_2][B_2]}$

1 mole of 'AB' was taken out

$$\text{Since } Q = \frac{[AB]^2}{[A_2][B_2]} < K_C = 1 = \frac{\left(\frac{1}{V}\right)^2}{\left(\frac{2}{V}\right)\left(\frac{2}{V}\right)}$$

Hence, A_2 and B_2 will react to form AB to regain to equilibrium $= \frac{1}{4} < K_C = 1$

$\longrightarrow$

Number of moles before equilibrium shift:	$A_2(g) + B_2(g)$ $\rightleftharpoons$		2 AB
	2	2	1
Number of moles reacted/formed:	x	x	2x
Final number of moles at regained equilibrium:	(2 – x)	(2 – x)	(1 + 2x)

So, the concentration of A_2, B_2 and AB at regained equilibrium are no follows.

$$[A_2]_e = \left(\frac{2-x}{V}\right)$$

$$[B_2]_e = \left(\frac{2-x}{v}\right)$$

$$[AB]_3 = \left(\frac{1+2x}{v}\right)$$

These concentration terms must satisfy the equilibrium constant K_C and K_C remains constant ($K_C = 1$) as temperature is constant.

$$\text{So, } K_C = \frac{[AB]^2}{[A_2][B_2]}] = \frac{\left(\frac{1+2x}{v}\right)^2}{\left(\frac{2-x}{v}\right)\left(\frac{2-x}{v}\right)} = 1$$

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

[Remember, $(2 - x) > 0$ or, $2 > x > 0$]

$$\frac{1+2x}{2-x} = \pm 1$$

We must take the value of 'x' within the practical domain.

Solving, we get $x = \frac{1}{3}$

Hence number of moles of A_2 at regained equilibrium = (2 – x) = 5/3

Number of moles of B_2 at regained equilibrium = (2 – x) = 5/3

Number of moles of 'AB' formed at equilibrium = 1 + 2x = 5/3

Case II:

Removal of reactants

Suppose one mole of A_2 is taken out and we have to find out fi l equilibrium concentration.

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

Moles at equilibrium:	2	2	2	.... $K_c = 1$
Moles after removal of one mole A_2:	1	2	2	.... $Q = \frac{[AB]^2}{[A_2][B_2]} > K_C = 1$

$$\text{Since } Q = \frac{[AB]^2}{[A_2][B_2]} \downarrow > K_C = \frac{\left(\frac{2}{V}\right)^2}{\left(\frac{1}{V}\right)\left(\frac{2}{V}\right)} = 2$$

The reaction will shift to reactant side to regain the equilibrium.

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

Moles before the shift of equilibrium:	1	2	2
Moles reacted or formed:	x	x	2x
Moles left at regained equilibrium:	(1 + x)	(2 + x)	(2 – 2x)

So, $[A_2]_e = \left(\frac{1+x}{V}\right)$

$[B_2]_e = \left(\frac{2+x}{V}\right)$

$[AB]_e = \left(\frac{2-2x}{V}\right)$

$$K_C = \frac{[AB]_e^2}{[A_2]_3[B_2]_e} = \frac{\left(\frac{2-2x}{V}\right)^2}{\left(\frac{1+x}{V}\right)\left(\frac{2+x}{V}\right)} = 1 \ (0 < x < 1)$$

Solving, we get, $x \simeq 0.19$

Hence, n_{A_2} (equilibrium) = (1 + x) = 1.19

n_{B_2} (equilibrium) = (2 + x) = 2.19

n_{AB} (equilibrium) = (2 – 2x) = 1.62

Case III:

Addition of reactant

Suppose one mole of 'A_2' is added to the equilibrium and we have to find the composition of final equilibrium mixture.

	$A_2(g)$ +	$B_2(g) \rightleftharpoons$	$2AB(g)$	
Moles at equilibrium:	2	2	2	.... $K_c = 1$
Moles after the addition of A_2:	3	2	2	.... Q

$$Q = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2}{V}\right)^2}{\left(\frac{3}{V}\right)\left(\frac{2}{V}\right)} = \frac{2}{3} < K_C = 1$$

$$\text{Since } Q < K_C \left(\Rightarrow Q \uparrow = \frac{[AB]^2}{[A_2][B_2]} \uparrow\right)$$

The reaction will be shifted to the product side to regain the equilibrium.

	$A_2(g)$ +	$B_2(g) \rightleftharpoons$	$2AB(g)$
Moles before the shift of equilibrium:	3	2	2
Moles reacted or produced:	x	x	2x
Final moles at regained equilibrium:	(3 – x)	(2 – x)	(2 + 2x)

So, $[A_2]_e = \left(\frac{3-x}{V}\right)$ $[B_2]_e = \left(\frac{2-x}{V}\right)$ $[AB]_e = \left(\frac{2+2x}{V}\right)$

$$K_C = \frac{[AB]_e^2}{[A_2]_e[B_2]_e} = \frac{\left(\frac{2+2x}{V}\right)^2}{\left(\frac{3-x}{V}\right)\left(\frac{2-x}{V}\right)} = 1$$

Solving we get, we $\approx \frac{1}{6}$

Hence, we can get the composition.

Case IV:

Simultaneous addition/removal of reactants or products

Suppose one mole of A_2 and one mole of AB are taken out but two moles of B_2 is added.

	$A_2(g)$ +	$B_2(g) \rightleftharpoons$	$2AB(g)$	
Moles at equilibrium:	2	2	2	..... $K_C = 1$
Moles after addition/removal	1	4	1	.... Q

$$Q = \frac{[AB]^2}{[A^2][B_2]} = \frac{\left[\frac{1}{V}\right]^2}{\left[\frac{1}{V}\right]\left[\frac{4}{V}\right]} = \frac{1}{4} < K_C$$

Since, $Q = \frac{[AB]^2}{[A_2][B_2]} \uparrow < K_C$

The reaction will be shifted to the product side to regain the equilibrium.

	$A_2(g)$	+ $B_2(g)$	$\rightleftharpoons$	2AB(g)
Moles before shift of reaction:	1	4		1
Moles reacted or produced:	x	x		2x
Final moles at regained equilibrium:	(1–x)	(4–x)		(1 + 2x)

So, $[A_2]_e = \left[\frac{1-x}{V}\right]$

$[B_2]_e = \left[\frac{4-x}{V}\right]$

$[AB]_e = \left(\frac{1+2x}{V}\right)$

$$K_C = \frac{[AB]_e^2}{[A_2]_e[B_2]_e} = \frac{\left(\frac{1+2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{4-x}{V}\right)} = \frac{(1+2x)^2}{(1-x)(4-x)} = 1$$

Solving we get, $x \approx 0.3$

It is not mandatory that we have to calculate the 'Q' and compare it with K_C to decide the shift of equilibrium.

We can say in general that,

(a) **When reactant is added, the reaction shifts to product side to regain the equilibrium.**

addition of reactant → shift of equilibrium →

$$R \rightleftharpoons P$$

(b) **When product is added, the reaction shifted to reactant side to regain the equilibrium.**

← shift of equilibrium ← Product is added

$$R \rightleftharpoons P$$

(c) **When reactant is withdrawn, the reaction is shifted to reactant side to regain equilibrium.**

← Reactant is removed $R \rightleftharpoons P$

(d) **When product is removed, reaction is shifted to product side to regain equilibrium.**

→ shift of equilibrium

$R \rightleftharpoons P$ → Product is removed

Note that the arrows in every case are pointed in the same direction.

- When more than one changes are made (consider case IV in numerical application) which tend to shift the reaction in opposite directions, it is wise to calculate the 'Q' value so as to decide the exact shift of the reaction.
- Addition or removal of pure solid or pure liquid cannot disturb the equilibrium. It is because the concentration of pure solid or pure liquid is constant. Moreover, the concentration of pure solid ore pure liquid is not involved in the expression of equilibrium constant K_C or K_P

  For example, addition ore removal of $CaCO_3$ or CaO in the following equilibrium has effect (no shift occurs)

  $$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)\uparrow$$

- Also note that concentration of a pure gas is not constant.

$$PV = nRT$$

$$\Rightarrow \quad P = \left(\frac{n}{V}\right) RT$$

$$\Rightarrow \quad P = CRT \qquad \left[C = \frac{n}{V} = \text{Molar concentration}\right]$$

It changes with the pressure of the gas.



Worked-out Examples

27. H_2 and I_2 are mixed at 400°C in a 1.0 L container and when equilibrium established, the following concentrations are present: [HI] = 0.49 M, $[H_2]$ = 0.08 M and $[I_2]$ = 0.06 M. If now an additional 0.3 mol of HI are added, what are the new equilibrium concentrations, when the new equilibrium $H_2 + I_2 \rightleftharpoons 2HI$ is reestablished?

Solution First determine the equilibrium constant

K_C for $H_2 + I_2 \rightleftharpoons 2HI$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.49)^2}{(0.08)(0.06)} = 50$$

When 0.3 mol of HI are added, equilibrium is disturbed. At the instant,

$$[HI] = 0.49 + 0.3 = 0.79 \text{ M}$$

$$\Rightarrow \quad Q > K_C, \text{ since } K_C = P_{O_2} = \frac{\frac{x}{2}}{1+\frac{x}{2}} P = \frac{0.475 \times 1.21}{1.475}$$

$\Rightarrow$ backward reaction dominate and the equilibrium shifts to the left.

Let 2x = concentration of HI consumed (while going left) then concentration of each of H_2 and I_2 formed = x

$\Rightarrow$ [HI] = 0.79 – 2x, $[H_2]$ = 0.08 + x, $[I_2]$ = 0.06 + x and K_C = 50

$$\Rightarrow \quad K_C = P_{O_2} = \frac{\frac{x}{2}}{1+\frac{x}{2}} P = \frac{0.475 \times 1.21}{1.475}$$

$\Rightarrow$ $46x^2 + 10.2x - 0.35 = 0$

$\Rightarrow$ x = 0.033 or – 0.25 (neglecting the –ve value)

Finally, the equilibrium concentrations are:

$$[HI] = 0.79 - 2x = 0.79 - 0.033 \times 2 = 0.724 \text{ M}$$

$$[H_2] = 0.08 + x = 0.08 + 0.033 = 0.113 \text{ M}$$

$$[I_2] = 0.06 + x = 0.06 + 0.033 = 0.093$$

28. At 800K a reaction mixture contained 0.5 mole of SO_2, 0.12 mole of O_2 and 3 mole of SO_3 at equilibrium. K_C for the equilibrium $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is 833 lit/mol. If the volume of the container is 1 litre. Calculate how much O_2 is to be added at this equilibrium in order to get 5.2 mole of SO_3 at the same temperature.

Solution Suppose x mole of O_2 is added by which equilibrium shifts to right hand side and y mole of O_2 changes to SO_3. The new equilibrium concentration may be represented as,

	$2SO_2$ +	O_2 $\rightleftharpoons$	$2SO_3$
First equilibrium,	0.5 mole	0.12 mole	5 mole
Second equilibrium,	(0.5 – 2y)	(0.12 + x – y)	(5 + 2y)

But $5 + 2y = 5.2$ (given) [$\therefore y = 0.1$]

Now, $K_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = \dfrac{(5+2y)^2}{(0.5-2y)^2(0.12+x-y)} = 833$ (volume = 1 lit)

Substituting, $y = 0.1$, we get x.

GASEOUS SYSTEMS



Homogeneous Equilibrium or One Phase Equilibrium

Degree of dissociation and mole fraction

Degree of dissociation is denoted as 'α' and it is the fraction of number of moles of reactant reacted.

$$\text{Hence, } \alpha = \frac{n_{reacted}}{n_{taken}}$$

Let us consider the dissociation of HI

	$2HI(g) \rightleftharpoons$	$H_2(g)$ +	$I_2(g)$
Number of moles taken initially:	a	–	–
Number of moles reacted or formed:	x	$\frac{x}{2}$	$\frac{x}{2}$
Number of moles left at equilibrium:	(a – x)	$\frac{x}{2}$	$\frac{x}{2}$

The degree of dissociation (α) of HI is given as,

$$\alpha = \frac{n_{reacted}}{n_{taken}} = \frac{x}{a} \Rightarrow x = a\alpha$$

The mole fraction of HI at equilibrium is given as,

$$X_{HI} = \frac{n_{HI}}{n_{total}} = \frac{a-x}{a-x+\frac{x}{2}+\frac{x}{2}} = \left(\frac{a-x}{a}\right) = \left(1-\frac{x}{a}\right) = 1-\alpha$$

Hence, we can see that mole fraction of any component can be expressed by 'α' alone. The initial number of moles 'a' does not appear in the expression of mole fraction.

If we take $a = 1 \Rightarrow x = a\alpha = \alpha$ ($\because a = 1$)

So we can write down:

	$2HI \rightleftharpoons$	H_2 +	I_2
Initial number of moles taken:	1	–	–
Number of moles at equilibrium:	(1–α)	$\alpha/2$	$\alpha/2$

Now the mole fraction of HI at equilibrium is,

$$X_{HI} = \frac{n_{HI}}{n_{Total}} = \frac{(1-\alpha)}{1-\alpha+\frac{\alpha}{2}+\frac{\alpha}{2}} = (1-\alpha)$$

So we can see the relation between mole fraction and α remains the same when we assume one mole of reactant to start with. We will frequently take one mole reactant initially to save time but this practice is correct as long as we relate mole fraction and 'α'.

We need to be careful about a common mistake as demonstrated,

	$2HI \rightleftharpoons$	H_2	+	I_2	
Number of moles at equilibrium when a = 1	$(1-2\alpha)$	α		α	...wrong
Number of moles at equilibrium when a = 1	$(1-\alpha)$	$\frac{\alpha}{2}$		$\frac{\alpha}{2}$	correct
Number of moles at equilibrium:	$(a-x)$	$\frac{x}{2}$		$\frac{x}{2}$	correct
Number of moles at equilibrium:	$(a-2x')$	x'		x'	

$$\alpha = \frac{n_{reacted}}{n_{taken}} = \frac{x}{a} = \frac{2x'}{a}$$

$\Rightarrow$ $a\alpha = x$ and $a\alpha = 2x'$

Hence, $n_{HI} = (a-x) = a - a\alpha = a(1-\alpha)$ So $n_{HI} = (a-2x') = a - a\alpha = a(1-\alpha)$

When, $a = 1$, $n_{HI} = (1-\alpha)$ When $a = 1$, $n_{HI} = (1-\alpha)$

Therefore, when we take one mole of reactant to start with, the number of moles of reactant reacted in always 'α' not 2α or 3α.

Application of average molar mass to equilibrium

From the knowledge of average molar mass of the equilibrium mixture we can find out the degree of dissociatioion of the reactant.

Let us consider the following equilibrium.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Suppose the average molar mass (twice of vapour density for gases) of the equilibrium system is 69 and we have to find out the degree of dissociation of $_2O_4$.

Method I $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium: $(1-\alpha)$ 2α

$$M_{av} = 69 = \frac{M_{N_2O_4}(1-\alpha) + M_{NO_2}(2\alpha)}{1-\alpha+2\alpha} = \frac{92(1-\alpha)+46\times 2\alpha}{1+\alpha}$$

$\Rightarrow$ $69 = \frac{92}{1+\alpha}$ or, $\alpha = \frac{1}{3}$

Method II We can apply the law of conservation of mass to solve the above problem

Initially: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium: a – [Here $\alpha = \frac{x}{a}$]

$(a-x)$ $2x$

Initial mass = Mass at equilibrium

$$92\,a = (a - x + 2x)\,M_{av} \Rightarrow 92\,a = (a+x)\,M_{av} \Rightarrow M_{av}\left(1+\frac{x}{a}\right) = 92$$

$69\,(1+\alpha) = 92$ Solving we get, $\alpha = \frac{1}{3}$



Worked-out Example

29. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm. and 348 K is 1.84 g dm^{-3}. Calculate the equilibrium constant of the reaction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g).$$

Solution Let us assume that we start with C moles of $N_2O_4(g)$ initially.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial,	0		0
At equilibrium,	$C(1-\alpha)$		$2C\alpha$

Where α is the degree of dissociation of $N_2O_4(g)$
Since,

$$\frac{\text{Total moles at equilibrium}}{\text{Total moles initially}} = \frac{\text{Vapour density initial}}{\text{Vapour density at equilibrium}} = \frac{\text{Initial molecular mass}/2}{\text{Average molecular mass}/2}$$

$$\text{Initial vapour density} = \frac{92}{2} = 46$$

$$\frac{C(1+\alpha)}{C} = \frac{46}{d}$$

Since vapour density and actual density are related by the equation,

$$\text{V.D.} = \frac{\rho RT}{2P} = \frac{1.84 \times 0.082 \times 348}{2} = 26.25$$

$$\therefore \quad 1 + \alpha = \frac{46}{26.25} = 1.752$$

$$\therefore \quad \alpha = 0.752$$

$$\therefore \quad K_p = \frac{\left(\frac{2\alpha}{(1+\alpha)} \times P_T\right)^2}{\frac{(1-\alpha)}{(1+\alpha)} \times P_T} = \frac{\left(\frac{2 \times 0.75}{1.752} \times 1\right)^2}{\frac{0.248}{1.752} \times 1} \quad \therefore = 5.2 \text{ atm.}$$

Effect of pressure at equilibrium (quantitative)

To understand the effect of pressure, let us consider the following equilibrium.

$$aA(g) + bB(s) \rightleftharpoons cC(g) + dD(g)$$

The expression of Kp for the above equilibrium will be,

$$K_p = \frac{P_C^c \, P_D^d}{P_A^a}$$

[We neglect the pressure of solid 'B' in the expression of Kp]
The partial pressures of A, C and D can be expressed in terms of total pressure 'P' and more fraction.

$$P_A = PX_A$$

$$P_C = PX_C$$

$$P_D = PX_D$$

Putting these expression in K_p we get,

$$K_P = \frac{P_C^c P_D^d}{P_A^a} = \frac{(PX_c)^C (PX_D)^d}{(PX_A)^a} = \frac{X_C^c X_D^d}{X_A^d} \quad [(C + d) - a]\ P$$

$$K_P = \frac{X_C^c X_D^d}{X_A^a} P^{\Delta n}$$

Where, $\Delta n = (c + d - a)$

'Constant temperature' When we change total pressure of the container it is actually changing the volume of the container. Also note that K_p cannot change as temperature is constant.

Case I: When $\Delta n = 0 \Rightarrow P^{\Delta n} = 1$ for any value of pressure.
Hence, pressure has no impact on the equilibrium.

Case II: When $\Delta n > 0 \Rightarrow (c + a) > a$

When pressure 'P' is increased, $P^{\Delta n}$ will increase as well. Because the K_p remains constant at constant temperature, the mole fraction ratio $\left(\frac{X_C^c X_D^d}{X_A}\right)\downarrow$ has to decrease to keep K_p constant.

Hence, the reaction will shift to the reactant of the gaseous component is less.

Case III: If $\Delta n < 0 \Rightarrow (c + d) < a$

When pressure 'P' is increased, $P^{\Delta n}$ will decreae because Δn is negative. Because K_p remains constant the molefraction ratio $\left(\frac{X_C^c X_D^d}{X_A^a}\uparrow\right)$ has to increase to keep the value of K_p constant.

Hence, the reaction will shift to the product side (where the sum of stoichiometric co-efficient of gaseous component is less).

(at constant temperature or the volume is decreased)

Note that when, total pressure is increased the reaction shifts to the side where the sum of stoichiometric co-efficient of the gases is less (to decrease the number of moles of gases) to regain the equilibrium

When the total pressure is decreased at constant temperature (or the volume is increased), the reaction shifts to the side where the sum of stoichiometric co-efficient of the gaseous component is greater (to increase the number of moles) to regain the equilibrium.



Worked-out Examples

30. At 127°C and 1 atm pressure N_2O_4 is 40% dissociated. Calculate the pressure at which it will be 80% dissociated at 127°C?

If degree of dissociation has to be increased then equilibrium will shift towards right. Stoichiometry coefficient on R H S has to be increased.

Since the degree of dissociation has to be increased, the pressure should be less than 1 atm. (when pressure will decrease and will increase).

Solution $N_2O_4 \rightleftharpoons 2NO_2$

Working plane

$P_T = 1$ atm $\qquad$ P_T

K_P (constant)

$\alpha_1 = 0.4 = \left(\frac{40}{100}\right)$ $\qquad$ $\alpha_2 = 0.8$

$$K_P = \left(\frac{4\alpha^2}{1-\alpha^2}\right)P_T$$

$$\left(\frac{4\alpha_1^2}{1-\alpha_1^2}\right)P_1 = \left(\frac{4\alpha_2^2}{1-\alpha_2^2}\right)P_2$$

$$\left(\frac{0.16}{1-0.16}\right)\underset{(1\,atm)}{P_1} = \left(\frac{0.64}{1-0.64}\right)P_2 \qquad P_2 = 0.107 \text{ atm}$$

31. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At Equilibrium the partial pressure of both the gases are 2 atm each at 27°C in a closed container

If the volume of the container is doubled at the same temperature what will be the final equilibrium pressure of the container.

Solution $K_P = \dfrac{P^2_{NO_2}}{P_{N_2O4}} = 2$ atm. The moment when volume is doubled the pressure becomes exactly half.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

1 atm 1 atm

$\Rightarrow$ Q = 1 atm < K_P

$$\left(\frac{1\times1}{1}\right) = 1 = \frac{P_{NO_2}}{P_{N_2O_4}} \uparrow P_T = 2 \text{ atm}$$

Increase in the volume or decrease in pressure are the same thing.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Final: (1–x) atm (1 + 2x) atm

$$K_P = 2\text{atm} = \frac{(1+2x)^2}{1-x} \quad o < x < 1$$

Solving we get, x = 0.16

$P_f = 1 - x + 1 + 2x = 2 + x = 2.16$ atm

If normal gas the pressure would have decreased exactly half. Here system has exhibited reactions opposing the change.

If any change is made to a system at equilibrium the system will adjust itself in such a way so that the change can be opposed to some extent.

In the study of equilibria, gas reactions are broadly classified into two groups:

(i) *First type gas reactions* in which total number of reactant molecules and of resultant molecules are the same, *i.e.*, $\Delta n = 0$, *e.g.;* $2HI \rightleftharpoons H_2 + I_2$

(ii) *Second type gas reactions* in which the number of molecules of reactants differ from that of the resultants, *i.e.*, $\Delta n \neq 0$; *e.g.*, $PC1_5 \rightleftharpoons PC1_3 + C1_2$.

(a) **Water gas reaction:** $H_2 + CO_2 \rightleftharpoons H_2O + CO$

This is a 1st type gas reaction. Starting with equimolecular mixture of the reactants, we have, when *x* is the extent of H_2 used up at equilibrium,

	H_2	+	CO_2	$\rightleftharpoons$	H_2O	+	CO		Total
Moles at eqm, :	$1-x$		$1-x$		x		x	=	2
Partial Pressure :	$\frac{1-x}{2}P$		$\frac{1-x}{2}P$		$\frac{x}{2}P$		$\frac{x}{2}P$	=	P

$$K_P = \frac{P_{H_2O} \times P_{CO}}{P_{H_2} \times P_{CO_2}} = \frac{\left(\frac{x}{2}P\right)^2}{\left(\frac{1-x}{2}P\right)^2} = \frac{x^2}{(1-x)^2}$$

Hence, x is independent of pressure, since K_p does not depend on pressure.

At 1260°K and 1 atmosphere, the equilibrium composition of this reaction is $CO_2 = 21.4$, $H_2 = 22.9$ and $CO = 27.8$ (moles per cent).

$$\text{Hence, } K_P = \frac{P_{H_2O \times P_{CO}}}{P_{CO_2} \times P_{H_2}} = \frac{(27.8)^2}{(21.4) \times (22.9)} = 1.58$$

It is often difficult to estimate x directly in this system, and an indirect method is employed. The eqm. constant is computed from the known values of eqm. constants of other reactions. Consider two other equilibria:

$$\text{(i) } 2CO_2 \rightleftharpoons 2CO + O_2;\ K_1 = \frac{P_{CO}^2 \times P_{O2}}{P_{CO_2}^2}$$

$$\text{(ii) } 2H_2 + O_2 \rightleftharpoons 2H_2O;\ K_2 = \frac{P_{H_2}^2 O}{P_{H_2}^2 \times P_{O_2}}$$

$$\text{so, } \quad K_1 \times K_2 \left[\frac{P_{CO} \times P_{H_2O}}{P_{H2} \times P_{CO_2}}\right]^2 = K_P^2$$

Since K_1 and K_2 can both be separately determined, K_P is known.

(b) **We may now consider some 2nd type gas reactions, such as the dissociation of phosphorus pentachloride:**

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Let us start with a gm-mole of PCl_5 and suppose the degree of dissociation is α at equilibrium. Then, the relative amounts of the components and their pressures would be:

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2	Total
Moles at eqm.	$1-\alpha$		α		α	$= 1+\alpha$
Partial pressure	$\frac{1-\alpha}{1+\alpha}P$		$\frac{\alpha}{1+a}P$		$\frac{\alpha}{1+\alpha}P$	$= P$
Concentrations	$\frac{1-\alpha}{V}$		$\frac{\alpha}{V}$		$\frac{\alpha}{V}$	$= \frac{1+\alpha}{V}$

$$\text{Hence, } K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PC_5}} = \frac{\left(\frac{\alpha}{1+\alpha}P\right)\left(\frac{\alpha}{1+\alpha}P\right)}{\frac{1-\alpha}{1+\alpha}P} = \frac{a^2}{1-\alpha^2}P. \quad \text{and } K_C = \frac{C_{PCl_3} \times C_{Cl_2}}{C_{PCl_5}} = \frac{\frac{\alpha}{V}\cdot\frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V}$$

Since the numbers of molecules of reactants and resultants are unequal, $K_P \neq K_C$. At any given temperature, K_P remains constant, hence with increase of pressure P, α will diminish. That is, the extent of dissociation will decrease with pressure increase.

(c) ***Synthesis of ammonia:*** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

This is a reaction in which the number of molecules of resultants is less than that of the reactants. Suppose we start with a mixture of N_2 and H_2 in 1:3 ratio in moles and let the extent of chemical transformation at equilibrium be *x* per mole of nitrogen. Then,

	N_2	+	$_3H_2$ $\rightleftharpoons$	$2NH_3$	Total
Initial moles	1		3	0	= 4
Moles at equilibrium	$1-x$		$3-3x$	$2x$	$= 4-2x$
Partial pressure	$\frac{1-x}{4-2x}P$		$\frac{3-3x}{4-2x}P$	$\frac{2x}{4-2x}P = P$	

$$\text{So, } K_P = \frac{P_{NH3}^2}{P_{N_2}.P_{H2}^3} = \frac{\left[\frac{2x}{4-2x}P\right]^2}{\left[\frac{1-x}{4-2x}P\right]\left[\frac{3-3x}{4-2x}P\right]^3} = \frac{4x^2(4-2x)^2}{27(1-x)^4.P^2}$$

If *x* is small,

It shows K_P, which is constant at any given temperature, is determined by the ratio x/P. Further, with increase of P, x must also increase proportionately,

$$\text{for } P^2 = \frac{64}{27K_P}.x^2, \text{ i.e., } P = k'x$$

This means that with higher pressures, the yield of ammonia would be larger. This is a valuable information to the manufacturer of ammonia. We can also calculate K_C from this,

$$K_C = K_P(RT)^{-\Delta n} = \frac{64x^2}{27}.\frac{1}{P^2}.(RT)^{-(2-4)} = \frac{64x^2}{27}(RT/P)^2$$

Since volume $V = (4-2x)\frac{RT}{P}$, we have, $K_C = \frac{64x^2}{27}\left(\frac{V}{4}\right)^2 = \frac{4x^2V^2}{27}$.

(d) ***The dissociation of nitrogen tetraoxide:*** $N_3O_4 \rightleftharpoons 2NO_2$

So, we have,

$$K_P = P_{NO_2}^2/P_{N_2O_4}$$

If we start with 1 mole of N_2O_4 and α be the degree of dissociation, then at equilibrium, there are in all $(1+\alpha)$ gm-moles of gas, of which 2α gm-moles are NO_2 and $(1-\alpha)$ gm-moles N_2O_4.

Hence, $$K_x = \frac{[2\alpha/(1+\alpha)]^2}{[(1-\alpha)/(1+\alpha)]} = \frac{4\alpha^2}{1-\alpha^2}$$

But $$K_P = Kx.P\Delta n,$$

Since, $$\Delta n = 1, K_P = \frac{4\alpha^2}{1-\alpha^2}P$$

'α' can be easily obtained from vapour-density measurements and hence K_p is evaluated.



Worked-out Examples

32. In an evacuated vessel of capacity 110 litres, 4 moles of Argon and 5 moles of PCl_5 were introduced and equilibriated at a temperature at 250°C. At equilibrium, the total pressure of the mixture was found to be 4.678 atm. Calculate the degree of dissociation, α of PCl_5 and K_P for the reaction

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ at this temperature.

Solution

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial moles	5		0		0
At equilibrium	5 – x		x		x

Total moles = 5 + x + 4 (including moles of Argon) = 9 + x

$$\text{Since total moles} = \frac{PV}{RT} = \frac{4.678 \times 110}{0.082 \times 523} = 11.99 \approx 12$$

$$\therefore \quad x = 3$$

$$\therefore \quad \alpha = \frac{3}{5} = 0.6$$

$$K_P = \frac{\left(\frac{3}{12} \times 4.678\right)^2}{\left(\frac{2}{12} \times 4.678\right)} = 1.75 \text{ atm.}$$

33. $N_2O_4(g) \rightleftharpoons 2NO_2$ Express α in terms of K_P and P for this equilibrium.

Solution

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initially,	1		–
At Equilibrium	1–α		2α

$$X_{N_2O_4} = \frac{1-\alpha}{1-\alpha+2\alpha} = \frac{1-\alpha}{1+\alpha}$$

$$P_{N_2O_4} = X_{N_2O_4} P_T = \left(\frac{1-\alpha}{1+\alpha}\right) P_T$$

$$K_P = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{4\alpha^2 . P_T^2}{\left(\frac{1-\alpha^2}{1+\alpha}\right) P_T} \quad \text{and} \quad P_{NO_2} = X_{NO_2} P_T = \frac{2\alpha}{1+\alpha} P_T$$

$$K_P = \left(\frac{4\alpha^2}{1-\alpha^2}\right) P_T$$

$$\frac{1}{\alpha^2} - 1 = \frac{1-\alpha^2}{\alpha^2} = \frac{4P_T}{K_P}$$

$$\alpha = \sqrt{\frac{K_P}{4P_T + K_P}}$$

Hence, value of α decreases with increasing pressure.

Note: When pressure is increased, the equilibrium is shifted to that side where the sum of the stoichiometry coefficients of the gaseous components is less

34. At 1000 K, the pressure of iodine gas is found to be 0.112 atm due to partial dissociation of $I_2(g)$ into I. Had there been no dissociation, the pressure would have been 0.074 atm. Calculate the value of K_p for the reaction: $I_2(g) \rightleftharpoons 2I(g)$.

Solution Analysing in terms of pressure directly,

Partial pressure	$I_2(g)$ $\rightleftharpoons$	2I (g)
Initial	0.074	0
at equilibrium	0.074- p	2p

$\Rightarrow$ total pressure at equilibrium
$= (0.074 - p) + 2p = 0.112$ (given)

$\Rightarrow$ $p = 0.038$ atm

$$K_p = \frac{(P_I)^2}{(P_{t_2}} = \frac{(2p)^2}{(0.074 - p)}$$

Substituting value of p $\Rightarrow K_p = 0.16$ atm

35. 5 g of PCl_5 were completely vaporized at 250°C in a vessel of 1.9 litre capacity. The mixture at equilibrium exerted a pressure of one atmosphere. Calculate the degree of dissociation K_C and K_p for this reaction.

Solution Number of mole of PCl_5

$$= \frac{\text{Weight}}{\text{Moelcular weight}}$$

$$= \frac{5}{208.5} = 0.024$$

The equilibrium for dissociation of PCl_5 maybe represented as,

	PCl_5 $\rightleftharpoons$	PCl_3	+	Cl_2
At t = 0	0.024	0		0
At equilibrium	$(0.024 - \alpha)$	α		α

Total moles of gas components,
$= 0.024 - \alpha + \alpha + \alpha$
$= (0.024 + \alpha)$

We know, $PV = nRT$

$$1 \times 1.9 = (0.024 + \alpha)\, 0.0821 \times 523$$

$$(0.024 + \alpha) = \frac{1.9}{0.0821 \times 523}$$

$$\alpha = 0.0202$$

Degree of dissociation $= \frac{0.0202}{0.024} = 0.843$

$$[PCl_5] = \frac{0.024 - \alpha}{1.9} = \frac{0.024 - 0.0202}{1.9} = \frac{0.0038}{1.9}$$

$$[PCl_3] = [Cl_2] = \frac{\alpha}{V} = \frac{0.0202}{1.9}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left[\frac{0.0202}{1.9}\right]^2}{\frac{0.0038}{1.9}} = \frac{4.08\times10^{-4}}{1.9\times0.0038} = 0.0565 \text{ mole/litre}$$

$K_p = K_c (RT)^{\Delta n}$

Where, $K_c = 0.0565$

$\Delta n = 2 - 1 = 1$

36. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K = (4x^2P)/(1-x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true? **[IITJEE-2001]**

(a) K_p increases with increase of P (b) K_p increases with increase of x

(c) K_p increases with decrease of x (d) K_p remains constant with change in P and x

Solution (d) With change of pressure, x will change in such a way that K remains a constant.

37. Consider the following equilibrium in a closed container: **[IITJEE-2002]**

$$N_2O_4(g) \rightleftharpoons 2N0_2(g)$$

At a fixed temperature, the volume of the reaction container is halved, For this change, which of the following statements holds true regarding the equilibrium constant (K) and degree of dissociation

(a) neither K nor α changes (b) both K_p and α change

(c) K_p changes, but α does not change (d) K_p does not change, but α changes

Solution (d) For the equilibria: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_p = K_c$ because here $\Delta n = 1$ [$K_P = K_c \times (RT)^{\Delta n}$] Since temperature is constant so K_c or K_p will remain constant. Further since volume is halved, the pressure will be doubled so a will decrease so as to maintain the constancy of K_c or K_p.

N_2O_4	$\rightleftharpoons$	$2NO_2$
a		0
a – x		2x

Let total pressure = P

$$\therefore \quad p_{NO_2} = \frac{2x}{a+x}\times P; p_{N_2O_4} = \frac{a-x}{a+x}\times P$$

$$K_p = \frac{(p_{NO_2})^2}{P_{N_2O_4}} = \frac{4x^2P^2}{(a+x)^2}\times\frac{(a+x)}{P(a-x)} = \frac{4x^2P}{(a^2-x^2)}$$

Since K_p = constant, so $\propto \frac{1}{\sqrt{p}}$

So when volume is halved, pressure gets doubled and thus x (or α) will decrease.

38. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when N_2O_4 (g) decomposes to $NO_2(g)$. If the resultant pressure is 2.4 atm, the percentage dissociation by mass of N_2O_4 (g) is

(a) 10% (b) 20%

(c) 30% (d) 40%

Solution $N_2O_4(g) \qquad 2NO_2(g)$

Equilibrium $1-\alpha \qquad 2\alpha$

Where α is the degree of dissociation

$$\frac{(P_2)\text{ Pressure of } N_2O_4 \text{ at } 600K}{(P_1)\text{ Pressure of } N_2O_4 \text{ at } 300K} = \frac{600}{300} \; (\because V \text{ is constant})$$

$\therefore \quad P_2 = 2$ atm

Ater dissociation of N_2O_4 at 600K,

$$P_{N_2O_4} = 2(1-\alpha) = 2-2\alpha$$

$$P_{N_2O_4} = 2 \times 2\alpha = 4\alpha$$

Total pressure $= 2-2\alpha+4\alpha = 2+2\alpha$

$2+2\alpha = 2.4$(Given)

$\alpha = 0.2$

$\therefore$ Percentage dissociation = 20%

$\therefore$ (b)

39. For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$

Show that the degree of dissociation of NH_3 is given as,

$$\alpha = \left[1+\frac{3\sqrt{3}}{4}\frac{P}{K_P}\right]^{-1/2}$$

where P is the equilibrium pressure. If K_P of the above reaction is 78.1, atm at 400°C, determine the value of K_C.

Solution Let n and α be the initial number of moles and degree of dissociation of NH_3 (g) respectively.

	$NH_3(g) \rightleftharpoons$	$\frac{1}{2}N_2(g) +$	$\frac{3}{2}H_2(g)$
Initially,	n	0	0
At equilibrium,	$n(1-\alpha)$	$n\frac{\alpha}{2}$	$\frac{3n\alpha}{2}$

Total number of moles $= n(1+\alpha)$

Partial pressure of NH_3, $p_{NH_3} = \frac{1-\alpha}{1+\alpha} \times P$

Partial pressure of N_2, $p_{N_2} = \frac{\alpha}{2(1+\alpha)} \times P$

Partial pressure of H_2, $p_{H_2} = \frac{3\alpha}{2(1+\alpha)} \times P$

$$\therefore \quad K_P = \frac{(p_{N_2})^{1/2}(p_{H_2})^{3/2}}{p_{NH_3}}$$

$$\frac{\left[\frac{\alpha P}{2(1+\alpha)}\right]^{1/2}\left[\frac{3\alpha P}{2(1+\alpha)}\right]^{3/2}}{\frac{1-\alpha}{1+\alpha}\times P} = \left[\frac{3\sqrt{3}P}{4}\right]\left[\frac{\alpha^2}{1-\alpha^2}\right]$$

$$\frac{1-\alpha^2}{\alpha^2} = \frac{3\sqrt{3}P}{4\,K_P}$$

$$\frac{1}{\alpha^2} = \left[1+\frac{3\sqrt{3}}{4}\frac{P}{K_P}\right] \text{ or, } \alpha = \left[1+\frac{3\sqrt{3}}{4}\frac{P}{K_P}\right]^{-1/2}$$

Δn, change in number of the moles of the given reaction = +1

$K_P = K_C(RT)^{\Delta n}$

or, $K_C = K_P (RT)^{-\Delta n}$

$K_C = 78.1\ [0.0821 \times 673]^{-1} = 1.413$ mol/l

40. PCl_5 dissociation a closed container as:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is α, the partial pressure of PCl_3 will be: **[AIEEE-2006]**

(a) $P.\left[\frac{\alpha}{\alpha+1}\right]$ (b) $P.\left[\frac{2\alpha}{1-\alpha}\right]$

(c) $P.\left[\frac{\alpha}{\alpha-1}\right]$ (d) $P.\left[\frac{\alpha}{1-\alpha}\right]$

Solution (a)

$PCl_{5(g)}$	$\rightleftharpoons$	$PCl_{3(g)}$	+	$Cl_{2(g)}$
1		0		0
1–α		α		α

$$P'_{PCl_3} = P \times X_{PCl_3} = \left[\frac{P.\alpha}{1+\alpha}\right]$$

41. A definite amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. NH_4HS decomposes to give NH_3 and H_2S and at equilibrium total pressure in flask is 0.84 atm. The equilibrium constant for the reaction is: **[AIEEE-2005]**

(a) 0.30 (b) 0.18

(c) 0.17 (d) 0.11

Solution (d)

$NH_4HS_{(s)}$	$\rightleftharpoons$	$NH_{3(g)}$	+	$H_2S_{(g)}$
Before eq.		0.5		0
After eq.		0.5 + P		P

$P_T = 0.84 = 0.5 + P + P \quad \therefore P = 0.17$ atm

$K_p = P'_{NH_3} \times P'_{H_2S} = (0.5 + 0.17) \times 0.17 = 0.11\ atm^2$

Liquid Systems

The principle of the law of mass action is universally applicable to reactions in liquid systems and also in heterogeneous systems where components may occur in different phases. The esterification of acids is a classical example of equilibrium study in liquid systems.

(e) ***Esterification of acetic acid:***

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

At eqm.: a—x $\quad b-x \quad x \quad x$ moles

Let the total volume of the liquid system be V and let the initial amounts of alcohol and acid be a and b gm-moles and at equilibrium the amount of acid esterified be x. Then at equilibrium, the concentrations are,

$$C_{alc} = \frac{a-x}{V},\ C_{acid} = \frac{b-x}{V},\quad C_{ester} = \frac{x}{V},\ C_{H_2O} = \frac{x}{V}$$

$$\text{So, } K_C = \frac{C_{ester} \times C_{H_2O}}{C_{alc} \times C_{acid}} = \frac{x^2}{(a-x)(b-x)}$$

The equilibrium constant is therefore independent of the volume of the system. If we start with 1 mole of each, then,

$$K_C = \frac{x^2}{(1-x)^2}, \quad \text{or} \quad x = \frac{2K_C \pm \sqrt{4K_C^2 - 4(K_C-1)K_C}}{2(K_C-1)}$$

Experimentally, at room temperature, $K_C = 4.0$. So, $x = 0.66$. It is obvious that with a given amount of acid and alcohol, we can calculate the expected yield of the ester at equilibrium.

(f) Another equilibrium studied carefully in a liquid system is esterfication with amylene ($_5H_{10}$);

$$CCl_3COOH + C_5H_{10} \rightleftharpoons CC1_3COOC_5H_{11}$$

Conc. $(a-x)/V \quad (b-x)/V \quad x/V$

If initial amounts of the acid and hydrocarbon be a and b moles in volume V and x moles be esterified at eqm., then

$$K_C = \frac{\frac{x}{V}}{\frac{(a-x)}{V}\frac{(b-x)}{V}} = \frac{xV}{(a-x)(b-x)}$$

Heterogeneous Systems

(g) ***Dissociation of calcium carbonate.*** This is a heterogeneous chemical reaction, as one of the products (CO_2) is in the gas-phase while others are solids.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

If, at a constant temperature, calcium carbonate is kept in a closed vessel, then the reaction proceeds with gradual increase in pressure of CO_2 until a constant pressure is obtained which is called the dissociation pressure of calcium carbonate.

It is the generally accepted convention that the activities of solids should be regarded as unity. In the case of liquids, the standard state is the pure state (under 1 atm.), when activity is unity. But if it be present in liquid solution, as a first approximation, activity may be taken as equal to its mol-fraction.

Now, for dissociation of calcium carbonate, $a_{CaCO_3} = 1,\ a_{CaO} = 1$

$$\therefore\ K_a = \frac{a_{CaO} \times a_{CO_2}}{a_{CaCO_3}} = a_{CO_2} \approx P_{CO_2}$$

Assuming that carbon dioxide behaves ideally, Hence, at any given temperature, the dissociation pressure of calcium carbonate would be a constant.

(h) ***Hydrogen from reduction of steam***

(a) *with iron:* $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

$$\text{when} \quad K_a = \frac{a_{Fe_3O_4} \times a_{H_2}^4}{a_{Fe}^3 \times a_{H_2O}^4} = \left(\frac{a_{H_2}}{a_{H_2O}}\right)^4 \approx \left[\frac{P_{H_2}}{P_{H_2O}}\right]^4$$

Thus, the ratio of $P_{H_2}/P_{H_2}O$ is constant, which has been substantiated from experiment. This mean that with increase of steam-pressure higher yield of hydrogen is obtained.

(b) *with carbon:* $C + H_2O \rightleftharpoons CO + H_2$

$$\text{where} \quad K_a = \frac{a_{CO} \times a_{H_2}}{a_C \times a_{H_2O}} \approx \frac{P_{CO} \times P_{H_2}}{P_{H_2O}} = \frac{P_{H_2}^2}{P_{H_2O}}, \text{ (since } P_{CO} = P_{H_2})$$

$$\text{Hence,} \quad K_P = \frac{P_{H_2}^2}{P_{H_2O}}, \qquad \text{i.e., } P_{H_2} \propto \sqrt{P_{H_2O}}$$

Some Typical Numerical Examples

1. Calculate the pressure in atmosphere necessary to obtain a 50% dissociation of PCl_5 at 250°C. The eqm. constant for the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, $K_p = 1.8$. If we start with 1 mole of PCl_5, the moles of different gases at eqm. are, $PCl_5 = 0.5$ moles, $PCl_3 = 0.5$ moles, $Cl_2 = 0.5$ moles, Total = 1.5 moles.

The partial pressure are $P_{PCl_5} = P_{PCl_3} = PCl_2 = \frac{0.5}{1.5}P$

where P is the required total pressure in atmosphere.

$$\text{Hence,} \quad K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\left(\frac{0.5}{1.5}\right)^2 P^2}{\frac{0.5}{1.5}P} = \frac{1}{3}P$$

$$\text{or} \quad \frac{1}{3}P = 1.8, \; P = 5.4 \text{ atmosphere.}$$

This shows that in a reaction of the type $AB \rightarrow A + B$, the total pressure required for 50% dissociation is numerically 3 times K_P.

2. At 25°C, 1 mole of acetic acid and 1 mole of ethanol are mixed. At equilibrium 0.667 moles of acid have reacted. Calculate K_C. How much ester would be obtained if 2 moles of acid were taken with 1 mole ethanol under the same conditions ?

$$K_C = \frac{C_{ester} \times C_{H_2O}}{C_{acid} \times C_{alcohol}} = \frac{(0.667/V)(0.667/V)}{(0.333/V)(0.333/V)} = 4.00$$

In the other experiment, let x moles of acid be transformed, then

	CH_3COOH	+	EtOH	$\rightleftharpoons$	CH_3COOEt	+	H_2O
Conc:	$(2-x)/V$		$(1-x)/V$		x/V		x/V

$$\therefore \quad K_C = 4 = \frac{x^2}{(2-x)(1-x)} = \frac{x^2}{2-3x+x^2}$$

Where x = 3.15 or 0.85,

Since the first solution is absurd, amount of ester at equilibrium is 0.85 moles.

3. At 1000°K for the equilibria,

(i) $CaCO_3 \rightleftharpoons CaO + CO_2$, $K_P = 4.0 \times 10^{-2}$ atm.
(ii) $C + CO_2 \rightleftharpoons 2CO$, $K'_P = 2.0$ atm.

Solid carbon, CaO and $CaCO_3$ are mixed and allowed to attain eqm. at 1000°K. What is the pressure of CO?

$$K_P = \frac{a_{CaO} \times a_{CO_2}}{a_{CaCO_3}} \approx P_{CO_2}\ ; K'_P = \frac{a^2_{CO}}{a_C . a_{CO_2}} = \frac{P^2_{CO}}{P_{CO_2}}$$

$$\therefore \quad K_P . K'_P = P^2_{CO} \text{ or } P_{CO} = \sqrt{K_P . K'_P} = \sqrt{4 \times 10^{-2} \times 2.0} = 0.28 \text{ atmosphere.}$$

4. At 1000°C, the pressure of iodine gas is found to be 0.112 atm. whereas the expected pressure is 0.074 atm. The increased pressure is due to dissociation; $I_2 \rightleftharpoons 2I$. Calculate K_P. Also find out the pressure at which I_2 will be 90% dissociated at 1000°C.

I_2	$\rightleftharpoons$	$2I$	Total
$I - \alpha$		2α	$1 + \alpha$; α = degree of dissociation

Since pressure is proportional to number of moles of entities of gases; $P/P_0 = 1 + \alpha$,
Where, P = observed pressure, P_a = calculated pressure (having no dissociation).

$$\therefore \qquad \alpha = \frac{P - P_0}{P_0}$$

Now,
$$P_I = \frac{2\alpha}{1+\alpha} P\ ; \qquad P_{I_2} = \frac{1-\alpha}{1+\alpha} P$$

Hence,
$$K_P = \frac{\left[\frac{2\alpha}{1+\alpha} P\right]^2}{\left(\frac{1-\alpha}{1+\alpha} P\right)} = \frac{4\alpha^2}{1-\alpha^2} \frac{4\left(\frac{P-P_0}{P_0}\right)^2}{1-\left(\frac{P-P_0}{P_0}\right)^2} P$$

$$= \frac{4(P-P_0)^2}{2P_0 - P} = \frac{4(0.038)^2}{0.036} = 1.52 \times 10^{-2}$$

When degree of dissociation $\alpha = 0.90$, we have,

$$P = K_P \frac{(1-\alpha^2)}{4a^2} = 1.52 \times 10^{-2} \times \frac{(1-0.81)}{4 \times 0.81} = 8.9 \times 10^{-2} \text{ atm.}$$

5. The ammonia in eqm. with a 1 : 3 N_2–H_2 mixture at 20 temperature and 427°C amounts to 16%. Calculate K_P and K_C for

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$$

For 100 moles of mixture, there are 16 moles of ammonia. Hence every mole of mixture contains 0.16 moles NH_3, 0.21 moles N_2 and 0.63 moles H_2. Their partial pressure are:

$$P_{NH_3} = \frac{0.16}{1} \times 20 = 3.2 \text{ atm; } P_{H_2} = \frac{0.63}{1} \times 20 = 12.6 \text{ atm; } P_{N_2} = \frac{0.21}{1} \times 20 = 4.2 \text{ atm.}$$

$$\therefore \quad K_P = \frac{P_{NH_3}}{P^{\frac{3}{2}}_{H_2} \times P^{\frac{1}{2}}_{N_2}} = \frac{3.2}{(12.6)^{\frac{3}{2}} \times (4.2)^{\frac{1}{2}}} = 3.49 \times 10^{-2}$$

and $K_C = K_P(RT)^{-\Delta n} = K_P(RT)^{+1} = 3.49 \times 10^{-2} \times 700 \times 0.082 = 2.003$

6. Ammonia in equilibrium with 1 : 3 $N_2 - H_2$ mixture at 44 atm and 350°C is 15% by weight. Calculate K_P

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$$

100 g mixture contains 15 g ammonia, $\frac{14\times 85}{17}$ g N_2 and $\frac{3\times 85}{17}$ g of H_2. Then,

	NH_3	N_2	H_2	Total	
in moles	0.88	2.5	7.5	10.88	
in pressure	$\frac{0.88\times 44}{10.88}$	$\frac{2.5\times 44}{10.88}$	$\frac{7.5\times 44}{10.88}$		44

$$\therefore \quad K_P = \frac{[0.88\times 44/10.88]}{[2.5\times 44/10.88]^{\frac{1}{2}}\,[7.5\times 44/10.88]^{\frac{3}{2}}} = 6.7\times 10^{-2}$$

7. At 127°C, the equilibrium constant K_P for the reaction

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$$

is 2.4 in atmosphere, 6.75 g of SO_2Cl_2 are placed in an empty 1-litre bulb and the temperature raised to 127°C. What would be the pressure of SO_2, Cl_2 and SO_2Cl_2 gases?

Also calculate the pressure of these gases if the same quantity of SO_2Cl_2 were taken into the bulb already containing chlorine at 1 atm. Compare if the results are consistent with the Le-Chatelier principle.

In absence of dissociation, the initial pressure (P) of SO_2Cl_2 is,

$$P \times 1 = \frac{6.75}{135}\times 0.082\times(273+127), \text{ or } P = 1.64 \text{ atm.}$$

Now, $$K_P = \frac{P_{SO_2}\times P_{Cl_2}}{P_{SO_2Cl_2}} = \frac{P^2_{SO_2}}{P - P_{SO_2}} \qquad [\text{since } P_{SO_2} = P_{Cl_2}]$$

$$\therefore \quad \frac{P^2_{SO_2}}{P - P_{SO_2}} = \frac{P^2_{SO_2}}{1.64 - P_{SO_2}} = 2.4$$

Solving: $P_{SO_2} = P_{Cl_2} = 1.118$ atm, $P_{SO_2Cl_2} = 0.522$ atm

(b) When the bulb already contains chlorine at 1 atm, let the partial pressure of SO_2 at equilibrium be π. Then, $P_{Cl2} = (\pi + 1)$ and $P_{SO_2Cl_2} = 1.64 - \pi$

$$\therefore \quad K_P = \frac{\pi(\pi+1)}{1.64-\pi} = 2.4$$

Solving: $\pi = 0.912$, i.e., $P_{SO_2} = 0.912$; $P_{Cl_2} = 1.912$; $P_{SO_2Cl_2} = 0.728$ atm.

The addition of chlorine has diminished the extent of dissociation of SO_2Cl_2. This is expected from Le-Chatelier principle, which predicts the removal of chlorine, obviously by the reverse process.

8. (a) In phosgene gas reaction at 400°C, the initial pressures are $P_{CO} = 342$ mm and $P_{Cl_2} = 352$ mm and the total pressure at eqm, is 440 mm $CO + Cl_2 \rightleftharpoons COCl_2$.
Calculate the percentage dissociation of phosgene at 400°C at 1 atmosphere.

(b) What will be the extent of dissociation if N_2 is present in the system with a pressure of 0.4 atm., the total pressure being the same 1 atmosphere.

(a) Let x be the partial pressure of phosgene gas at eqm. At equilibrium then,

$P_{CO} = (342 - x)$ mm, $PCl_2 = (.352 - x)$mm, $P_{COCl_2} = x$ mm

$\therefore$ $(352 - x) + (342 + x) + x = 440$, i.e., $x = 254$ mm $= 0.334$ atm

$\therefore$ $P_{CO} = 342 - 254 = 88$ mm $= 0.116$ atm., $P_{Cl_2} = 352 - 254 = 98$ mm $= 0.128$ atm. The eqm. constant for the dissociation of phosgene:

$COCl_2 = CO + Cl_2$

$1 - \alpha \quad \alpha \quad \alpha$

$$\therefore \quad K_P = \frac{P_{CO} \times P_{Cl_2}}{P_{COCl_2}} = \frac{0.116 \times 0.128}{0.334} = 4.4 \times 10^{-2}$$

But $K_P = \dfrac{\alpha^2 P}{1-\alpha^2} = 4.4 \times 10^{-2}$

Since $P = 1$, $\alpha = 0.206$, i.e., dissociation is 20.6%

(b) When inert N_2 is present with $P_{N_2} = 0.4$ atm, the total pressure of the reactant and resultants at eqm. = 0.6 atm

Hence, $K_P = \dfrac{\alpha_1^2 P}{1-\alpha_1^2}$, where α_1 is the degree of dissociation in presence of N_2

or $\dfrac{\alpha_1^2 (0.6)}{1-\alpha_1^2} = 4.4 \times 10^{-2}$, where $\alpha_1 = 0.26$, i.e., 26%

The presence of N_2 has enhanced the extent of dissociation.

Effect of temperature (quantitative)

Now we will derive the dependence of K_p on temperature.

Starting with Arrhenius equation of rate constant,

$$k_f = A_f e^{-E_{a_f}/RT} \qquad \text{(i)}$$

Where, k_f = rate constant for forward reaction, A_f = Arrhenius constant of forward reaction,

E_{a_f} = Energy of activation of forward reaction

$$k_r = A_r e^{-E_{a_r}/RT} \qquad \text{(ii)}$$

Dividing (2) by (3) we get,

$$\frac{k_f}{k_r} = \frac{A_f}{A_r} e^{\frac{(E_{a_r} - E_{a_f})}{RT}}$$

We know that, $\dfrac{k_f}{k_r} = K$ (equilibrium constant)

$$\therefore \quad K = \frac{k_f}{k_r} = \frac{A_f}{A_r} e^{\frac{(E_{a_r} - E_{a_f})}{RT}}$$

At temperature T_1,

$$K_{T_1} = \frac{A_f}{A_r} e^{\frac{(E_{a_r} - E_{a_f})}{RT_1}} \qquad \text{(iii)}$$

At temperature T_2,

$$K_{T_2} = \frac{A_f}{A_r} e^{\frac{(E_{a_r} - E_{a_f})}{RT_2}} \qquad \text{(iv)}$$

Dividing (5) by (4) we get,

$$\frac{K_{T_2}}{K_{T_1}} = e^{\left(\frac{E_{ar} - E_{af}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$\Rightarrow \quad \log \frac{K_{T_2}}{K_{T_1}} = \frac{E_{a_r} - E_{a_f}}{2.303\ R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The enthalpy of a reaction is defined in terms of activation ene gies as $E_{a_f} - E_{a_r} = \Delta H$

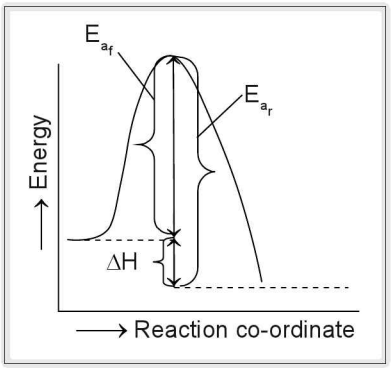


Fig. 6.3

$$\therefore \quad \log \frac{K_{T_2}}{K_{T_1}} = \frac{-\Delta H}{2.303\ R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\therefore \quad \log \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{(v)}$$

For an exothermic reaction, ΔH would be negative. If we increase the temperature of the system ($T_2 > T_1$), the right hand side of the equations (V) becomes negative.

$\therefore$ $K_{T_2} < K_{T_1}$, that is, the equilibrium at the higher temperature would be less than that at the lower temperature.

Now, let us analyse our question. Will the reaction go forward or backward?

Before answering this, we must first encounter another problem. If temperature is increased, the new K_P would either increase or decrease or may remain same. Let us assume it increases.

Now, Q_P can also increase, decrease or remain unchanged. If K_P increases and Q_P decreases, than $Q_{P_{T_2}} < K_{P_{T_2}}$, therefore, the reaction moves forward. If K_P increases and Q_P remains same, then $Q_{P_{T_2}} \left(Q_{P_{T_1}}\right) < K_{P_{T_2}}$. Again, the reaction moves forward. What, if K_P increase and Q_P also increases?

$\therefore$ K_P would still be greater than Q_P and the reaction moves forward again.

Therefore, to see the temperature effect, we need to look at K_P only. If it increases the reaction moves forward, if it decreases, reaction moves backward and if it remains fixed, then, no change at all.

Worked-out Examples

42. K_p for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.6×10^{-4} atm^{-2} at 400°C. What will be K_p at 500°C. Heat of reaction in this temperature range is – 25.14 kcal.

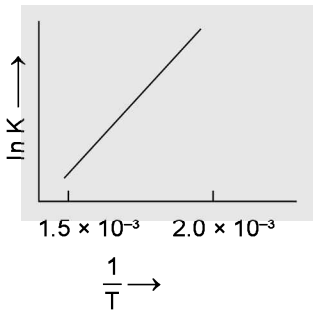
Solution We know that,

$$\log \frac{k_{p_2}}{k_{p_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{1.6\times10^{-4}}{K_{p_2}} = \frac{-25.14}{2.303\times2\times10^{-5}}\left[\frac{773-673}{773\times673}\right]$$

$\Rightarrow \quad k_{p_1} = 1.46 \times 10^{-5}$ atm^{-2}

43. The graph relates ln $K_{eq.}$ vs $\frac{1}{T}$ for a reaction. The reaction must be: **[AIEEE-2005]**



(a) Exothermic
(b) Endothermic
(c) ΔH is negligible
(d) High spontaneous at ordinary temperature

Solution (a) $\ln \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

Since K increase with decrease of temperature and thus, ΔH = –ve.

Influences of inert gases on the equilibrium of gaseous reactions

It would be of interest to know if the equilibrium. concentrations of the components would alter by the presence of some inert gases i.e., gases which do not interact chemically with the components.

Consider a gaseous reaction: $aA + bB \rightleftharpoons cC + dD$

Let x_A, x_B, x_C, x_D denote the-mol-fractions of the components at equilibrium. At a constant temperature, the equilibrium constant K_p remains constant.

Now,

$$K_P = \left(\frac{x_C^c \times x_D^d}{x_A^a \times x_B^b}\right).(p)^{\Delta n}$$

Let n_0 gm-moles of an inert gas be introduced into the system. If n-term denote the gm-moles of the components, then,

$$x_A = \frac{n_A}{n_0 + n_A + n_B + n_C + n_D} = \frac{n_A}{\Sigma n}, \ \Sigma n = \text{total number of moles.}$$

Similarly, $x_B = \frac{n_B}{\Sigma n}$; $x_C = \frac{n_C}{\Sigma n}$; etc.

Hence, $$K_p = \frac{(n_C/\Sigma n)^c \times (n_D/\Sigma n)^d}{(n_A/\Sigma n)^a \times (n_B/\Sigma n)^b} \times (P)^{\Delta n} = \left[\frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}\right] \times \left(\frac{P}{\Sigma_n}\right)^{\Delta n} \quad \ldots. (A)$$

The introduction of an inert gas would always increases Σn. The effect may be considered separately in different cases.

1. When the inert gas is added at constant pressure:

(a) For a reaction in which $\Delta n = 0$, $(P/\Sigma n)^{\Delta n} = 1$. Hence in such a reaction, the first term $\left[\frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}\right]$ of equation (A) will remain unaltered to keep K_p constant. That is, the equation remains undisturbed.

(b) For a reaction in which Δn is positive, $(P/\Sigma n)^{\Delta v}$ diminishes with increase in Σn; hence the first factor of equation (A) will increase in magnitude to keep K_p constant. This is possible by increasing the concentrations of resultants in the numerator and decreasing the concentrations in the denominator. In other words, there would be more of the reaction. At constant pressure, the presence of nitrogen would increase the dissociation of phosphorus pentachloride.

(c) For a reaction in which Δn is negative, $(P/\Sigma n)^{\Delta n}$ increases with increase in Σn; hence the equilibrium will shift to reactent side.

When inert gas is introduced at constant pressure, the equilibrium shifts to that side where the sum of stoichiometric coefficient of gaseous component is g eater.



Worked-out Examples

44. For the reaction: **[IIT-JEE-1991]**

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

Solution (c, d, e) Introduction of an inert gas at constant pressure causes the equilibrium to shift in a direction in which number of moles increases. The forward reaction is further accelerated by increase in the quantity of substrate, i.e., PCl_5 and by the increase of space, i.e., volume of container.

45. The equilibrium: **[IIT-JEE-1989]**

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?

(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 do not change
(b) More chlorine is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl, is formed.

Solution (a) At constant volume, concentrations do not change.

A quantitative version is given by the reaction quotient

J.W. Gibbs suggested in 1873 that equilibrium is attained when the Gibbs energy of the system is at its minimum value (assuming the reaction is carried out under constant pressure). What this means is that the derivative of the Gibbs energy with respect to reaction coordinate (a measure of the extent of reaction that has occurred, ranging from zero for all reactants to a maximum for all products) vanishes, signalling a stationary point. This derivative is usually called, for certain technical reasons, the Gibbs energy change. This criterion is both necessary and sufficient. If a mixture is not at equilibrium, the liberation of the excess Gibbs energy (or Helmholtz energy at constant volume reactions) is the "driving force" for the composition of the mixture to change until equilibrium is reached. The equilibrium constant can be related to the standard Gibbs energy change for the reaction by the equation,

$$\Delta_r G^{\ominus} = -RT \ln K_{eq}$$

Where R is the universal gas constant and T the temperature.

dG_r relates to Q and T (temperature) in the following equation:

$$dG_r = dG_r^{\circ} + RT \ln(Q)$$

Where dG_r° is the Gibbs free energy associated with a specific reaction at standard conditions

When dG_r is negative, the forward reaction is spontaneous and thus the reverse reaction nonspontaneous. When dG_r is positive, the forward reactions is nonspontaneous, thus, the reverse reaction is spontaneous. This is true to Q's deviation from K and Le Chatlier's Principle at standard temperature. When Q is larger than K, more products are present initially than at equilibrium, according to Le Chatlier's Principle, the equilibrium shifts towards the reactants. In other words, the reverse reaction is spontaneous, which corresponds to a positive dG_r value. When Q is smaller than K, more reactants are present initially than at equilibrium, the reaction shifts towards the products, thus the forward reaction is spontaneous. This corresponds to a negative dG_r value. The relationship between Q and dG_r can be represented by this graph.

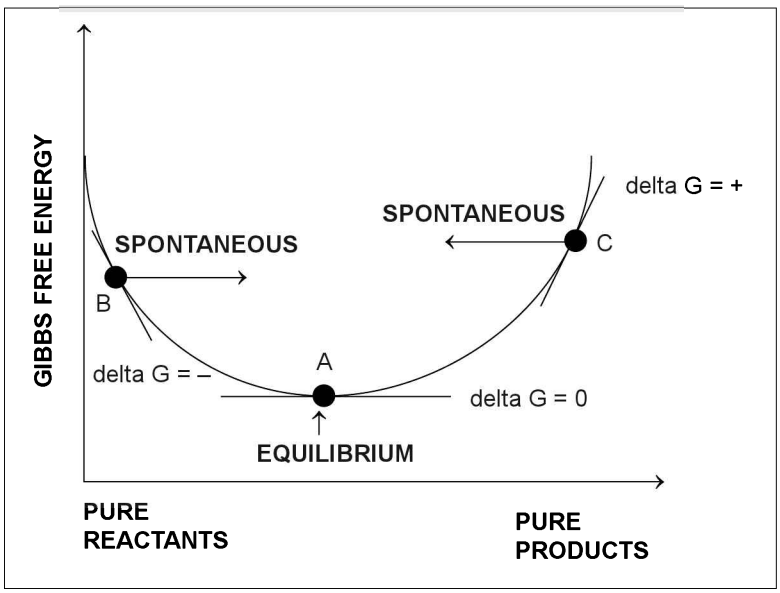


Fig. 6.4

Point **A** refers to a point where the system is in equilibrium, thus, Q=K and dG_r=0. Point **B** refers to a point when Q<K, therefore, the forward reaction is spontaneous to reach equilibrium and dG_r=negative.

Point **C** refers to a point when Q>K, therefore, the reverse reaction is spontaneous to reach equilibrium and dG_r=positive.

$$\Delta G = \Delta G^0 + 2.303\ RT\ \log Q \quad \ldots (1)\ (Q = \text{Reaction Quotient})$$

Under equilibrium condition, $Q = K_C$ or K_P

The Gibbs free energy G for a system is defined as $G = H - TS$

$$\Delta G = \Delta H - T\Delta S \quad \ldots (2)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \ldots (3)\ (\text{standard condition})$$

For a process occurring at constant T and P if (1) $\Delta G < O$, the process is spontaneous.

(2) $\Delta G > O$, the process is non-spontaneous

(3) $\Delta G = 0$, the process is at equilibrium

$\therefore$ At equilibrium,

$$0 = \Delta G^0 + 2.303\ RT\ \log K$$

$$\therefore \quad \Delta G^0 = -2.303\ RT\ \log K \quad \ldots (4)$$

$$\therefore \quad \log K = -\frac{\Delta G^0}{2.303RT} \Rightarrow \ln K = \frac{\Delta G^0}{RT}$$

From equation (3) and (4),

$$-2.303\ RT\ \log K = \Delta H^0 - T\Delta S^0$$

$$\Rightarrow \quad \log K = \frac{-\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303RT}$$

$$\log K_1 = -\frac{\Delta H^0}{2.303RT_2} + \frac{\Delta S^0}{2.303R}\ (\text{At temperature } T_1)$$

$$\log K_2 = -\frac{\Delta H^0}{2.303RT_2} + \frac{\Delta S^0}{2.303R}\ (\text{At temperature } T_2,\ T_1 < T_2)$$

(Assuming $\Delta H°$ to be constant in temperature range T_1 and T_2)

$$\therefore \quad \text{lok}\ \frac{K_2}{K_{11}} = \frac{\Delta H^0}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\Rightarrow \quad \log \frac{K_2}{K_1} = \frac{\Delta H^0}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\text{Also,}\ \frac{d \log K_C}{dT} = \frac{\Delta E^0}{2.303RT^2}$$

Similarly, $\frac{d \log K_C}{dT} = \frac{\Delta E^0}{2.303RT^2}$ where ΔE is the change in internal energy associated with the system.

Graph between logK and $\frac{1}{T}$

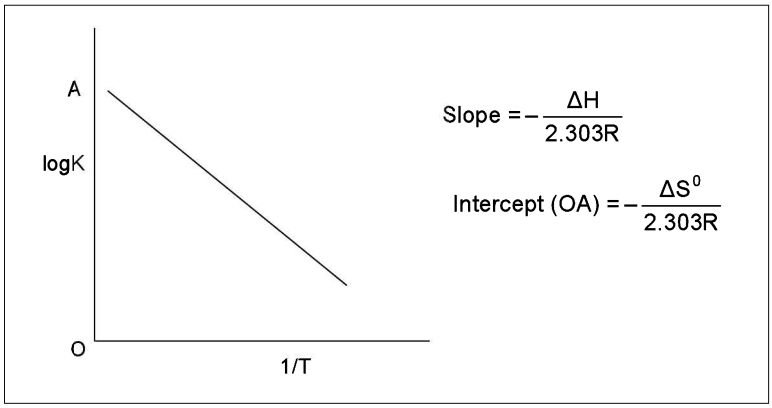


Fig. 6.5

K is referred to as thermodynamic equilibrium constant and can be replace by K_C or K_p for general reaction.

$$aA + bB \rightleftharpoons mC + nD$$

$$K = \frac{(a_c)^m (a_D)^n}{(a_A)^a (a_B)^b} \text{ (Thermodynamic equilibrium constant)}$$

(i) For pure solids and liquids a = 1
(ii) For gases ideal behaviour is considered and activity is equal to its pressure in (atm)
(iii) For components in solution a = molar concentration.

Further, for changes in standard states,

$$\left.\begin{aligned} \Delta G° &= -RT \ln K_p \\ \Delta G° &= -RT \ln K_c \end{aligned}\right\}$$

(the standard states should be specified in each case

These relations are of unique importance of the chemist.

The knowledge of ΔG would therefore allow the evaluation of the equilibrium constant K_p or K_c. The methods for the determination of free energy change ΔG of a process have been discussed. Most commonly used relations for this purpose are:

(i) $\Delta G^o = \Delta H^o - T\Delta S^0$
(ii) $\Delta G^o = \Sigma \Delta G^0_{f(\text{products})} - \Sigma \Delta G^0_{f(\text{reactiants})}$

We shall see later that ΔG for reactions occurring in voltaic cells can also be estimated from measurement of emf of these cells.

Alternatively, experimental determination of K_p or K_c will enable us to estimate the free energy change of the process.

Since, $\Delta G^0 = -RT \ln K$(K, the appropriate equilibrium constant)

Now, $\Delta G^0 = \Delta H^o - T\Delta S^o$, hence, $K = e^{\frac{-\Delta H^\circ}{eRT}} \cdot \frac{\Delta S^\circ}{e^R}$

It is evident that,

(i) When $\Delta G^0 < 0$ i.e., ΔG is negative, K will be greater than unity. As ΔG^o becomes more and more negative, K will be larger and larger.
(ii) The more negative the value of ΔH^o, the larger will be the value of K.
(iii) The larger the value of ΔG^o, the higher will be magnitude value of K.

The higher values of K indicates greater extent of reaction to produce the resultants. The reaction will be favoured by negative values of ΔH° and ΔG° and by increase of randomness i.e., positive values of ΔS°. As G° is a state function, the standard free energy changes and hence, the equilibrium constants of related reactions are also related. For example,

(i) $2NO + O_2 \rightleftharpoons 2NO_2; \Delta G_1^\circ = -RT \ln K_1$

Adding, (ii) $2NO_2 \rightleftharpoons N_2O_4; \Delta G_2^\circ = -RT \ln K_2$

$2NO + O_2 \rightleftharpoons N_2O_4; \Delta G_2^\circ = -RT \ln K_1$

(ii) $2NO + O_2 \rightleftharpoons N_2O_4; \Delta G_2^\circ = -RT \ln K_3$

Since, dG° is a perfect differential, ΔG_3^0

$\therefore \quad -RT \ln K_3 = -RT \ln K_1K_2$

or $\quad K_3 = K_1 \times K_2$

That is, the equilibrium constant of a reaction which is the sum of two other reactions is the product of the equilibrium constants for those two reactions. A few illustrative examples are given.



Worked-out Examples

46. ΔG^0 for $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$ is –16.5 kJ/mol. Find out K_p for the reaction. Also report K_p and ΔG^0 for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 25°C.

Solution $-\Delta G^0 = 2.303\ RT \log K_p$

$-(16.5 \times 10^3) = 2.303 \times 8.314 \times 298 \log K_p$

$\Rightarrow K_p = 779.4\ atm^{-1}$

Also, k_p' for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$k_p{}^1 = (k_p)^2 = (779.4)^2$

$= 6.06 \times 10^5\ atm^{-2}$

Also, $\Delta G^0 = 2.303\ RT \log k_p'$

$= 2.303 \times 8.314 \times 298 \log (6.07 \times 10^5) \Rightarrow -32.989$ kJ/mole

47. The equilibrium constant for the reaction,

$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$ as a function of temperature can be expressed as

$KT \ln k_p = -40900 + 4.9T \ln T - 4.95 \times 10^{-2} T^2 + 5.1 \times 10^{-7} T^3 + 12.66T$

In the range of 1100 to 1500 K. If the p_{CO_2} at 1200 K is 1.2 atm calculate p_{CO}.

Solution For the given reaction,

$$k_p = \frac{p_{CO}^2}{p_{CO_2}} \text{ or}$$

$$\Rightarrow p_{CO} = \left(k_p p_{CO_2}\right)^{1/2}$$

k_p at 1200 K can be calculated from the reaction

$$\ln k_p = \frac{1}{1200 \times 8.314}[-40900 + 4.9\,(1200)$$

$$\ln 1200 - (4.95 \times 10^{-2})\,(1200)^2 + (5.1 \times 10^{-7})\,(1200)^3 + (12.66)\,(1200)]$$

$$\ln k_p = -5.454$$

$$\Rightarrow k_p = 4.28 \times 10^{-3}$$

putting the value of k_p

$$p_{CO} = (4.28 \times 10^{-3} \times 1.2)^{1/2} = 0.072 \text{ atm}$$

1. At 1000°K, the value of K_p for the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, is 3.5. What would be the thermodynamic potential change if 2 moles of SO_3 at 1 atm are formed from SO_2 at 0.1 atm and O_2 at 0.2 atm at this temperature? [Use R in litre-atm.]

$$\Delta = -RT \ln K_p + RT \ln \frac{P^o_{SO_2}}{P^2_{SO_2} \times P_{O_2}}$$

$$= -RT \ln 3.5 + RT \ln \frac{(1)^2}{(0.1)^2 \times (0.2)} = 9890 \text{ cal}$$

2. For the reaction, $H_2 + S \rightleftharpoons H_2S$, calculate K_p at 25°C if the standard thermodynamic potential of H_2S is –7.88 Kcal.

We have, $\Delta G^\circ = [\Delta G^\circ_f]_{H_2S} - [\Delta G^0_f]_{H_2} - [\Delta G^0_f]_s$

$$= -7880 \quad -0 \quad -0 = -7880 \text{ cal}$$

Hence, $\log K = -\frac{\Delta G^\circ}{2.3RT} = \frac{7880}{2.3 \times (1.98)(298)} = 5.78$

$\therefore \quad K = 6.02 \times 10^5$

ΔG° can be evaluated from standard heat of reaction Δ° and the entropy change ΔS°.

3. The value of K for the reaction,

$$O_3(g) + OH(g) \rightleftharpoons H(g) + 2O_2(g)$$

changed from 0.096 at 298 K to 1.4 at 373 K. Above that what temperature will the reaction become thermodynamically spontaneous in the forward direction assuming that ΔH° and ΔS° values for the reaction do not change with change in temperature? Given that, $\Delta S^0_{298} = 102.96 \text{ JK}^{-1}$
We have,

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \frac{(T_2 - T_1)}{T_1 T_2}$$

$$\log \frac{1.4}{0.096} = \frac{\Delta H^\circ}{2.303 \times 8.314}\left(\frac{373 - 298}{373 \times 298}\right)$$

$$\Delta H^\circ = 33025 \text{ J.}$$

Now the temperature above which the forward reaction will be spontaneous is actually the temperature at which the reaction attains equilibrium, that is, when K = 1 or log K = 0.

$\therefore \quad \Delta G^\circ = -2.303\ RT\ lo\ K$

$= -2.303\ RT \log 1.0$

$= 0$

From thermodynamics, we have,

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$0 = 33025 - T \times 102.96$

or $T = 320.75\ K$



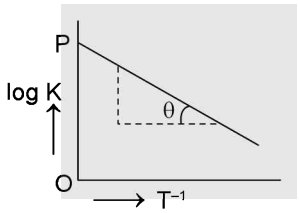
Worked-out Examples

48. Variation of equilibrium constant K with temperature T is given by Van't Hoff equation,

$$\log K = \log A - \frac{\Delta H^\circ}{2.303\ RT}$$

A graph between log K and T^{-1} was a straight line as shown and having OP = 10 and $\tan\theta = 0.5$. Calculate:

(i) equilibrium constant at 298 K, and
(ii) and equilibrium constant at 798 K, assuming ΔH° to be independent of temperature.



Solution To calculate equilibrium constant, we need to know A and ΔH°, which are calculated as

The given equation represents a straight line of slope,

$$= \frac{-\Delta H^\circ}{2.303\ R}$$

$= -\tan\theta = -0.5$

$\therefore \quad \Delta H^\circ = 2.303 \times 8.314 \times 0.5 = 9.574\ J/mol$

Intercept = log A = OP = 10

$$\therefore \quad \log K = \log A - \frac{\Delta H^\circ}{2.303\ RT} = 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$\therefore \quad K = 9.96 \times 10^9$

Now, to calculate equilibrium constant at some other temperature, we will use the expression

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314}\left[\frac{500}{798 \times 298}\right]$$

$\therefore \quad K_2$ (equilibrium constant at 798 = 9.98×10^9)

49. K_c for the reaction, $N_2O_4 \rightleftharpoons 2NO_2$ in chloroform at 291 K is 1.14. Calculate the free energy change of the reaction when the concentration of the two gases are 0.5 mol dm^{-3} each at the same temperature. (R = 0.082 lit atm K^{-1} mol^{-1}.)

Solution From the given data,

$T = 291$ K; $R = 0.082$ lit atm K^{-1} mol^{-1}

$K_c = 1.14$; $C_{NO_2} = C_{N_2O_4} = 0.5$ mol dm^{-3}

The reaction quotient Q_c for the reaction $N_2O_4 \rightleftharpoons 2NO_2$,

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.5 \times 0.5}{0.5} = 0.5$$

Since $Q_p = Q_c(RT)^{\Delta n}$ and $\Delta n = 2 - 1 = 1$ in this case

$\therefore$ $Q_c = 0.5\ (0.082 \times 291) = 11.93$

$K_p = K_c(RT)^{\Delta n} = 1.14\ (0.082 \times 291) = 27.1$

Substituting these values in the equation

$\Delta G = \Delta G^0 + RT\ln Q_p = -RT \ln K_p + RT \ln Q_p$, we get

$= -2.303\ RT\ (\log K_p - \log Q_p)$

$\Delta G = -(0.082 \times 291 \times 2.303)\ [\log 27.2 - \log 11.93]$

$= -54.95\ (1.4346 - 1.0766) = -9.67$ lit atm

ONE CORRECT OPTION TYPE QUESTIONS

1. The equilibrium constant K_c for the reaction

$$P_4(g) \rightleftharpoons 2P_2(g)$$

is 1.4 at 400°C. Suppose that 3 moles of $P_4(g)$ and 2 moles of $P_2(g)$ are mixed in 2 litre container at 400°C. What is the value of reaction quotient (Q)?

(a) $\frac{3}{2}$ (b) $\frac{2}{3}$

(c) 1 (d) None of these

2. The equilibrium constant for a reaction is 1C, and the reaction quotient is Q. For a particular reaction mixture, the ratio $\frac{K}{Q}$ is 0.33. This means that:

(a) the reaction mixture will equilibrate to form more reactant species

(b) the reaction mixture will equilibrate to form more product species

(c) the equilibrium ratio of reactant to product concentrations will be 3

(d) the equilibrium ratio of reactant to product concentrations will be 0.33

3. In the presence of excess of anhydrous $SrCl_2$, the amount of water taken up is governed by $K_p = 10^{12}$ atm^{-4} for the following reaction at 273 K

$$SrCl_2 . 2H_2O(s) + 4H_2O(g) \rightleftharpoons SrCl_2 . 6H_2O(s)$$

What is equilibrium vapour pressure (in torr) of water in a closed vessel that contains

$SrCl_2 . 2H_2O(s)$?

(a) 0.001 torr (b) 10^3 torr

(c) 0.76 torr (d) 1.31 torr

4. When heated, ammonium carbamate decomposes as follows:

$$NH_4COONH_2(g) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

At a certain temperature, the equilibrium pressure of the system is 0.318 atm. K_p for the reaction is:

(a) 0.128 (b) 0.426

(c) 4.76×10^{-3} (d) None of these

5. The equilibrium constant K_p for the reaction

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

is 4.0 at 1660°C. Initially 0.80 mole H_2 and 0.80 mole CO_2 are injected into a 5.0 litre flask. What is the equilibrium concentration of $CO_2(g)$?

(a) 0.533 M (b) 0.0534 M

(c) 0.535 M (d) None of these

6. At 273 K and 1 atm, 10 litre of N_2O_4 decomposes to NO_2 according to equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

What is degree of dissociation (α) when the original volume is 25% less than that of existing volume?

(a) 0.25 (b) 0.33

(c) 0.66 (d) 0.5

7. The equilibrium constant for the reaction $CO(g) + H_2O(g)$ f5* $CO_2(g) + H_2(g)$ is 5. How many moles of CO_2 must be added to 1 litre container already containing 3 moles each of CO and H_2O to make 2M equilibrium concentration of CO?

(a) 15 (b) 19

(c) 5 (d) 20

8. At 27°C and 1 atm pressure, N_2O_4 is 20% dissociation into NO_2. What is the density of equilibrium mixture of N_2O_4 and NO_2 at 27°C and 1 atm?

(a) 3.11 g/litre (b) 2.11 g/litre

(c) 4.5 g/litre (d) None of these

9. $COCl_2$ gas dissociates according to the equation, $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$. When heated to 700 K the density of the gas mixture at 1.16 atm and at equilibrium is 1.16 g/litre. The degree of dissociation of CO_2 at 700 K is:

(a) 0.28 (b) 0.50

(c) 0.72 (d) 0.42

10. At 87°C, the following equilibrium is established

$$H_2(g) + S(s) \rightleftharpoons H_2S(g); \quad K_p = 7 \times 10^{-2}$$

If 0.50 mole of hydrogen and 1.0 mole of sulphur are heated to 87°C in 1.0 L vessel, what will be the partial pressure of H_2S at equilibrium?

(a) 0.966 atm (b) 1.38 atm

(c) 0.0327 atm (d) 1 atm

11. Pure PCl_5 is introduced into an evacuated chamber and comes to equilibrium at 247°C and 2.0 atm. The

equilibrium gaseous mixture contains 40% chlorine by volume. Calculate K_p at 247°C for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a) 0.625 atm (b) 4 atm
(c) 1.6 atm (d) None of these

12. For the reaction $XCO_3(s) \rightleftharpoons XO(s) + CO_2(g)$, K_p =1.642 atm at 727°C. If 4 moles of $XCO_3(s)$ was put into a 50 litre container and heated to 727°C.
What mole per cent of the XCO_3 remains unreacted at equilibrium?
(a) 20 (b) 25
(c) 50 (d) None of these

13. $Fe_2O_3(s)$ may be converted to Fe by the reaction

$$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2FeCs) + 3H_2O(g),$$

for which $K_c = 8$ at temp. 720°C.
What percentage of the H_2 remains unreacted after the reaction has come to equilibrium?
(a) ≃ 22% (b) ≃ 34%
(c) ≃ 66% (d) ≃ 78%

14. $AB_3(g)$ is dissociates as

$$AB_3(g) \rightleftharpoons AB_2(g) + \frac{1}{2}B_2(g).$$

When the initial pressure of AB_2 is 800 torr and the total pressure developed at equilibrium is 900 torr. What fraction of $AB_3(g)$ is dissociated?
(a) 10% (b) 20%
(c) 25% (d) 30%

15. Pure nitrosyl chloride (NOCl) gas was heated to 240°C in a 1.0 L container. At equilibrium the total pressure was 1.0 atm and the NOC1 pressure was 0.64 atm. What would be the value of K_p?
(a) 1.02 atm (b) 16.875×10^{-3} atm
(c) 16×10^{-2} atm (d) None of these

16. For the dissociation reaction N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g), the degree of dissociation (a) in terms of K_p and total equilibrium pressure P is:
(a) $\alpha = \sqrt{\frac{4P + K_P}{K_P}}$ (b) $\alpha = \sqrt{\frac{K_P}{4P + K_P}}$
(c) $\alpha = \sqrt{\frac{K_P}{4P}}$ (d) None of these

17. The vapour pressure of mercury is 0.002 mm Hg at 27°C. K_c for the process $Hg(l) \rightleftharpoons Hg(g)$ is:
(a) 0.002 (b) 8.12×10^{-5}
(c) 6.48×10^{-5} (d) 1.068×10^{-7}

18. K_p has the value of 10^{-6} atm^3 and 10^{-4} atm^3 at 298 K and 323 K respectively for the reaction

$$CuSO_4 . 3H_2O(s) \rightleftharpoons CuSO_4(s) + 3H_2O(g)$$

$\Delta_r H°$ for the reaction is:
(a) 7.7kJ/mol (b) –147.41 kJ/mol
(c) 147.41 kJ/mol (d) None of these

19. The following equilibrium constants were determined at 1120 K:

$$2CO(g) \rightleftharpoons C(s) + CO_2(g);$$
$$K_{P_1} = 10^{-14} \text{ atm}^{-1}$$

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g);$$
$$K_{P_2} = 6 \times 10^{-3} \text{ atm}^{-1}$$

What is the equilibrium constant K_c for the following reaction at 1120 K:

$$C(s) + CO_2(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g)$$

(a) 3.31×10^{11} M^{-1} (b) 5.5×10^{10} M^{-1}
(c) 5.51×10^{6} M^{-1} (d) None of these

20. Assume that the decomposition of HNO_3 can be represented by the following equation

$$4HN0_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$$

and the reaction approaches equilibrium at 400 K temperature and 30 atm pressure. At equilibrium partial pressure of HNO_3 is 2 atm.
Calculate K_c in (mol/L)^3 at 400 K:
(Use: R = 0.08 atm-L/mol-K)
(a) 4 (b) 8
(c) 16 (d) 32

21. For the equilibrium

$$LiCl.3NH_3(s) \rightleftharpoons LiCl.NH_3(s) + 2NH_3(g);$$

K_p = 9 atm^2 at 37°C. A 5 litre vessel contains 0.1 mole of $LiCl.NH_3$. How many moles of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion?
Use: R = 0.082 atm-L/mol K
(a) 0.2 (b) 0.59
(c) 0.69 (d) 0.79

22. For the reaction $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$ K_p is 5×10^{-2} atm. Calculate the mole per cent of $C_2H_6(g)$ at equilibrium if pure C_2H_6 at 1 atm is passed over a suitable catalyst at 900 K:
(a) 20 (b) 33.33
(c) 66.66 (d) None of these

23. Consider the partial decomposition of A as

$$2A(g) \rightleftharpoons 2B(g) + C(g)$$

At equilibrium 700 mL gaseous mixture contains 100 mL of gas C at 10 atm and 300 K. What is the value of K_p for the reaction?

(a) $\frac{40}{7}$ (b) $\frac{1}{28}$

(c) $\frac{10}{28}$ (d) $\frac{28}{10}$

24. 0.020 g of selenium vapour at equilibrium occupying a volume of 2.463 mL at 1 atm and 27°C. The selenium is in a state of equilibrium according to reaction

$$3Se_2(g) \rightleftharpoons Se_6(g)$$

What is the degree of association of selenium?
(At. wt. of Se = 79)

(a) 0.205 (b) 0.315

(c) 0.14 (d) None of these

25. Determine the degree of association (polymerization) for the reaction in aqueous solution

$$6HCHO \rightleftharpoons C_6H_{12}O_6$$

If observed (mean) molar mass of HCHO and $C_6H_{12}O_6$ is 150:

(a) 0.50 (b) 0.833

(c) 0.90 (d) 0.96

26. A reaction system in equilibrium according to reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ in one litre vessel at a given temperature was found to be 0.12 mole each of SO_2 and SO_3 and 5 mole of O_2. In another vessel of one litre contains 32 g of SO_2 at the same temperature. What mass of O_2 must be added to this vessel in order that at equilibrium 20% of SO_2 is oxidized to SO_3?

(a) 0.4125 g (b) 13.2 g

(c) 1.6 g (d) None of these

27. A vessel of 250 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain the equilibrium at 440°C as

$$Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$$

After equilibrium, the H_2S formed was analysed by dissolved it in water and treating with excess of Pb^{2+} to give 1.19 g of PbS as precipitate. What is the value of K_c at 440°C?

(a) 1 (b) 2

(c) 4 (d) 8

28. For the reaction $2A(g) + B(g) \rightleftharpoons C(g) + D(g)$; $K_c = 10^{12}$. If the initial moles of A, B, C and D are 2,1, 7 and 3 moles respectively in a one litre vessel. What is the equilibrium concentration of A?

(a) 4×10^{-4} (b) 2×10^{-4}

(c) 10^{-4} (d) 8×10^{-4}

29. The equilibrium constant for the reaction in aqueous solution

$$H_3BO_3 + \text{glycerin} \rightleftharpoons$$

$(H_3BO_3\text{–glycerin})$ is 0.90.

How many moles of glycerin should be added per litre of 0.10 M H_3BO_3 so that 80% of the H_3BO_3 is converted to the boric-acid-glycerin complex?

(a) 4.44 (b) 4.52

(c) 3.6 (d) 0.08

30. Rate of diffusion of ozonized oxygen is $0.4\sqrt{5}$ times that of pure oxygen. What is the per cent degree of association of oxygen assuming pure O_2 in the sample initially?

(a) 20 (b) 40

(c) 60 (d) None of these

31. One mole of SO_3 was placed in a two litre vessel at a certain temperature. The following equilibrium was established in the vessel:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

The equilibrium mixture reacted with 0.2 mole $KMnO_4$ in acidic medium. Hence, K_c is:

(a) 0.50 (b) 0.25

(c) 0.125 (d) None of these

32. At 800°C, the following equilibrium is established as

$$F_2(g) \rightleftharpoons 2F(g)$$

The composition of equilibrium may be determined by measuring the rate of effusion of the mixture through a pin hole. It is found that at 800°C and 1 atm mixture effuses 1.6 times as fastasSO_2 effuses under the similar conditions. (At. wt. of F = 19). What is the value of K_p (in atm)?

(a) 0.315 (b) 0.685

(c) 0.46 (d) 1.49

33. The equilibrium constant for the ionization of $RNH_2(g)$ in water as

$$RNH_2(g) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$

is 8×10^{-6} at 25°C. Find the pH of a solution at equilibrium when pressure of $RNH_2(g)$ is 0.5 bar:

(a) ≈ 12.3 (b) ≈11.3
(c) ≈ 11.45 (d) None

34. When N_2O_5 is heated at certain temperature, it dissociates as $N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g)$ $K_c = 2.5$. At the same time N_2O_3 also decomposes as: $N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g)$. I initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to dissociatior concentration of O_2 at equilibrium is 2.5 M. Equilibrium concentration of N_2O_5 is:

(a) 1.0 M (b) 1.5 M
(c) 2.166 M (d) 1.846 M

35. Two solid compounds X and Y dissociates at a certain temperature as follows:

$$X(s) \rightleftharpoons A(g) + 2B(g);\ K_{P_1} = 9 \times 10^{-3}\ atm^3$$
$$Y(s) \rightleftharpoons 2B(g) + C(g);$$
$$K_{P_2} = 4.5 \times 10^{-3}\ atm^3$$

The total pressure of gases over a mixture of X and Y is:

(a) 4.5 atm (b) 0.45 atm
(c) 0.6 atm (d) None of these

36. For a reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the value of K_C would depend upon

(a) initial concentration of the reactants
(b) pressure
(c) temperature
(d) all of these

37. K for the synthesis of HI(g) is 50. The degree of dissociation of HI is

(a) 0.10 (b) 0.14
(c) 0.18 (d) 0.22

38. In the dissociation of PCl_5 as:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

if the degree of dissociation is a at equilibrium pressure P, then equilibrium constant for the reaction is:

(a) $k_p = \dfrac{\alpha^2}{1-\alpha^2 P}$ (b) $k_p = \dfrac{\alpha^2 P^2}{1-\alpha^2}$

(c) $k_p = \dfrac{\alpha P^2}{1-\alpha^2}$ (d) $\dfrac{\alpha^2 P}{1-\alpha^2}$

39. The vapour density of N_2O_4 at certain temperature is 30. What is the percentage dissociation of N_2O_4 at this temperature?

(a) 53.3 (b) 106.6
(c) 26.7 (d) None.

40. If $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

$K_1 = 1.8 \times 10^7$

$$Ag^+ + Cl^- \rightleftharpoons AgCl$$

$K_2 = 5.6 \times 10^9$

Then for

$$AgCl + 2NH_3 \rightleftharpoons [Ag(NH_3)2]^+ + Cl^-$$

equilibrium constant will be

(a) 0.32×10^{-2} (b) 3.11×10^2
(c) 10.08×10^{16} (d) 1.00×10^{-17}

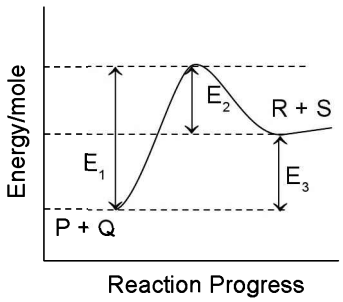
41. In the following reaction:

$$3A + B \rightleftharpoons 2C + D$$

Initially moles of B is double' than A. At equilibrium, moles of A and C are equal. Hence % age dissociation of B is

(a) 10% (b) 20%
(c) 40% (d) 5%.

42. The energy profile for a reversible reaction $P + Q \rightarrow R + S$ is given on the right hand side. For this reaction, it can be inferred from the diagram,



(a) The forward reaction is exothermic
(b) The increase in temperature will increase the value of E_3
(c) The addition of a catalyst will alter the value of e! and E_2
(d) The increase in temperature will decrease the value of E_1.

43. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the reaction connecting the degree of dissociation (α) of $N_2O_4(g)$ with the equilibrium constant K_p is

(a) $\alpha = \dfrac{\frac{K_p}{P}}{4+\frac{K_p}{P}}$ (b) $\alpha = \dfrac{K_p}{4+K_p}$

(c) $\alpha = \left[\dfrac{K_p/P}{4+K_p/P}\right]^{\frac{1}{2}}$ (d) $\alpha = \left[\dfrac{K_p}{4+K_p}\right]^{\frac{1}{2}}$

44. The activation energies of two reactions are E_{q_1}, E_{q_2} with $E_{q_1} > E_{q_2}$. If the temperature of the reacting system is increased from T_1 to T_2, predict which of the following alternatives is correct.

(a) $\dfrac{K_1^1}{K_1} = \dfrac{K_2^1}{K_2}$ (b) $\dfrac{K_1^1}{K_1} > \dfrac{K_2^1}{K_2}$

(c) $\dfrac{K_1^1}{K_1} < \dfrac{K_2^1}{K_2}$ (d) $\dfrac{K^1}{K_1} < \dfrac{2K_2^1}{K_2}$

45. What is the activity of 10^{-3} NHCl, the activity coefficient of HCl at this concentration is 0.996?

(a) $1.0^3 \times 0.996$ (b) $10^{-3}/0.996$

(c) $0.996/10^{-3}$ (d) None of these.

46. For the reaction:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g);$$

the degree of dissociation (α) of HI(g) is related to equilibrium constant K_p by the expression

(a) $\dfrac{1+2\sqrt{K_p}}{2}$ (b) $\sqrt{\dfrac{1+2K_p}{2}}$

(c) $\sqrt{\dfrac{2K_p}{1+2K_p}}$ (d) $\dfrac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

47. Given $X \rightleftharpoons$ nyx decomposes to give y (in one litre vessel) If degree of dissociation is α, then K_c and its unit is:

(a) $\dfrac{na}{1-\alpha}$ mol^{n-1} lit^{n-1}

(b) $\dfrac{(na)^n}{1-\alpha}$ mol^n lit^{-n}

(c) $\dfrac{na}{1-\alpha}$, K_c is unitless

(d) $\dfrac{(na)^n}{1-\alpha}$, K_c is unitless

48. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction

$$2AB_2(g) = 2AB + B_2(g)$$
$$(g)$$

With degree of dissociation *a,* which is small compared with unity. The expression of K_p, in terms of *a* and total pressure P_T is:

(a) $P_T \dfrac{a^3}{2}$ (b) $\dfrac{P_T a^2}{3}$

(c) $P_T \dfrac{a^3}{3}$ (d) $\dfrac{P_T a^2}{2}$

49. If $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(v)$ $K_p = 1.086 \times 10^{-4}$ atm^2 at 25°C. The efflorescent nature of $CuSO_4.5H_2O$ can be noticed when vapour pressure of H_2O in atmosphere is:

(a) > 7.92 mm (b) < 7.92 mm

(c) $\gtrless$7.92mm (d) None of these

50. Sulphide ions in alkaline solution react with solid sulphur to form polyvalent sulphide ions. The equilibrium constant for the formation of S_2^{2-} and S_3^{2-} from S and S^{2-} ions are 1.7 and 5.3 respectively. Equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S is:

(a) 1.33 (b) 3.11

(c) 4.21 (d) 1.63

51. In an aqueous solution of volume 500 mL, when the reaction of $2Ag^+ + Cu \rightleftharpoons Cu^{2+} + 2Ag$ reached equilibrium the $[Cu^{2+}]$ was x M. When 500 mL of water is further added, at the equilibrium $[Cu^{2+}]$ will be:

(a) 2*x*M

(b) *x*M

(c) Between *x*M and *x*/2 M

(d) Less than *x*/2 M

52. The vapour density of completely dissociated NH_4Cl would be:

(a) Slightly less than half of that of ammonium chloride

(b) Half of that of ammonium chloride

(c) Double that of ammonium chloride

(d) Determined by the amount of solid ammonium chloride used in the experiment

53. The values of K_C for the following reactions are given as below

$$A \rightleftharpoons B,\ K_C = 1,\ B \rightleftharpoons C,\ K_C = 3$$

and $C \rightleftharpoons D,\ K_C = 5$

Evaluate the value of K_C for $A \rightleftharpoons D$

(a) 15 (b) 5
(c) 3 (d) 1

54. For a reversible reaction between A and B. A and B react in the ratio 2 : 3 and form C and D in the ratio 2 : 1. Initially, the concentrations of A and B are equal. The concentrations of A and C are equal at equilibrium. Calculate the concentration of A, B, C, D at equilibrium respectively.

(a) $\frac{1}{2}, \frac{1}{4}, \frac{1}{2}, \frac{1}{4}$ (b) $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}, \frac{1}{4}$
(c) $\frac{1}{2}, \frac{1}{4}, \frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}, \frac{1}{2}$

55. Formaldehyde polymerizes to form glucose according to the reaction

$$6HCHO \rightleftharpoons C_6H_{12}O_6$$

The theoretically computed equilibrium constant for this reaction is found to be 6×10^{22}. If 1 M solution of glucose dissociates according to the above equilibrium, the concentration of formaldehyde in the solution will be

(a) 1.6×10^{-2} M (b) 1.6×10^{-4} M
(c) 1.6×10^{-6} M (d) 1.6×10^{-8} M

ANSWER KEYS

1. (b)	**2.** (a)	**3.** (c)	**4.** (c)	**5.** (b)	**6.** (b)	**7.** (b)	**8.** (a)	**9.** (c)	**10.** (a)
11. (c)	**12.** (d)	**13.** (b)	**14.** (c)	**15.** (b)	**16.** (b)	**17.** (d)	**18.** (c)	**19.** (a)	**20.** (d)
21. (d)	**22.** (c)	**23.** (c)	**24.** (b)	**25.** (d)	**26.** (b)	**27.** (a)	**28.** (a)	**29.** (b)	**30.** (c)
31. (c)	**32.** (d)	**33.** (b)	**34.** (d)	**35.** (b)	**36.** (c)	**37.** (d)	**38.** (d)	**39.** (a)	**40.** (a)
41. (a)	**42.** (c)	**43.** (c)	**44.** (a)	**45.** (a)	**46.** (d)	**47.** (d)	**48.** (a)	**49.** (b)	**50.** (b)
51. (d)	**52.** (b)	**53.** (a)	**54.** (a)	**55.** (b)					

HINTS AND EXPLANATIONS

1. (b) $Q_c = \frac{[P_2(g)]^4}{[P_4(g)]} = \frac{(1)^2}{(3/2)} = \frac{2}{3}$

2. (a) $Q_c = \frac{\left(\frac{6}{2}\right)^2}{\left(\frac{2}{2}\right)\left(\frac{4}{2}\right)^3} = \frac{9}{8}$ $Q_c < K_c$ so reaction will proceed in forward direction.

3. (c) $K_P = \frac{1}{P^4_{H_2O(g)}} \Rightarrow P_{H_2O(g)} = \left(\frac{1}{K_P}\right)^{1/4} \Rightarrow (10^{-12})^{1/4}$

10^{-3} atm

$\therefore K_p = 10^{-3} \times 760 = 0.76$ torr

4. (c) $P_{total} = 3P \Rightarrow P = \frac{0.318}{3} = 0.106$

$\therefore K_p = 4P^3 = 4.76 \times 10^{-3}$

5. (b) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

moles of eqm 0.8–x .8–x x x

conc. At equm $\frac{0.8-x}{5}\left(\frac{0.8-x}{5}\right)\left(\frac{x}{5}\right)\left(\frac{x}{5}\right)$

$\because \Delta n_g = 0 \therefore K_c = \frac{\left(\frac{x}{5}\right)^2}{\left(\frac{0.8-x}{5}\right)^2}$

$$\Rightarrow 2 = \frac{x}{0.8-x} \Rightarrow x = 0.533 \quad [CO_2(g)]$$

$$= \frac{0.8-0.533}{5}$$

6. (b) For ideal gas mole % ≡ volume %

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Initial moles a 0

At eqm $a(1-\alpha)$ $2a\alpha$

As per given original volume = $\frac{75}{100}$ × Volume at eqm at constant T and P : V∝ n

$\therefore a = 0.75 \times a(1+\alpha) \Rightarrow \alpha = 0.33$

7. (b) $CO + H_2O \rightleftharpoons CO_2 + H_2$

Initial conc. 3 3 x 0

At eqm 2 2 (x+1) 1

$$5 = \frac{(x+1)}{4} = 20 = x+1 \Rightarrow x = 19$$

8. (a) $\alpha = \frac{M_T - M_O}{(n-1)M_O} \Rightarrow 0.2 = \frac{92-M_O}{M_O} \Rightarrow M_O$

$= 76.66$ $d_{mixture}$

$$= \frac{PM_{mixture}}{RT} = \frac{1\times 76.66}{0.821\times 300} = 3.11 \text{ g/litre}$$

9. (c) $M_O = \frac{dRT}{P} = 57.47$ $\alpha = \frac{99-57.47}{57.47} = 0.72$

10. (a) $H_2(g) + S(s) \rightleftharpoons H_2S(g)$

Conc. at equm 0.5–x – x

$$K_c = \frac{[H_2S]}{[H_2]} \Rightarrow 7\times 10^{-2} = \frac{x}{0.5-x}$$

$\Rightarrow x = 0.0327$ $P_{H_2S} = \left(\frac{n_{H_2S}}{V}\right) RT$

$= 0.0327 \times 0.0821 \times 360 = 0.966$

11. (c) The gaseous mixture contains 40% Cl_2 and 40% PCl_3, since they are produced in 1 : 1 mole ratio. The PCl_5 % is 20.

For ideal gases mole % ≡ volume %

$P_{Cl_2} = P_{PCl_3} \Rightarrow 2 \times 0.40 = 0.80$ atm P_{PCl_5}

$= 2 \times 0.2 = 0.40$ atm

$$\therefore K_P = \frac{P_{PCl_3}.P_{Cl_2}}{P_{PCl_5}} = \frac{0.80\times 0.80}{0.40}$$

$= 1.6$ atm

12. (d) Moles of CO_2 present at equilibrium

$$= \frac{1.642\times 50}{0.0821\times 1000} = 1$$

Mole % of XCO_3 decomposed $= \frac{1}{4}\times 100 = 25\%$

Hence, 75% remains undecomposed

13. (b) Let initial moles of $H_2(g)$ is 1

$$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2Fe(s) + 3H_3O(g)$$

at eqm — 1–3x — 3x

$$K_c = \frac{\left(\frac{3x}{V}\right)^3}{\left(\frac{1-3x}{V}\right)^3} \Rightarrow 8 = \left(\frac{3x}{1-3x}\right)^3$$

$\Rightarrow$ x = 0.22 % of H_2 unreacted

$$= \frac{1-3\times 0.22}{1}\times 100 = 34$$

14. (c) $AB_3(g) \rightleftharpoons AB_2(g) + \frac{1}{2}B_2(g)$

At eqm 800–x x x/2

$$800-x+x+\frac{x}{2} = 900 \Rightarrow x = 200$$

$$\% \text{ dissociated} = \frac{200}{800}\times 100 = 25$$

15. (b) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

At eqm p–2x 2x x

P + x = 1; P–2x = 0.64, x = 0.12

$$K_P = \frac{(0.24)^2(0.12)}{(0.64)^2} = 16.875\times 10^{-3} \text{ atm}$$

16. (b)

17. (d) $K_c = [Hg(g)]$; P = CRT

$$C = \left(\frac{0.002}{760}\right)\times \frac{1}{(0.0821\times 300)}$$

$= 1.068 \times 10^{-7}$ M

18. (c) $\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \ln\left(\frac{10^{-4}}{10^{-6}}\right)$

$= \frac{\Delta H^\circ}{8.314}\left(\frac{25}{298\times 323}\right)$ $\Delta_r H^\circ = 147.41$ kJ/mol

19. (a) $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$; ...(1)

$K_{P_1} = 10^{14}$ atm

$2CO(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g)$; ...(2)

$K_{P_2} = (6 \times 10^{-3})^2$ atm^{-2}

Add (1) and (2)

$C(s) + CO_2(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g)$;

$K_P = 10^{14} \times 36 \times 10^{-6} = 36 \times 10^8$

For given reaction $\Delta n_g = -1$

$\therefore$ $K_c = K_p(RT) = 36 \times 10^8 \times 0.0821 \times 1120$

$K_c = 3.31 \times 10^{11}$ M^{-1}

20. (d) $P_{total} = P_{HNO_3} + P_{NO_2} + P_{H_2O} + P_{O_2}$ ℓ $P_{NO_2} = 4P_{O2}$

and $P_{H_2O} = 2P_{O_2}$

$\therefore$ $P_{total} = P_{HNO_3} + 7P_{O_2} \Rightarrow 30 - 2 = P_{O_2} \times 7$

$\Rightarrow$ $P_{O_2} = \frac{28}{7} = 4$

$K_P = \frac{P^4_{NO_2}.P_{H_2O}.P_{O_2}}{P^4_{HNO_3}} = \frac{(4\times 4)^4 \times (2\times 4)^2 \times 4}{2^4} = 2^{20}$

$K_p = K_c (RT)^{\Delta n_g} = K_c (0.08 \times 400)^3$

$\Rightarrow$ $K_c = \frac{2^{20}}{(32)^3} = 32$

21. (d) $LiCl.\ 3NH_3(s) \rightleftharpoons LiCl\ .\ NH_3(s) + 2NH_3(g)$; $[K_p = 9\ atm^2]$

Therefore,

$LiCl\ .\ NH_3(s) + 2NH_3(g) \rightleftharpoons LiCl.3NH_3(s)$;

Initial moles	0.1	a	0
Final moles at eqm	0	(a–0.2)	0.1

$\left[K'_P = \frac{1}{9}(atm)^{-2}\right]$

Let initial moles of NH_3 is a for completion of reaction.

At eqm $K'_P = \frac{1}{(P'_{NH_3})^2}$ or $\frac{1}{9} = \frac{1}{(P'_{NH_3})^2}$

$\therefore$ $P'_{NH_3} = 3$ atm

$\therefore$ $PV = nRT \Rightarrow 3 \times 5 = n \times 0.0820 \times 310$

$\therefore$ $n = 0.59$ i.e., $(a–0.2) = 0.59$

$\therefore$ initial moles of $NH_3 = 0.79$

22. (c) $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

At eqm 1–x x x

$K_p = \frac{P_{C_2H_4}.P_{H_2}}{P_{C_2H_6}} \Rightarrow \frac{x^2}{1-x} = 5 \times 10^{-2}$

$x^2 + 0.05\,x - 0.05 = 0$

$x = \frac{-0.05 + \sqrt{(0.05)^2 + 4\times 0.05}}{2} = 0.20$ atm

Partial pressure of C_2H_6 = mole fraction × total pressure $\Rightarrow$ 0.80 = mole fraction × 1.2

$\therefore$ mole % of $C_2H_6 = \frac{0.8}{1.2} \times 100 = 66.66$

23. (c) ℓ Initially, only A is present so at eqm B and C should be present in 2 : 1

$2A(g) \rightleftharpoons 2B(g) + C(g)$

at eqm 400 mL 200 mL 100 mL

for ideal gases volume % = mole %

$K_p = \frac{\left(\frac{200}{700}\times 10\right)^2 \left(\frac{100}{700}\times 10\right)}{\left(\frac{400}{700}\times 10\right)^2} = \frac{10}{28}$

24. (b) $3Se_2(g) \rightleftharpoons Se_6(g)$

moles at eqm $a(1-\alpha)$ $\frac{a\alpha}{3}$

$\frac{\text{Observed no. of moles at equilibrium}}{\text{Initial no. of moles of reactant}} = \frac{M_T}{M_O}$,

$\Rightarrow$ $\frac{a(1-\alpha) + \frac{a\alpha}{3}}{a} = \frac{M_T}{M_O} = \alpha = 0.315$

where molar mass of Se_2 $(M_T) = 79 \times 2 = 158$

and molar mass of mixture

$(M_O) = \frac{wRT}{PV} = \frac{0.02\times 24.63}{1\times 2.463\times 10^{-3}} = 200$

25. (d) $6HCHO \rightleftharpoons C_6H_{12}O_6$

Conc. at eqm $C(1-\alpha)$ $\frac{C\alpha}{6}$

$$\frac{\text{Observed moles concentration}}{\text{Initial moles concentration}} = \frac{M_T}{M_O}$$

M_T = Theoretical molar mass of HCHO

$$\frac{C(1-\alpha)+\frac{C\alpha}{6}}{C} = \frac{M_T}{M_O} = \frac{30}{150} \Rightarrow \alpha = 0.96$$

26. (b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ K_c

$$= \frac{(0.12)^2}{(0.12)^2 \times 5} = 0.2$$

Another vessel

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

moles at eqm 0.5–2x y–x 2x

as per given $2x = \frac{20}{100} \times 0.5 = 0.1$ K_c

$$= \frac{(0.1)^2}{(0.4)^2(y-0.1)} = 0.20 \quad y = 0.4125 \text{ mole}$$

$\therefore$ mass of O_2 added = 13.2 g

27. (a) $Sb_2S_3(s) + 3H_2(g) \longrightarrow 2Sb(s) + 3H_2S(g)$

0.01–x 0.01–x x x

where r = 0.005

$H_2S + Pb^{2+} \longrightarrow PbS + 2H^+$ number of moles

of PbS formed $= \frac{1.19}{238} = 0.005$ mole

At eqm $[H_2] = \left(\frac{0.005}{250}\right)$; $K_c = \left(\frac{0.005}{0.005}\right)^3 = 1$

28. (a) $2A(g) + B(g) \rightleftharpoons C(g) + D(g)$

Initial moles	1	1	7	3
At eqm	2–2x	1–x	7+x	3+x

Due to very high value of K_c we can assume that reactant almost converted into products so

$1-x = y$; $2-2x = 2y \Rightarrow x \simeq 1$ $10^{12} = \frac{8 \times 4}{(2y)^2 y}$

$\Rightarrow y^3 = 8 \times 10^{-12}$

$\therefore$ equilibrium concentration of A = $2y = 4 \times 10^{-4}$

29. (b) $K_c = \frac{[\text{complex}]}{[H_3BO_3][\text{glycerin}]} = 0.90 \Rightarrow \frac{[\text{complex}]}{[H_3BO_3]}$

$$= \frac{80}{20} \quad \therefore \quad [\text{glycerin}] = \frac{80}{20 \times 0.9} = 4.44 \text{ M}$$

$H_3BO_3 + \text{glycerin} \rightleftharpoons (H_3BO_3 - \text{glycerin})$

At eqm 0.1–x a–x x

$x = 0.1 \times \frac{80}{100} = 0.08$; $a - x = 4.44$

$\Rightarrow$ a = 4.44 + 0.08 = 4.52 M or Initial moles = 4.52

30. (c) $\frac{r_{mix}}{r_{O_2}}\sqrt{\frac{32}{M_{mix}}} = 0.4\sqrt{5} \Rightarrow M_{mix} = 40 \text{g/mol}$

$$O_2(g) \rightleftharpoons \frac{2}{3}O_3(g)$$

Initial moles	1	0
At eqm	1–α	$\frac{2}{3}\alpha$

$\frac{32}{40} = \frac{1-\alpha+\frac{2}{3}\alpha}{1} \Rightarrow \alpha = 0.6 \quad \therefore \quad \% \alpha = 60$

31. (c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

moles at eqm 1–2x 2x x

Only SO_2(O. No. = 4) will oxidized

So equivalent of SO_2 = equivalent of $KMnO_4$

$2x \times 2 = 0.2 \times 5$

$\Rightarrow$ 2x = 0.5 $K_c = \frac{\left(\frac{0.5}{2}\right)^2\left(\frac{0.25}{2}\right)}{\left(\frac{0.5}{2}\right)^2} = 0.125$

32. (d) $\frac{r_{mix}}{r_{SO_2}} = \sqrt{\frac{M_{SO_2}}{M_{mix}}} \Rightarrow 2.56 = \frac{64}{M_{mix}}$

$\Rightarrow M_{mixture} = 25$

Let mole fraction of F_2 is x $25 = \frac{38 \times x + (1-x) \times 19}{1}$

x = 0.315;

$\Rightarrow K_p = \frac{P_F^2}{P_{F_2}} = \frac{(0.6885)^2}{(0.315P)} \simeq 1.49$ atm

33. (b) $8 \times 10^{-6} = \frac{x^2}{0.5} \Rightarrow x = 2 \times 10^{-3}$ $\therefore$ pOH = 2.7

So, pH = 11.3

34. (d) $N_2O_5 \rightleftharpoons N_2O_3 + O_2$

4–x x–y x+y

$N_2O_3 \rightleftharpoons N_2O + O_2$

x–y N_2O y+x

ℓ $[O_2] = x + y = 2.5$ and 2.5

$= \frac{(x+y)(x-y)}{4-x}$ $\therefore$ x = 2.166

$[N_2O_5] = 4–x = 1.846$

35. (b) Let x is partial pressure of A and y is partial pressure of C when both equilibrium simultaneously established in a vessel

$X(s) \rightleftharpoons A(g) + 2B(g)$

X $(2x+2y)$; $K_{P_1} = P_A.P^2_{B(total)}$

$Y(s) \rightleftharpoons C(g) + 2B(g)$

y $(2y+2x)$; $K_{P_2} = P_C.P^2_{B(total)}$

$\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y} \Rightarrow x = 2y$ $K_{P_1} = x(2x + 2y)^2$

$\Rightarrow$ x = 0.1 atm;

$\therefore$ y = 0.05 atm

Total pressure of gases $= P_A + P_B + P_C = 3(x + y)$ = 0.45 atm.

36. The equilibrium constant K_C of a reaction depends only on temperature and nature of reactants

$\therefore$ (c)

37. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

1–α $\frac{\alpha}{2}$ $\frac{\alpha}{2}$ where α is the degree of dissociations

$K_{diss} = \frac{1}{K_{synthesis}} = \frac{1}{50}$

$\frac{1}{50} = \frac{\frac{\alpha}{2} \times \frac{\alpha}{2}}{(1-\alpha)^2}$

$\frac{\alpha}{2(1-2)} = \frac{1}{5\sqrt{2}}$

$5\sqrt{2}\ \alpha = 2–2\alpha$

$2+5\sqrt{2}\ \alpha = 2$

$\alpha = \frac{2}{2+5\sqrt{2}} = 0.22$

$\therefore$ (d)

38. (d) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initial moles 1 0 0

Equilibrium 1–a a a moles

Total moles = 1 – a + a + a = 1 + a

Total pressure: P

$\therefore$ $P_{PCl_5} = \frac{(1-a)P}{(1+a)}$; $P_{PCl_3} = \frac{a.P.}{1+a}$.

$PCl_2 = \frac{a.P}{1+a}$.

Now, $K_P = \frac{P_{PCl_3}.P_{Cl_2}}{P_{PCl_3}}$

$= \frac{a^2.P^2}{(1+a)(1-a)P} = \frac{a^2P}{1-a^2}$

39. (a) Vapour density, $D = \frac{Mol.wt.}{2} = \frac{92}{2} = 46$

$d = 30°$

$d = \frac{D-d}{d} = \frac{46-30}{30}$

$= \frac{16}{30} = 0.533 = 53.3\%$

40. (a) $K_1 = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$

$K_2 = \frac{[AgCl]}{[Ag^+][Cl^-]}$

$K_n = \frac{[Ag(NH_3)_2]^+[Cl^-]}{[AgCl][NH_3]^2} = \frac{K_1}{K_2}$

$\therefore$ $\frac{K_1}{K_2} = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \times \frac{[Ag^+][Cl^-]}{[AgCl]}$

$= \frac{1.8\times10^7}{5.6\times10^9} = 0.32 \times 10^{-2} = K$

41. (a) $3A + B \rightleftharpoons 2C + D$

Initial 1 2

At eqm $1-x$ $2-\frac{x}{3}$ $\frac{2}{3}x$

At Eqbm. [A] = [C]

$$1 - x = \frac{2x}{3}; x = \frac{3}{5}$$

$$\frac{x}{3} = \frac{1}{3} \times \frac{3}{5} = \frac{1}{5}$$

Out of 2 moles, moles dissociated to give

$\therefore$ % age dissociation $= \frac{100}{2} \times \frac{1}{5} = 10\%$

42. (c) From the given energy profile diagram, it is evident that forward reaction is endothermic and the addition of a catalyst decreases the value of E_1 and E_2.

43. (c) $N_2O_4 \rightleftharpoons 2NO_2$

$1-\alpha$ 2α at equilibrium

Total number of moles at equilibrium

$= 1 - \alpha + 2\alpha = 1 + \alpha$

and $K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{\left[\frac{2\alpha}{1+\alpha}P\right]^2}{\frac{1-\alpha}{1+\alpha}.P}$

$\therefore \quad K_p = \frac{4\alpha^2 P}{1-\alpha^2}$

or $K_p = 4\alpha^2 P + K_p\alpha^2$

or $\alpha = \left[\frac{\frac{K_p}{P}}{4+\frac{K_p}{P}}\right]^{\frac{1}{2}}$

44. (a) As the temperature of reacting system is increased, the equilibrium constant of reaction is also increased for endothermic reactions. So for two reactions on increasing the temperature by equal amounts,

$$\frac{K_1'}{K_1'} = \frac{K_1'}{K_2}$$

45. (a) activity = activity coefficient × concentration

(f) (c)

$\therefore \quad a = 0.996 \times 10^{-3}$

46. (d) $2HI \rightleftharpoons H_2(g) + I_2(g)$

$1-a$ $\frac{a}{2}$ $\frac{a}{2}$

$$K_P = \frac{(a/2\ P)^2}{(1-a)^2P^2}$$

$$\frac{a}{1} - a = 2\sqrt{K_P}$$

$$a = \frac{2\sqrt{K_P}}{1+2\sqrt{K_P}}$$

47. (d) As K_c is the expression in terms of activity (which itself is unitless) it is unit less quantity.

1 0

$X \rightleftharpoons nY$

$1-a$ $n-a$

$$K_c = \frac{(na)^n}{1-a}$$

48. (a) For the given equilibrium, the equilibrium constants are

$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

Equilibrium $c(1-a)$ ca $\frac{ca}{2}$

conc.

$\therefore \quad K_P = \frac{(P_{B_2})(P_{AB})^2}{(P_{AB_2})^2} = \frac{\frac{ca}{2} \times (ca)^2 \times P_T}{[c(1-a)]^2[c(1+\frac{a}{2})]}$

$$K_p = \frac{a^3 \times P_T}{2(1-a)^2(1+\frac{a}{2})}$$

Since $a << 1$,

$\therefore \quad K_p = \frac{a^3 \times P_T}{2}$

49. (b) An efforescent salt is one that loses H_2O to atmosphere.

For the reaction

$CuSO_4 . 5H_2O(s) \rightleftharpoons$

$CuSO_4 . 3H_2O(s) + 2H_2O(v)$

$K_p = (P'_{H_2O})^2 = 1.086 \times 10^{-4}$

$P'_{H_2O} = 1.042 \times 10^{-2}$ atm $= 7.92$ mm

ℓ If P'_{H_2O} at 25°C < 7.92 mm only then, reaction will proceed in forward direction.

50. (b) Given, $S(s) + S^{2-} \rightleftharpoons S_2^{2-}$ $\quad K_{C_1} = 1.7$

$2S(s) + S^{2-} \rightleftharpoons S_3^{2-}$ $\quad K_{C_2} = 5.3$

$\therefore \quad K_{C_1} = \dfrac{[S_2^{2-}]}{[S^{2-}]} = 1.7$ ...(1)

$K_{C_1} = \dfrac{[S_3^{2-}]}{[S^{2-}]} = 5.3$ ...(2)

Now for, $S_2^{2-}(s) + S(s) \rightleftharpoons S_3^{2-}$

$K_c = \dfrac{[S_3^{2-}]}{[S_2^{2-}]}$

$\therefore \quad K_c = 3.11$

51. (d) $2Ag^+ + Cu \rightleftharpoons Cu^{2+} + 2Ag$

a x

if V is 500 mL

$$K_c = \frac{\left(\frac{x \times 1000}{500}\right)}{\left(\frac{a \times 1000}{500}\right)^2} = \frac{x}{2a^2}$$

If volume is doubled, then a becomes a/2; Let x be x', then if V = 1000 mL

$$K_c = \frac{x'}{(a/2)^2} = \frac{4x'}{a^2}$$

$$\therefore \quad \frac{x}{2a^2} = \frac{4x'}{a^2}$$

or $x' = \dfrac{x}{8}$ or $x' < \dfrac{x}{2}$

$$K_c = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{x}{(a)^2}$$

to have K_c constant $[Cu^{2+}]$ will be less than $\dfrac{x}{2}$.

52. (b) $\dfrac{\text{normal mol. wt.}}{\text{exp. mol. wt.}} = 1 + \alpha$

For, $NH_4CI \rightleftharpoons NH_3 + HCI$;

ℓ $\alpha = 1$

$\therefore$ Exp. mo. wt. $= \dfrac{\text{normal mol. wt.}}{2}$

53. (a) $A \rightleftharpoons B$, $\quad K_C^{I} = 1$, $\quad B \rightleftharpoons C$, $\quad K_C^{II} = 3$

$C \rightleftharpoons D$, $\quad K_C^{III} = 5$ $\quad A \rightleftharpoons D$, $\quad K_C^{IV}$

$$K_C^{IV} = \frac{[D]}{[A]}$$

$$= K_{C_I} . K_{C_{II}} . K_{C_{III}} = \frac{[B]}{[A]} . \frac{[C]}{[B]} . \frac{[D]}{[C]}$$

$= 1 \times 3 \times 5 = 15$

54. (a) A and B ract in the ratio 2 : 3 and C and D are formed in the ratio 2 : 1

Hence equation is

$2A + 3B \rightleftharpoons 2C + D$

Initial conc.	1	1	0	0
Final conc. at equilibrium	1–2n	1–3n	2n	n

Note: At equilibrium, conc. of A and C are equal

$\Rightarrow \quad 1 - 2n = 2n$

$\Rightarrow \quad 1 = 4n \Rightarrow n = \dfrac{1}{4}$

$\Rightarrow$ concentrations at equilibrium:

$A = 1 - 2 \times \dfrac{1}{4} = \dfrac{1}{2}$ $\quad B = 1 - 3 \times \dfrac{1}{4} = \dfrac{1}{4}$

$C = 2 \times \dfrac{1}{4} = \dfrac{1}{2}$ $\quad D = \dfrac{1}{4} = n$

55. (b) A very high value of K for the given equilibrium shows that dissociation of glucose to form HCHO is very very small. Hence at equilibrium, we can take $[C_6H_{12}O_6] = 1$ M

$$K = \frac{[C_6H_{12}O_6]}{[HCHO]^6} \text{ i.e.,}$$

$$6 \times 10^{6} = \frac{1}{[HCHO]^6}$$

Or $[HCHO] = \left(\dfrac{1}{6 \times 10^{22}}\right)^{1/6}$

$= 1.6 \times 10^{-4}$ M

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. Which of the following is correct?
(a) $\Delta G^\circ = -RT \ln K_p$ (at unit pressure)
(b) $\Delta G^\circ = -RT \ln K_c$ (at activity)
(c) $\Delta G = -RT \ln K_c$ (at unit activity)
(d) $\Delta G = -RT \ln K_p$ (at unit pressure)

2. A system in equilibrium is described by the gaseous phase equation

$$\text{Heat} + SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$$

Which of the following statements is true?
(a) Addition of Cl_2 will shift the equilibrium towards right and temperature is raised
(b) Addition of Cl_2 will shift the equilibrium towards left and temperature is raised
(c) Withdrawal of Cl_2 and SO_2 will shift the equilibrium towards left and temperature is raised
(d) Withdrawal of SO_2 and Cl_2 will shift the equilibrium towards left and temperature is lowered.

3. For the gas phase reaction,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6;\ \Delta H = -137 \text{ kJ mol}^{-1}$$

Carried out in a closed vessel, the equilibrium concentration of C_2H_4 can be increased by
(a) Increasing the temperature
(b) Decreasing the pressure
(c) Removing some C_2H_6
(d) Adding some H_2

4. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal
(a) Intermolecules forces
(b) Potential energy
(c) Kinetic energy
(d) Both kinetic energy and potential energy

5. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on adding graphite. The total pressure at equilibrium was found to be 0.8 atm.
(a) The equilibrium is achieved as soon as Q = K, K value = 0.18 atm^2
(b) The equilibrium is achieved as soon as Q = K, K value = 1.8 atm
(c) The $p_{CO_2} = 0.2$ atm at equilibrium
(d) The $p_{CO} = 0.6$ atm at equilibrium

6. Consider the following reaction:

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)};\ \Delta H^\circ = -196$ KJ for the forward reaction.

Which of the following is (are) correct?
(a) an increase in temperature from 500° to 1000°C will increase the proportion of SO_3 in the equilibrium mixture.
(b) $K_c = \dfrac{[SO_{3(g)}]^2}{[SO_{2(g)}]^2[O_{2(g)}]}$ L/mol
(c) $K_p = K_c$ for this reaction
(d) the yield of SO_3 can be increased by removing it continously

7. For the reaction $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$ which of the following representation is correct?
(a) $K_p = (P_{H_2O})^2$ (b) $K_c = [H_2O]^2$
(c) $K_p = K_c(RT)^2$ (d) All

8. The equilibrium constants for the reactions are:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-;\ K_1$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-};\ K_2$$

$$HPO_4^{2-} \rightleftharpoons H^+ PO_4^{3-};\ K_3$$

The equilibrium constant for the reaction $H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$ will be
(a) K_1/K_2K_3 (b) $K_1 \times K_2 \times K_3$
(c) K_2/K_1K_3 (d) $K_1 + K_2 + K_3$

9. The condition for spontaneity in a chemical reaction is

(a) $\dfrac{d \ln K_c^\circ}{dT} = \dfrac{\Delta U^\circ}{RT^2}$

(b) $\left(\dfrac{\partial \ln K_x^\circ}{\partial T}\right)_p = \dfrac{\Delta S^\circ}{RT^2}$

(c) $\left(\dfrac{\partial \ln K_x^\circ}{\partial T}\right)_T = -\dfrac{\Delta n/\text{mol}}{p}$

(d) $\dfrac{\partial \ln K_p^\circ}{dT} = -\dfrac{\Delta H^\circ}{RT^2}$

10. In the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(a) $K_p = K_x(RT)^2$ (b) $K_p = K_p \frac{K_N}{(RT)^2}$

(c) $K_c = \frac{K_p}{(RT)^{-2}}$ (d) $K_p = \frac{K_c}{(RT)^2}$

11. Which of the following is correct for the equilibrium of the reaction (Assume there was no product when the reaction started)

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$?

(a) $p_{H_2} \propto p_{H_2O}$

(b) $p_{H_2} \propto \sqrt{p_{H_2O}}$

(c) $p_{H_2} \propto p_{H_2O^2}$

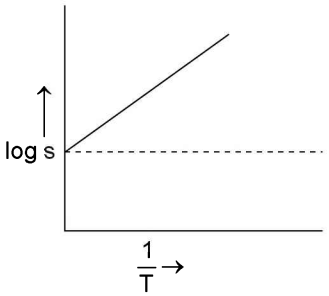
(d) $p_{H_2} \propto \frac{p_{H_2O^2}}{pCO}$

12. Solubility of a solute in water is dependent on temperature as given by,

$S = Ae^{-\Delta H/RT}$ where ΔH = heat of solution

Solute + $H_2O(l) \rightleftharpoons$ Solution $\Delta H = \pm x$

For a given solution, variation of logS with temperature is shown graphically. Hence solute is:



(a) $CuSO_4.5H_2O$ (b) NaCl

(c) Sucrose (d) CaO

ANSWER KEYS

1. (a,b) **2.** (b) **3.** (a,b) **4.** (c) **5.** (b,c,d) **6.** (b,d) **7.** (a) (b) (c) (d) **8.** (b)

9. (a) (c) **10.** (d) **11.** (b) **12.** (d)

HINTS AND EXPLANATIONS

1. (a,b)

2. (b)

3. (a, b)

4. (c) Vapours and liquid are at the same temperature.

5. (b, c, d) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

Initial pressure	0.5 atm	0
At equilibrium	0.5–x	2x

$\Rightarrow P_{Total} = p_{CO_2} + p_{CO}$

$P_{Total} = 0.5 - x + 2x = 0.5 + x$

$\Rightarrow 0.8 = 0.5 + x$

$\Rightarrow x = 0.3$ atm

$p_{CO_2} = 0.5 - 0.3 = 0.2$ atm, choice (c) is correct

$p_{CO} = 2x = 0.3 \times 2 = 0.6$ atm, choice (d) is correct

$Q = K$ at equilibrium $= \frac{p_{CO}^2}{p_{CO_2}} = \frac{0.6 \times 0.6}{0.2}$

$\Rightarrow Q = K = 1.8$ atm

6. (b, d)

7. (a, b, c, d)

8. (b)

9. (a, c)

10. (d)

11. (b)

12. (d)

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

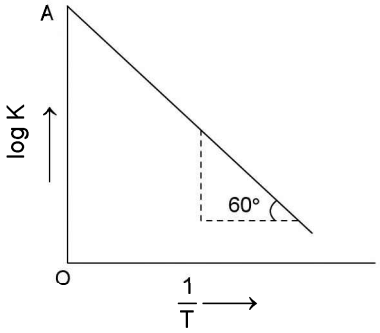
The approach of the following equilibrium was observed kinetically from the both directions:

$$[PtCl_4^{-2}] + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^- + Cl^- \text{ at } 25^\circ C.$$

It was found that $\frac{-d[PtCl_4^{2-}]}{dt}$

$= K_1[PtCl_4^{2-}] - K_{-1} = [Pt(H_2O)_3Cl^-]\,[Cl^-]$

The variation of equilibrium constant of the above reaction with temperature is as shown by the graph as under:



Given OA = 5

1. From the above graph, what will be the value of ΔH° (in joules) of the reaction at 25°C temperature? Assume R = 8 cal/mol/K

(a) 805 (b) 1105
(c) 31.95 (d) 41.95

2. What will be the value of pre-exponential factor i.e., A?

(a) 10^5 (b) 10^4
(c) 10^{-4} (d) None

3. What will be the value of the equilibrium constant at 25°C for the forward reaction?

(a) 9.86×10^4 (b) 10^5
(c) 5×10^3 (d) None

4. What will be the value of the equilibrium constant at 25°C when the fourth Cl^- gets complexed?

(a) 10^{-7} (b) 1.01×10^{-7}
(c) 10^{-6} (d) 1.01×10^{-5}

5. What will be the value for the K_{-1}, when K_1 is equal to 10^{-3}?

(a) 10^{-6} (b) 10^{-5}
(c) 10^{-7} (d) 10^{-8}

6. If ΔH° be assumed independent of temperature, what will be the equilibrium constant at 100°C?

(a) 4.98×10^4 (b) 9.86×10^4
(c) 9.86×10^8 (d) None

7. What will be the value of ΔS° at 25°C at equilibrium?

(a) 42.09 J/mol/K (b) 60.9 J/mol/K
(c) 92.09 J/mol/K (d) None

COMPREHENSION-II

For a reaction; $aA + bB \rightleftharpoons cC + dD$, the reaction quotient $Q = \frac{[C]_0^c[D]_0^d}{[A]_0^a[B]_0^b}$, where $[A]_0$, $[B]_0$, $[Cl_0,[D]_0$ are initial concentrations. Also $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ where [A], [B], [C], [D] are equilibrium concentrations. The reaction proceeds in forward direction if $Q < K_c$ and in backward direction if $Q > K_c$. The variation of K_c with temperature is given by: $2.303 \log \frac{K_{C_2}}{K_{C_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$. For gaseous phase reactions $K_p = K_c(RT)^{\Delta n}$ where Δn = moles of gaseous products–moles of gaseous reactants. Also $-\Delta G^\circ = 2.303\ RT \log_{10} K_c$.

8. A hydrated salt show efflorescent nature by losing water molecule. Under what pressure of moisture in atmosphere, $CuSO_4.5H_2O$ will show efflore scense nature if

$CuSO_4.5H_2O_{(s)} \rightleftharpoons CuSO_4.3H_2O + 2H_2O_{(v)}$; $K_p = 62.72\ mm^2$:

(a) $P'_{H_2O} > 62.72$ mm (b) $P'_{H_2O} < 62.72$ mm
(c) $P'_{H_2O} < 7.92$ mm (d) $P'_{H_2O} > 7.92$ mm

9. The moisture content of a gas is o ten expressed as dew point-the temperature at which if gas is cooled becomes saturated with vapour pressure of water at that temperature. Dew point of H_2O is 43°C having vapour pressure 0.07 torr. $CaCl_2.2H_2O_{(s)} \rightleftharpoons CaCl_{2(s)} + 2H_2O_{(g)}$;
The equilibrium constant should not be more than ... $(atm)^2$ if $CaCl_2$ is to be used as desiccant.

(a) 8.5×10^{-9} (b) 8.5
(c) 8.5×10^{-3} (d) 4.9×10^{-3}

10. The equilibrium constants for the reaction:

$CaC_{2(s)} + 5O_{2(g)} \rightleftharpoons 2CaCO_{3(s)} + 2CO_{2(g)}$ is/are given by:

(a) $K_c = \frac{[CO_2]^2}{[O_2]^5}$ (b) $K_p = \frac{(n_{CO_2})^2}{(n_{O_2})^5} \times \left[\frac{P}{\Sigma n}\right]^{-3}$

(c) $K_2 = \frac{(P_{CO_2})^2}{(P_{O_2})^5}$ (d) either of these

11. For the reactions: $2H_2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$; $K_{c_1} = 2.1 \times 10^{-13}$ and $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$; $K_{c_2} = 1.4 \times 10^{-12}$. The equilibrium constant for $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$ at the same temperature would be:

(a) 2.58 (b) 0.066
(c) 15 (d) 0.38

12. The equilibrium constant K_c for $A_{(g)} \rightleftharpoons B_{(g)}$ is 1.1. The gas having concentration ≥ 1 is

(a) [B] if [A] = 0.91
(b) [B] if $0.9 < [A] \leq 1$
(c) Both [A] and [B] if [A] > 1
(d) all are correct

13. Which relation is correct?

(a) $2.303 \log_{10} K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

(b) $\Delta G = \Delta G^\circ + 2.303\ RT \log_{10} Q$

(c) $K = A e^{-\Delta H^\circ/RT}$

(d) all are correct

14. The heat of reaction for an endothermic reaction in equilibrium is 1200 cal at constant volume is more than at constant pressure at 300 K. The ratio of K_p/K_c is:

(a) 1.648×10^{-3} (b) 16.48×10^{-3}
(c) 606.6 (d) 60.66

COMPREHENSION-III

Influence of pressure, temperature, concentration and addition of inert gas on a reversible chemical reaction in equilibrium can be explained by formulating the expression for equilibrium constant K_c or K_p for the equilibrium. On the other hand Le Chatelier principle can be theoretically used to explain the effect of *P, T* or concentration on the physical or chemical equilibrium both.

15. For a reversible reaction:

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$, the rate expression is given as $\left(\frac{dx}{dt}\right)_{net} = 2.6 \times 10^3[NO]^2[O_2] - 4.1[NO_2]^2$. The equilibrium constant of reaction is:

(a) 1.58×10^{-3} (b) 634.15
(c) 10.66×10^3 (d) 1.06×10^3

16. For the reaction: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, increase of pressure shows:

(a) An increase in degree of dissociation and a decrease in K_c
(b) A decrease in degree of dissociation and a decrease in K_c
(c) An increase in degree of dissociation but K_c remains constant
(d) A decrease in degree of dissociation but K_c remains constant

17. For the reaction: $2SO_2 + O_2 \rightleftharpoons 2SO_3$; ΔH = –ve, An increase in temperature shows:

(a) More dissociation of SO_3 and a decrease in K_c
(b) Less dissociation of SO_3 and an increase in K_c
(c) More dissociation of SO_3 and an increase in K_c.
(d) Less dissociation of SO_3 and a decrease in K_c.

18. For the reaction:

$$\underset{\text{Yello}}{Fe^{3+}_{(aq)}} + SCN^-_{(aq)} \rightleftharpoons \underset{\text{Red}}{[Fe(NCS)]^{2+}_{(aq)}}$$

in equilibrium if little more aqueous solution of $FeCl_3$ is added, than:

(a) Forward reaction becomes more and red colour is deepened
(b) Backward reaction becomes more and red colour faintens
(c) Solution becomes colourless
(d) None of these

19. n moles of a reactant A gives one mole of B and C. If degree of dissociation of A is independent of initial concentration of A then n is:

(a) 1 (b) 2
(c) 3 (d) 4

20. N_2O_4 is 66% dissociation into NO_2 at 340 K and 1 atmospheric pressure. The volume occupied by 10 g N_2O_4 under these conditions is:

(a) 5.03 litre (b) 10.04 litre
(c) 2.58 litre (d) 3.24 litre

ANSWER KEYS

1. (c)	**2.** (a)	**3.** (a)	**4.** (d)	**5.** (d)	**6.** (b)	**7.** (c)	**8.** (c)	**9.** (a)	**10.** (d)
11. (a)	**12.** (d)	**13.** (d)	**14.** (a)	**15.** (b)	**16.** (d)	**17.** (a)	**18.** (a)	**19.** (b)	**20.** (a)

HINTS AND EXPLANATIONS

COMPREHENSION-I

1. (c) $\ell \log K = \log A - \dfrac{\Delta H}{2.303RT}$

From question,

$$\frac{-\Delta H}{2.303R} = -m = -1.732$$

$\therefore \quad \Delta H = 1.732 \times 2.303 \times 8$

$= 31.9$ J

2. (a) Since intercept $= \log_{10} A = 5$

$\Rightarrow \quad A = 10^5$

3. (a) $K = Ae^{\frac{-\Delta H}{RT}}$

$$= 10^5 e^{\frac{-2.303\times1.732\times8}{R\times T}}$$

$$= e^{\frac{-2.303\times1.732}{298}}$$

$= 10^5 \times 0.986$

$= 9.86 \times 10^4$

4. (d) Let the equilibrium constant when the fourth Cl^- gets complexed is K'

$$\therefore \quad K' = \frac{1}{K} = \frac{1}{9.86} \times 10^{-4}$$

$= 1.01 \times 10^{-5}$

5. (d) $\ell \dfrac{K_1}{K_{-1}} = 10^{-5}$

$$\Rightarrow \quad K_{-1} = \frac{K_1}{10^5} = \frac{10^{-3}}{10^5} = 10^{-8}$$

6. (b) $\ln \dfrac{K_2}{K_1} = \dfrac{31.6}{R}\left[\dfrac{1}{298} - \dfrac{1}{373}\right]$

$$= 3.98 \times \frac{75}{298\times373}$$

$$\Rightarrow \quad \frac{K_2}{K_1} \approx 1 \approx K_2 \approx K_1 = 9.86 \times 10^4$$

7. (c) $\ell \quad \Delta S^\circ = \dfrac{\Delta H^\circ}{T} + R \ln K_{eq}$

$$= \frac{31.9}{298} + \ln [9.86 \times 10^4]$$

$= 92.09$ 5/mole/K

COMPREHENSION-II

8. (c) $K_p = (P_{H_2O})^2$

$\therefore \quad P_{H_2O} = \sqrt{62.72} = 7.92$ mm

If $P'_{H_2O} < K_p$ reaction will show forward reaction.

9. (a) $K_p = (P_{H_2O})^2 = (0.07)^2 = 4.9\times10^{-3}(\text{torr})^2$

$$= \frac{4.9\times10^{-3}}{(760)^2} = 8.5\times10^{-9}\,\text{atm}^2$$

If $CaCl_2$ is to be used as desiccant K_p should be lesser than 8.5×10^{-9} atm.

10. (d) All are correct.

11. (a) $K_{c_1} = 2.1\times10^{-13} = \dfrac{[H_2]^2[O_2]}{[H_2O]^2}$

$$K_{c_2} = 1.4\times10^{-12} = \frac{[CO]^2[O_2]}{[CO_2]^2}$$

$$K_{c_3} = \frac{[H_2O][CO_2]}{[H_2][CO]}$$

$$= \sqrt{\frac{K_{c_1}}{K_{c_2}}} = \sqrt{\frac{1.4\times10^{-12}}{2.1\times10^{-13}}} = 2.58$$

12. (d) $K_c = \dfrac{[B]}{[A]} = 1.1$ See all are correct;

13. (d) All are correct;

$\Delta G^\circ = -2.303\ RT \log_{10} K_c$ (at eq. $\Delta G = 0$)

$\Delta H^\circ - T\Delta S^\circ = -2.303\ RT \log_{10} K$

$$2.303 \log_{10} K_c = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}$$

14. (a) $\Delta H = \Delta U + \Delta nRT$

$$\Delta n = \frac{1200}{2\times 300} = -2$$

$$\therefore \quad \frac{K_p}{K_c} = (RT)^{\Delta n} = (0.0821\times 300)^{-2}$$

$$= 1.648 \times 10^{-3}$$

COMPREHENSION-III

15. (b) $K_f = 2.6 \times 10^3$; $K_b = 4.1$;

$$\therefore \quad K_c = \frac{K_f}{K_b} = \frac{2.6\times 10^3}{4.1} = 634.15$$

16. (d) $K_c = \dfrac{\alpha^2}{V(1-\alpha)}$; Increase in pressure will decrease volume. To have K_c constant α i.e., degree of dissociation of PCl_5 should decrease.

17. (a) An increase in temperature will favour backward reaction (endothermic).
Also K_c for $2SO_2 + O_2 \rightleftharpoons 2SO_3$ will

$$2.303 \log\frac{K_{c_2}}{K_{c_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

ΔH = –ve

$\therefore \quad K_{c_2} < K_{c_1}$ if $T_2 > T_1$

18. (a) Addition of Fe^{2+} will favour forward reaction.

19. (b)

$nA \rightleftharpoons$	B	+	C
	1	0	0
	$(1-\alpha)$	α/n	α/n

$$\therefore \quad K_c = \frac{\alpha^2 \cdot V^{n-2}}{n^2(1-\alpha)^n}$$

If α is independent of conc.,
then $n - 2 = 0 \quad \therefore n = 2$

20. (a)

$N_2O_4 \rightleftharpoons$	$2NO_2$
1	0
$(1 - 0.66)$	(2×0.66)
0.34	1.32

Total mole = 1.32 + 0.34 = 1.66 for 1 mole N_2O_4

$$\text{Total mole} = 1.66 \times \frac{10}{92}$$

for 10 g N_2O_4

$\therefore \quad PV = nRT$

$$1 \times V = \frac{1.66\times 10}{92} \times 0.0821 \times 340$$

$\therefore \quad V = 5.03$ atm

MATCH THE COLUMN TYPE QUESTIONS

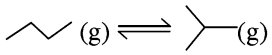
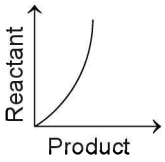
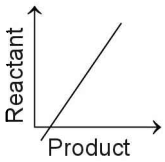
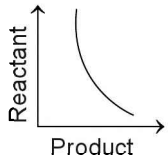
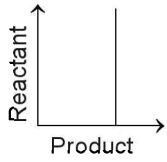
1.

Column-I (Reaction)	Column-II (If α is negligiable w.r.t 1)
(a) $2X(g) \rightleftharpoons Y(g) + Z(g)$	(p) $\alpha = 2 \times \sqrt{K_c}$
(b) $X(g) \rightleftharpoons Y(g) + Z(g)$	(q) $\alpha = 3 \times \sqrt{K_c}$
(c) $3X(g) \rightleftharpoons Y(g) + Z(g)$	(r) $\alpha = (2K_c)^{1/3}$
(d) $2X(g) \rightleftharpoons Y(g) + 2Z(g)$	(s) $\alpha = \sqrt{K_c}$

2.

Column-I	Column-II
(a) $\dfrac{K_{10+T°C}}{K_{T°C}} = 2$	(p) Endothermic
(b) $\dfrac{K_{10+T°C}}{K_{T°C}} = \dfrac{1}{2}$	(q) Not affected by pressure
(c) $A(g) + B(g) \rightleftharpoons C(g)$	(r) Exothermic
(d) $X(s) + Y(g) \rightleftharpoons Z(g)$	(s) Affected by volume

3.

Column-I	Column-II
(a) 	(p) 
(b) $I_2(s) \rightleftharpoons I_2(aq)$	(q) 
(c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$	(r) 
(d) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	(s) 

ANSWER KEYS

1. (a); (p) (b); (s) (c); (q) (d); (r) **2.** (a); (p) (b); (s) (c); (q) (d); (r) **3.** (a); (p) (b); (s) (c); (q) (d); (r)

TRUE/FALSE TYPE QUESTIONS

1. If equilibrium constant for a reaction $A_2 + B_2 \rightleftharpoons 2AB$ is K, then for the reaction $\frac{1}{2}A_2 + \frac{1}{2}B_2 \rightleftharpoons AB$ the equilibrium constant is K^2.

2. K_p is less than K_C if Δn is positive

3. The reaction will be fast in backward direction if $Q < K_C$.

4. The equilibrium reaction $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ is independent of pressure.

5. More PCl_5 will dissociate at low pressure.

ANSWER KEYS

1. F **2.** F **3.** F **4.** F **5.** T

HINTS AND EXPLANATIONS

1. False: It will be $\sqrt{K}$, as in this reaction half of the substances are taken.

2. False: $K_p > K_C$ when Δn is positive

3. False:

4. False: Number of moles are increasing thus low pressure will favour the formation of NO_2 and Cl_2.

5. T

ASSERTION/REASON TYPE QUESTIONS

Instructions: In the following questions, an Assertion (A) is given followed by a Reason (R). Mark your responses from the following options.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'.
(b) Both Assertion and Reason are true and Reason is not the correct explanation of 'Assertion'.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true.

1. **Assertion:** The melting point of ice decreases with increase of pressure.
   Reason: Ice contracts on melting.

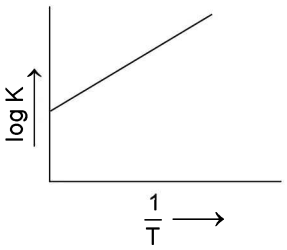
2. **Assertion:** For a reaction at equilibrium, the Gibb's free energy of reaction is minimum at constant temp, and pressure.
   Reason: The Gibb's free energy of both reactants and products increases and become equal at equilibrium.

3. **Assertion:** The physical equilibrium is not static but dynamic in nature.
   Reason: The physical equilibrium is a state in which two opposing process are proceeding at the same rate.

4. **Assertion:** The equilibrium constant of the exothermic reaction at high temperature decreases.
   Reason: Since In $\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ I and for exothermic reaction, ΔH° = –ve and thereby; $\frac{K_2}{K_1} < 1$.

5. **Assertion:** For the reaction at certain temperature
   $$A(g) + B(g) \rightleftharpoons C(g)$$
   there will be no effect by addition of inert gas at constant volume.
   Reason: Molar concentration of all gases remains constant.

6. **Assertion:** The graph of log K and $\frac{1}{T}$ for endothermic process is shown as under:



   Reason: For endothermic process, on increasing temperature the value of equilibrium constant increases monotonically.

ANSWER KEYS

1. (a) 2. (c) 3. (a) 4. (a) 5. (a) 6. (a)

SUBJECTIVE QUESTIONS

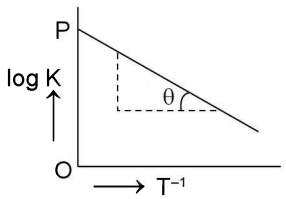
1. NH_3 is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at the equilibrium of the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$. Calculate % of mole of NH_3 actually decomposed.

2. Variation of equilibrium constant K with temperature T is given by Van't Hoff equation

$$\log K = \log A - \frac{\Delta H^\circ}{2.303RT}$$

A graph between log K and T^{-1} was a straight line as shown and having OP = 10 and tan θ = 0.5. Calculate

(i) equilibrium constant at 298 K, and
(ii) and equilibrium constant at 798 K, assuming ΔH° to be independent of temperature.



3. Would 1% CO_2 in the air be sufficient to prevent any lose in weight when Ag_2CO_3 is dried at 120°C? $Ag_2CO_{3(s)} \rightleftharpoons Ag_2O_{(s)} + CO_{2(g)}$, $K_p = 0.0095$ atm at 120°C. How low would the partial pressure of CO_2 have to be promote this reaction at 120°C?

4. The equilibrium constant for the reaction

$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$ as a function of temperature can be expressed as

$$KT \ln k_p = -40900 + 4.9T \ln T - 4.95 \times 10^{-2} T^2 + 5.1 \times 10^{-7} T^3 + 12.66T$$

In the range of 1100 to 1500 K. If the p_{CO_2} at 1200 K is 1.2 atm calculate p_{CO}.

5. For the reaction $NH_3\,(g) \rightleftharpoons \frac{1}{2} N_2\,(g) + \frac{3}{2} H_2\,(g)$

Show that the degree of dissociation of NH_3 is given as

$$\alpha = \frac{1-\alpha^2}{\alpha^2} = \frac{3\sqrt{3}P}{4\,K_P}$$

where P is the equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400°C, determine the value of K_C.

HINTS AND EXPLANATIONS

1. $2NH_3 \rightleftharpoons N_2 + 3H_2$

Initial mol	a	0	0
	(a – 2α)	α	3α

Initial pressure of NH_3 of a mol = 15 atm, at 27°C
The pressure of a mol of NH_3 = P atm at 347°C

$$\frac{15}{300} = \frac{P}{620} \quad \therefore P = 31 \text{ atm}$$

At constant volume at 347°C mole ∝ pressure
a ∝ 31 atm (before equilibrium)
(a + 2x) ∝ 50 atm (after equilibrium)

$$\therefore \quad \frac{a+2x}{a} = \frac{50}{31}$$

$$\therefore \quad x = \frac{19}{62}a \qquad \therefore \text{ \% of } NH_3 \text{ decomposed} = \frac{2x}{a} \times 100 = \frac{2 \times \frac{19}{62}}{a} \times 100 = 61.3\%$$

2. To calculate equilibrium constant, we need to know A and ΔH°, which are calculated as –

The given equation represents a straight line of slope

$$= \frac{-\Delta H^\circ}{2.303\,R}$$

$$= -\tan\theta = -0.5$$

$$\therefore \quad \Delta H^\circ = 2.303 \times 8.314 \times 0.5 = 9.574 \text{ J/mol}$$

Intercept = log A = OP = 10

$$\therefore \quad \log K = \log A - \frac{\Delta H^\circ}{2.303\,RT}$$

$$= 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$$\therefore \quad K = 9.96 \times 10^9$$

Now, to calculate equilibrium constant at some other temperature, we will use the expression

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314}\left[\frac{500}{798 \times 298}\right]$$

$$\therefore \quad K_2 \text{ (equilibrium constant at 798)} = 9.98 \times 10^9$$

3. $K_p = \frac{P_{Ag_2O} \times P_{CO_2}}{P_{Ag_2CO_3}} = P_{CO_2}$

$\therefore P_{CO_2} = 0.0095$ atm = constant at 120°C

Thus if Ag_2CO_3 is taken in a closed container, a small amount of it would decompose to give CO_2 gas until the partial pressure of CO_2 reaches 0.0095 atm. As this is equilibrium pressure of CO_2, the decomposition would then stop.

Now since partial pressure of CO_2 in air is 0.01 atm (since CO_2 is 1% in air) which is much greater

than 0.0095 atm, the equilibrium would practically shift to left hand side completely on in other wards, there would be no loss in weight of Ag_2CO_3 (by decomposition) if placed in air containing 1% CO_2.

Further, if the partial pressure of CO_2 in air is less than the equilibrium pressure of 0.0095 atm the decomposition of Ag_2CO_3 would continue till the CO_2 pressure around Ag_2CO_3 becomes 0.0095 atm.

4. For the given reaction

$$k_p = \frac{p_{CO}^2}{p_{CO_2}} \text{ or } \Rightarrow p_{CO} = (k_p p_{CO_2})^{1/2}$$

k_p at 1200 K can be calculated from the reaction

$$\ln k_p = \frac{1}{1200 \times 8.314}[-40900 + 4.9\,(1200)\ln 1200 - (4.95 \times 10^{-2})\,(1200)^2 + (5.1 \times 10^{-7})\,(1200)^3 + (12.66)\,(1200)]$$

$\ln k_p = -5.454 \quad \Rightarrow k_p = 4.28 \times 10^{-3}$

putting the value of k_p

$p_{CO} = (4.28 \times 10^{-3} \times 1.2)^{1/2} = 0.072$ atm

5. Let n and α be the initial number of moles and degree of dissociation of NH_3 (g) respectively.

$$NH_3\,(g) \rightleftharpoons \frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g)$$

Initially	n	0	0
At equilibrium	$n(1-\alpha)$	$n\frac{\alpha}{2}$	$\frac{3n\alpha}{2}$

Total number of moles = $n(1+\alpha)$

Partial pressure of NH_3, $p_{NH} = \frac{1-\alpha}{1+\alpha} \times P$

Partial pressure of N_2, $p_{N_2} = \frac{\alpha}{2(1+\alpha)} \times P$

Partial pressure of H_2, $p_{H_2} = \frac{3\alpha}{2(1+\alpha)} \times P$

$$\therefore \quad K_P = \frac{(p_{N_2})^{1/2}(p_{H_2})^{3/2}}{p_{NH_3}}$$

$$\frac{\left[\frac{\alpha P}{2(1+\alpha)}\right]^{1/2}\left[\frac{3\alpha P}{2(1+\alpha)}\right]^{3/2}}{\frac{1-\alpha}{1+\alpha} \times P} = \left[\frac{3\sqrt{3}P}{4}\right]\left[\frac{\alpha^2}{1-\alpha^2}\right]$$

$$\frac{1-\alpha^2}{\alpha^2} = \frac{3\sqrt{3}P}{4\,K_P}$$

$$\frac{1}{\alpha^2} = \left[1 + \frac{3\sqrt{3}}{4}\frac{P}{K_P}\right] \text{ or, } \alpha = \left[1 + \frac{3\sqrt{3}}{4}\frac{P}{K_P}\right]^{-1/2}$$

Δn, change in number of the moles of the given reaction = +1

$K_P = K_C(RT)^{\Delta n}$

or, $K_C = K_P\,(RT)^{-\Delta n}$

$K_C = 78.1\,[0.0821 \times 673]^{-1} = 1.413$ mol/l

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

1. Two flasks A and B of equal volume containing 1 mole and 2 mole of O_3 respectively, are heated to the same temperature. When the reaction $2O_3 \rightleftharpoons 3O_2$ practically stops, then both the flasks shall have

(a) the same ratio $[O_2]/[O_3]$

(b) the same ratio : $[O_2]^{3/2}/[O_3]$

(c) only O_2

(d) the same time to reach equilibrium

2. A 10 litre container at 300 K contains CO_2 gas at pressure of 0.2 atm and an excess solid CaO (neglect the volume of solid CaO). The volume of container is now decreased by moving the movable piston fitted in the container. What will be the maximum volume of container when pressure of CO_2 attains its maximum value given that

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad K_{ph} = 0.800 \text{ atm}$$

(a) 5 L

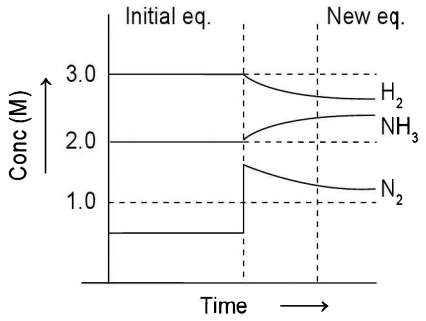
(b) 2.5 L

(c) 1 L

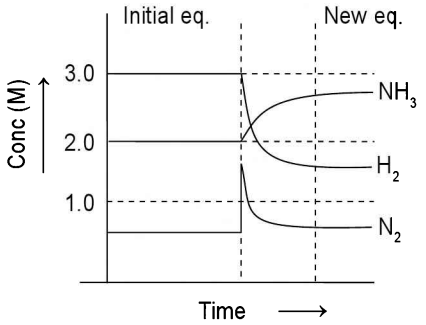
(d) The information is insufficient

3. An equilibrium mixture at 700 K of 0.50 M N_2, 3.00 M H_2 and 2.00 M NH_3 is present in a container. Now if this equilibrium is disturbed by adding N_2, so that its concentration becomes 1.50 M just after addition, then which of the following graphs represents the above situation more appropriately

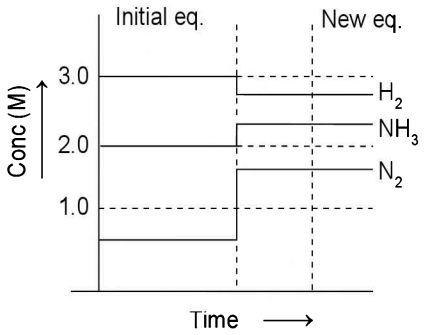
(a)



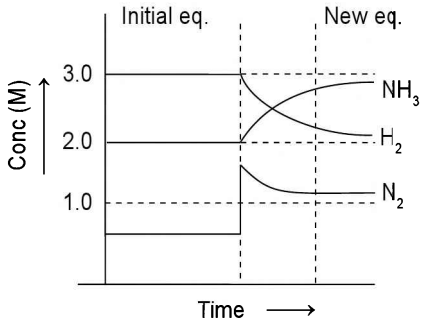
(b)



(c)



(d)

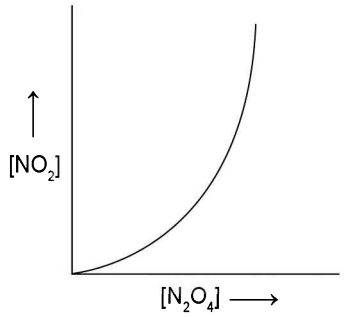


4. The graph which will be representing all the equilibrium concentrations for the reaction

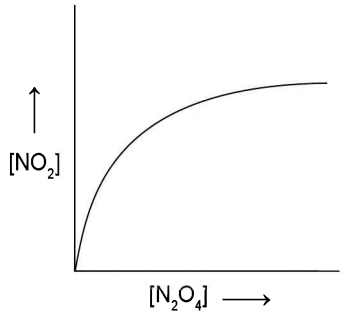
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ will be:

(the concentrations of N_2O_4 (g) and of NO (g) for which the following reaction will be at equilibrium will lie

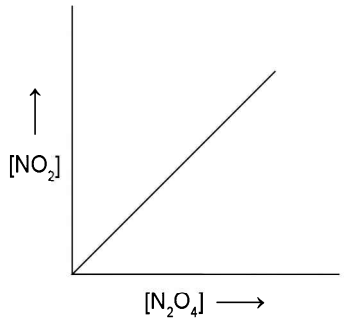
(a)



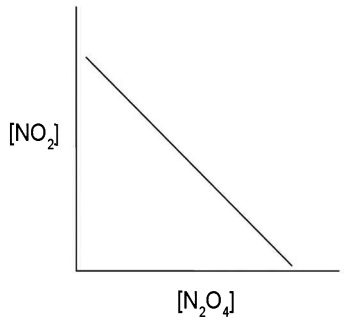
(b)



(c)



(d)



5. In a basic aqueous solution chloromethane undergoes a substitution reaction in which Cl is replaced by OH^- as.

$$CH_3Cl\ (aq) + OH^- \rightleftharpoons CH_3OH(aq) + Cl\ (aq)$$

The equilibrium constant of above reaction C, =1 × 10'6. If a solution is prepared by mixing equal volumes of 0.1 M CH_3Cl and 0.2 M NaOH (100% dissociated) then $[OH^-]$ concentration at equilibrium in mixture will be:

(a) 0.1 M (b) 0.5 M
(c) 0.2 M (d) 0.05 M

6. At a certain temperature the following equilibrium is established, $CO(g) + NO_2(g) \rightleftharpoons CO(g) + NO(g)$ One mole of each of the four gas is mixed in one litre container and the reaction is allowed to reach equilibrium state. When excess of baryta water ($Ba(OH)_2$) is added to the equilibrium mixture, the weight of white ppt ($BaCO_3$) obtained is 236.4 gm. The equilibrium constant C_c of the reaction is (Ba = 137)

(a) 1.2 (b) 2.25
(c) 2.1 (d) 3.6

7. At temperature T' the compound AB_2 (g) dissociates according to the reaction, $2AB_2$ (g) $\rightleftharpoons$ 2 AB(g) + B_2(g).With a degree of dissociation x, which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p and the total pressure, P.

(a) $x = \left[\frac{2K_p}{P}\right]^{-1/3}$ (b) $x = \left[\frac{K_p}{P}\right]^{1/3}$

(c) $x = \left[\frac{K_p}{2P}\right]^{1/3}$ (d) $x = \left[\frac{6K_p}{3P}\right]^{1/3}$

8. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows:

$$NH_2COONH_4(s) \rightleftharpoons 2\ NH_5(g) + CO_2(g)$$

At equilibrium, ammonia is added such that partial pressures of NH_5 now equals the original total pressure. Calculate the ratio of the total pressures to the original total pressure.

(a) $\frac{31}{27}$ (b) $\frac{60}{40}$

(c) $\frac{31}{9}$ (d) $\frac{62}{27}$

9. The reactions, $PCI_5(g) \rightleftharpoons PCI_5(g) + CI_2(g)$ and $CI_2(g) \rightleftharpoons CO_2(g) + Cl_2(g)$ are simultaneously in an equilibrium box at constant volume. A few moles of CO(g) are later introduced into the vessel. After some time, the new equilibrium concentration of

(a) PCI_5 will remain unchanged
(b) CI_2 will be greater
(c) PCI_5 will become less
(d) PCI_5 will become greater

10. For the equilibrium of the reaction, $HgO(s) \rightleftharpoons Hg(g) + \frac{1}{2}O_2(g)$, k_p for the reaction at total pressure of P is:

(a) $K_P = \frac{2}{3^{3/2}}p^{3/2}$

(b) $K_P = \frac{2}{3^{1/2}}p^{1/2}$

(c) $K_P = \frac{1}{3^{2/3}}p^{3/2}$

(d) $K_P = \frac{1}{3^{2/3}}p$

11. What is the minimum mass of $CaCO_5$ (s), below which it decomposes completely, required to establish equilibrium in a 6.50 litre container for the reaction : [K_C = mole/litre]

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(a) 32.5 g
(b) 24.6 g
(c) 40.9 g
(d) 8.0 gm

12. The value of k_p for the reaction at 27°C

$Br_2(\ell) + Cl_2(g) \rightleftharpoons 2\,BrCl(g)$

is '1 atom'. At equilibrium in a closed container partial pressure of BrCI gas is 0.1 atm and at this temperature the vapour pressure of $Br_2(\ell)$ is also 0.1 atm. Then what will be the minimum moles of $Br_2(\ell)$ to be added to 1 mole of $C1_2$, initially, to get above equilibrium situation:

(a) $\frac{10}{6}$ moles (b) $\frac{5}{6}$ moles

(c) $\frac{15}{6}$ moles (d) 2 moles

13. 5 mole $PCI_3(g)$ tand one mole N_2 gas is placed in a closed vessel. At equilibrium $PCI_5(g)$ decomposes 20% and total pressure in to the container is found to be 1 atm. The k_p for equilibrium $PCI_3(g) \rightleftharpoons PCI_3(g) + Cl_2(g)$

(a) $\frac{1}{24}$ atm (b) $\frac{1}{4}$ atm

(c) $\frac{1}{16}$ atm (d) $\frac{1}{28}$ atm

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

14. Solid ammonium carbamate, $NH_4\,CO_2NH_2$ (s) dissociates into ammonia and carbon dioxide when it evaporates as shown by

$NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

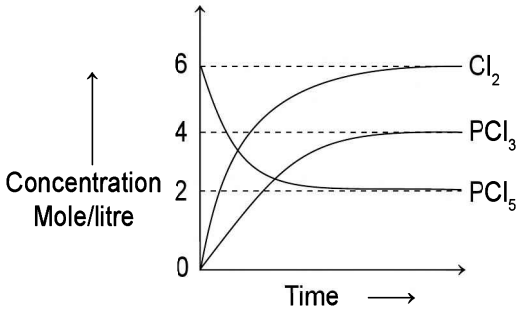
At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. If 0.1 atm of CO_2 is introduced after equilibrium is reached then:

(a) final pressure of CO_2 will be less than 0.1 atm
(b) final pressure of CO_2 will be more than 0.1 atm
(c) pressure of NF_{I3} will decrease due to addition of CO_2
(d) pressure of NH_3 will increase due to addition of CO_2

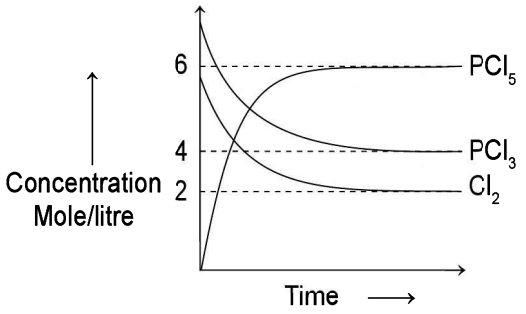
15. For the equilibrium, $PCI_3 \rightleftharpoons PCI_3(g) + CI_2(g)$

Which of the following sketches may represent above equilibrium. Assume equilibrium can be achieved from either side and by taking any one or more components initially. (Given K_c for the reaction < 2)

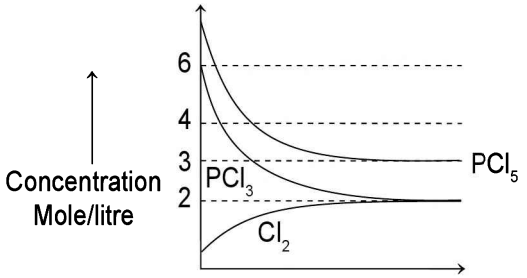
(a)



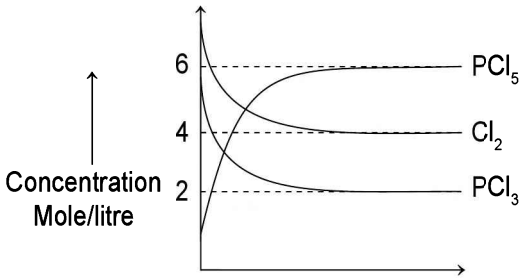
(b)



(c)



(d)



16. 138 gm of $N_2O_4(g)$ is placed in 8.2 L container at 300 K. The equilibrium vapour density of mixture was found to be 30.67. Then (R = 0.082 L atm $mol^{-1}K^{-1}$)

(a) = degree of dissociation of N_2O_4 = 0.25

(b) K_P of $N_2O_4 \rightleftharpoons 2NO_2(g)$ will be 9 atm.

(c) Total pressure at equilibrium = 6.75 atm

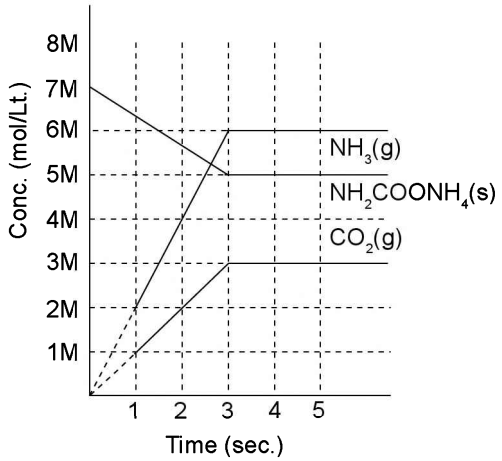
(d) The density of equilibrium mixture will be 16.83 gm/litre.

17. Solid ammonium carbamate dissociate to give ammonia and carbon dioxide as follows

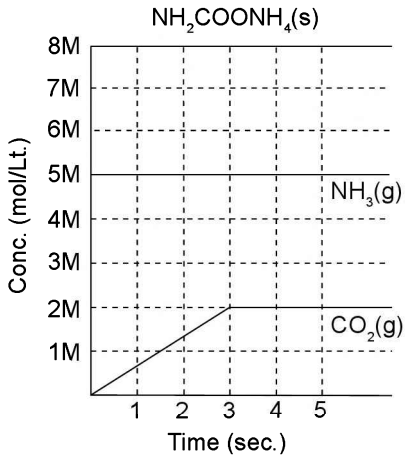
$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

which of the following graph incorrectly represents the equilibrium.

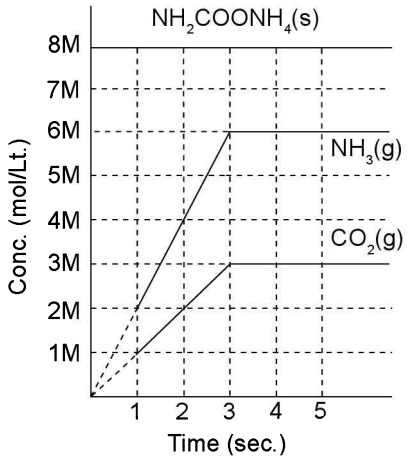
(a)



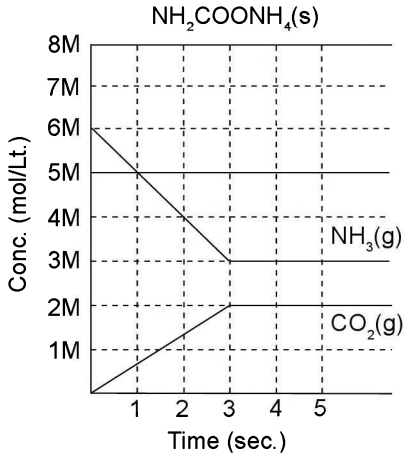
(b)



(c)



(d)



18. $2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g)$, $\Delta H > 0$

Above equilibrium is established by taking sufficient amount of $CaSO_4(s)$ in a closed container at 1600 K.

Then which of the following may be correct option (Assume that solid $CaSO_4$ is present in the container in each case)

(a) moles of CaO(s) will increase with the increase in temperature

(b) If tile volume of the container is doubled at equilibrium then the partial pressure of $SO_2(g)$ will change at new equilibrium.

(c) If the volume of the container is halved the partial pressure of $O_2(g)$ at new equilibrium will remain same

(d) If two moles of the He gas is added at constant pressure then the moles of CaO(s) will increase.

19. $CuSO_4\ 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$ $K_p = 10^{-10}$ (atm). 10^{-2} moles of $CuSO_4\ 5H_2O(s)$ is taken in a 2.5L container at 27°C then at equilibrium [Take: R = $\frac{1}{12}$ litre atm $mol^{-1}\ K^{-1}$]

(a) Moles of $CuSO_4 . 5H_2O$ left in the container is 9×10^{-3}

(b) Moles of $CuSO_4 . 5H_2O$ left in the container is 9.8×10^{-3}

(c) Moles of $CuSO_4$ left in the container is 10^{-3}

(d) Moles of $CuSO_4$ left in the container is 2×10^{-4}

20. A closed jar having waters vapours in equilibrium with liquid. Suddenly all the vapours of the jar is transferred to another, identical jar and is subjected to compression. Assume initial temperature to be the same and negligible volume occupied by the liquid water. Select the observation in the record jar

(a) liquid water will start forming in the jar

(b) vapour will undergo gradual compression without any condensation.

(c) temperature of the vapour will increases.

(d) final pressure will be the same as initial pressure.

21. For a reversible reaction $ad + bB \rightleftharpoons cC + dD$; the variation of K with temperature is given by

$$\log\frac{K_2}{K_1} = \frac{-\Delta H^\circ}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ then,}$$

(a) $K_2 > K_1$ if $T_2 > T_1$ for an endothermic change.

(b) $K_2 < K_1$ if $T_2 > T_1$ for an endothermic change.

(c) $K_2 > K_1$ if $T_2 > T_1$ for an exothermic change.

(d) $K_2 < K_1$ if $T_2 > T_1$ for an exothermic change.

COMPREHENSION BASED QUSTIONS

COMPREHENSION-1

Le chateliees principle

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure temperature, the system adjusts itself in such a way as to (Nulify) the effect of that change.

Change of pressure: If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume will now be more and the equilibirum will shift in the direction in which there is decrease in number of moles i.e., towards the direction in which there is decrease in volume.

Effect of pressure on melting point: There are two types of solids:

(a) Solids whose volume decreases on melting, egg, ice, diamond, carborundum, magnesium nitride and quartz

Solid (higher volume) $\rightleftharpoons$ Liquid (lower volume)

Then the process of melting is facilitated at high pressure, thus melting point is lowered.

(b) Solids whose volume increase on melting, e.g., Fe, Cu, Ag, Au, etc.

Solid (lower volume) $\rightleftharpoons$ Liquid (higher volume)

In this case the process of melting become difficult at high pressure; thus melting point becomes high.

Solubility of substances: When solid substances are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

$$KCI + aq \rightleftharpoons KCl(aq) - \text{heat}$$

In such cases, solubility increase with the increase in temperature.

Consider the case of KOH; when this is dissolved, heat is evolved.

$$KOH + aq \rightleftharpoons KOH(aq) + \text{heat}$$

In such cases, solubility decrease with the increase in temperature.

Solubility of gases in liquids: When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

Effect of temperature: Le-Chatelier's principle predicts a system at equilibrium will tend to shift in the endothermic direction when temperature is raised, for then energy is absorbed as heat and the rise in temperature is opposed. Conversely, an equilibrium will shift in the exothermic direction, if the temperature is lowered, for then that energy is released and the reduction in temperature is opposed. Van't Hoff equation shows the dependence of equilibrium constant K on temperature as:

$$\frac{d}{dT}\ell nK = \frac{\Delta H^\circ}{RT^2} \text{ or } \ell nK = \text{constant} - \frac{\Delta H^\circ}{R}.\frac{1}{T}$$

22. A gas 'X when dissolved in water heat is evolved. Then solubluty of 'X' will increase
(a) Low pressure, high temperature
(b) Low pressure, low temperature
(c) High pressure, high temperature
(d) High pressure, low temperature

23. $Au(s) \rightleftharpoons Au(\ell)$
Above equilibrium is favoured at:
(a) High pressure low temperature
(b) High pressure high temperature
(c) Low pressure, high temperature
(d) Low pressure, low temperature

24. For the reaction, $\frac{1}{2}N_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons NO(g)$
pressure is increased by reducing the volume of the container then
(a) total pressure at equilibrium will change.
(b) concentration of all the component at equilibrium will change.
(c) concentration of all the component at equilibrium will remain same.
(d) equilibrium will shift in the forward direction.

COMPREHENSION-2

In gaseous dissociation reactions, the total mass remains unchanged and the number of moles increases as a result of the reaction. Thus, the average molecular weight and hence the vapour density decreases. In other words, the volume increases at constant temperature and pressure, hence the vapour density decreases.The relationship between vapour density in the beginning and vapour density at equilibrium can be found as follows:

At constant temperature and constant pressure for a fixed mass of gaseous mixtures

$$\text{Vapour density } \alpha \text{ density } \alpha \frac{1}{\text{volume}}$$

$\therefore$ PV = nRT

$\therefore$ Volume $\propto$ number of moles

$\therefore$ $\text{Vapour density } \alpha \frac{1}{\text{Number of moles}}$

$\therefore$ $\frac{D}{D_0} = \frac{n_0}{n}$

Where D_o and D are the vapour densities in the beginning and at equilibrium and n_o and n are the number of moles in the beginning and at equilibrium.The vapour density of PCI_5 at 200°C and 252°C are 70.2 and 57.2 respectively at one atmosphere

25. The observation shows that the dissociation constants (K_p) for the reaction are
(a) 1 and 2 respectively
(b) 1.19 and 0.37 respectively
(c) 0.307 and 1.19 respectively
(d) 2 and 1 respectively

26. This observation shows that
(a) The reaction is endothermic
(b) The reaction is exothermic
(c) The reaction is not affected by the change in pressure
(d) The reaction is not affected by adding inert gas at constant pressure

27. From the given data, it can be interpreted that
(a) If degree of dissociation is more, then vapour density is more for PCI_5
(b) More the degree of dissociation, less is the vapour density of PCI_5
(c) Degree of dissociation and vapour density cannot be correlated
(d) α is independent of temperature

COMPREHENSION-3

The rate of chemical reaction at a particular temperature is proportional to the product of the molar concentration of reactants with each concentration term raised to the power equal to the number of molecules of the respective reactant taking part in the reaction. aA + bB $\rightarrow$ products, rate of reaction a [Aka [Bib = k [Aka [Bib, where k is the rate constant of the reaction.

EQUILIBRIUM CONSTANT (k)

For a general reaction aA + bB <=> cC + dD, forward rate $r_f = k_f [A]^a [B]^b$, backward rate $r_b = k_b$ [Cicpyi, concentrations of reactants & products at equilibrium are related by

$\frac{K_f}{K_b} = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ where all the concentrations are expressed in mole/litre.

e.g., $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

In the expression of equilibrium constant those components are kept whose concentration changes with time.

If equilibrium is estabilished by taking all the components in the reaction then to predict the direction of reactions we calculate the reaction quotient (Q).

The values of expression $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ at any time during reaction is called reaction quotient if Q > Kc reaction proceed in backward direction until equilibrium in reached if Q < Kc reaction will proceed in forward direction until equilibrium is established if $Q = K_C$ Reaction is at equilibrium

28. $A(g) + B(g) \rightleftharpoons 2C(g)$

Initial concentration of 'A' is twice the initial concentration of 'B'. At equilibrium concentration of 'A and a' are same then equilibrium constant for the reaction is

(a) $\frac{4}{3}$ (b) $\frac{4}{9}$

(c) $\frac{16}{9}$ (d) 4

29. $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

Above homogeneous reaction is carried out in a 2 litre container at a particular temperature by taking 1 mole each of A, B, C and D respectively. If K_c for the reaction is then equilibrium concentration of C is

(a) $\frac{1}{3}$ M (b) $\frac{2}{3}$ M

(c) $\frac{4}{3}$ M (d) $\frac{1}{2}$ M

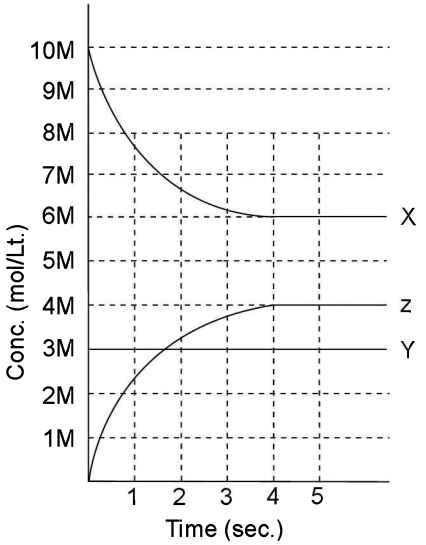
30. When C_2H_5OH and CH_3COOH are mixed in equivalent proportion equilibrium is reached when 2/3 of acid and alcohol are used. How much ester will be present when 2 moles of acid were to react with 2 moles of alcohol?

(a) 1.33 (b) 1

(c) 2.33 (d) 2

COMPREHENSION-4

X,Y and Z react in the 1 : 1 : 1 stoichiometric ratio. The concentration of X, Y and Z was found to vary with time as shown in the figure belo .



31. Which of the following equilibrium reaction represents the correct variation of concentration with time.

(a) $x(g) + y(g) \rightleftharpoons z(g)$

(b) $x(g) + y(s) \rightleftharpoons z(g)$

(c) $z(g) + y(s) \rightleftharpoons x(g)$

(d) $z(g) + x(g) \rightleftharpoons y(g)$

32. Value of the equilibrium constant (K_c) for the equilibrium represented in above sketch will be.

(a) $\frac{9}{2}$ (b) $\frac{21}{4}$

(c) $\frac{2}{3}$ (d) $\frac{12}{7}$

33. If above equilibrium is established in a 2 litre container by taking reactants in sufficient amount then how many moles of component Y must have reacted to establish the equilibrium.

(a) 0 (b) 6

(c) 12 (0) 8

COMPREHENSION-6

$2A_2 \rightleftharpoons A_4$ (i) $K_{P1} = \frac{2}{81}\ atm^{-1}$

$A_2 + 2C \rightleftharpoons A_2C_2$ (ii)

$A_2C_2 \rightleftharpoons 2AC$ (iii)

A_2 and C are taken in 3 : 1 mole ratio in a closed container of a certain volume at a fixed temperature and

above three equilibriums are established simultaneously. K_{opf} for the first reaction is 2/81 atm^{-1}. At equilibirum partial pressure of $A_4(g)$ and AC(g) are found to be 1/2 atm each and the total pressure at equilibirum is found to be $\frac{27}{4}$ atm. Then

34. The partical pressure of A_2C_2 at equilibrium is
(a) 1/2 (b) 1/4
(c) 2/4 (d) 1

35. The mole ratio of gases A_2 and AC at equiliburm is
(a) 9/2 (b) 7I2
(c) 8 (d) 9

36. Equilibrium constant K_p for the reaction, $2AC \rightleftharpoons A_2C_2$ is
(a) 2/4 (b) 2
(c) 4 (d) ½

MATCH THE COLUMN TYPE QUSTIONS

37. Match the following

Column-I	Column-II
(a) $C_2H_4(g) + H_2(g)$ C_2H_6 + Heat	(p) Doubling the volume causes forward shift
(b) $2HH_3$ + Heat $\rightleftharpoons$ H_2 + $2H_2$	(q) Kp is less than Kc
(c) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ + Heat	(r) Yield of reactant can be increased by increasing
(d) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ + Heat	(s) Forward reaction is forward on decreasing temperature

38. Match the following (multiple)

Left column: Represents an equilibrium situation through a chemical equation and below each equation a stimulus is given which may or may not disturb the equilibrium situation.

Right coloumn: Represents the responses immediately after the disturbance is created.

With R_1: Rate of forward reaction.
R_b: Rate of backward reaction.
Q: Reaction quotient
K: Equilibrium constant

Column-I	Column-II
(a) $H_{2(g)} + I \rightleftharpoons 2HI_{(g)}$ Pressure is increased	(p) R_f increases
(b) $\frac{1}{2}N_{2(g)} + \frac{3}{4}H_{2(g)} \rightleftharpoons$ $NH_{3(g)}$ Volume is halved	(q) R_b increases
(c) $PCl_{3(g)}$ + Cl PCI_5 is added	(r) $R_1 = Rb$
(d) $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ Inert gas added at court volume.	(s) $Q \neq K$

39.

Column-I	Column-II
(a) $N_2O_4(g) \rightleftharpoons 2NO_{+2}(g)$ On increase in volume at constant Temperature	(p) Density of reacting mixture remain constant
(b) $H_2(g) + I_2(g) \rightleftharpoons$ 2HI(g) On addition of inert gas at constant P & T	(q) Density of reacting mixture Decreases
(c) $2NO(g) + Br_2(g) \rightleftharpoons$ 2NOBr(g) On decrease in pressure at constant Temperature	(r) Average molar mass of reacting mixture increases.
(d) $2ICI_3(g) \rightleftharpoons I_3(g) +$ $3Cl_2(g)$, ΔO On increase in pressure at constant	(s) Average molar mass of reacting mixture decreases Temperature

40.

Column-I	Column-II
(a) NH_2COON_4 (s) $\rightleftharpoons 2NH_3(g) +$ $CO_2(g)$; $\Delta H < 0$	(p) High pressure and low temperature will favour formation of products.
(b) $CaCO_3$ (S) $\rightleftharpoons$ CaO(s) + $CO_2(g)$; $\Delta H > 0$	(q) Increase in the amount of any of the product will definitely favour backward reaction.

(c) $N_2(g) + O_2(g) \rightleftharpoons 2O(g)$; $\Delta H > 0$ — (r) Increase in temperature and doubling the volume of reaction vessel will cause the equilibrium to shift in similar direction.

(d) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H < 0$ — (s) A decrease in temperature will cause decrease in the value of equilibrium constant.

41. Match the following:

Column-I	Column-II
(a) For the equilibrium $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$, if pressure is increased at equilibrium	(p) Forward shift
(b) For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium volume is increased at equilibrium	(q) No change
(c) For the equilibrium $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ inert gas is added at constant pressure at equilibrium	(r) Backward shift
(d) For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is removed at equilibrium	(s) Final Pressure is more than initial pressure

SUBJECTIVE TYPE QUESTIONS

SHORT SUBJECTIVE

42. The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K,

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 C.

43. For the reaction; $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO(g) and a catalyst, until the pressure is 4.92 atmosphere. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate the equilibrium constants K_p & K_c.

44. NH_3 is heated initially at 15 atm from 27°C to 127°C at constant volume. At 127°C equilibrium is established. The new pressue at equilibrium at 127°C becomes 30 atm for the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$.

Then find the % of moles of NH_3 actually decomposed.

45. For the equilibrium

$LiCl.3NH_3(S) \rightleftharpoons LiCl.NH_3(s) + 2NH_3(g)$ $[K_p = 9\ atm^2]$

at 40°C. A 5litre vessel contains 0.1 mole of LiCl. NH_3. How many mole of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion?

46. Following two equilibria are established on mixing two gases A_2 and C.

(i) $3A_2(g) \rightleftharpoons A_6(g)$ $\quad K_p = 1.6\ atm^2$

(ii) $A_2(g) + C(g) \rightleftharpoons A_2C(g)$

If A_2 and C are mixed in 2:1 molar ratio, calculate the equilibrium partial pressure of A_2, C, A_2C and C_{ps} for the reaction (ii). Given that the total pressure to be 1.4 atm and partial pressure of A_6 to be 0.2 atm at equilibrium.

ANSWER KEYS

1. (b)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (d)	**6.** (b)	**7.** (d)	**8.** (a)	**9.** (c)	**10.** (a)
11. (a)	**12.** (c)	**13.** (d)	**14.** (b, c)	**15.** (b, d)	**16.** (b, c, d)	**17.** (a, b, d)	**18.** (a, c, d)	**19.** (b, d)	
20. (a, d)	**21.** (a, d)	**22.** (d)	**23.** (c)	**24.** (a, b)	**25.** (c)	**26.** (a)	**27.** (b)	**28.** (d)	**29.** (a)
30. (a)	**31.** (b)	**32.** (c)	**33.** (d)	**34.** (c)	**35.** (d)	**36.** (b)			

37. (a – q, s), (b – p, r), (c – q, s), (d – p, r)

38. (a – p, q, r), (b – p, q, s), (c – q, s), (d – p, q, r)

39. (a – q, s), (b – p), (c – q, s), (d – r)

40. (a – q), (b – r, s), (c – q, s), (d – p, q, r)

41. (a – r, s), (b – r), (c – q), (d – p, s)

43. $K_c = 279.64\ litre^2\ mol^{-2}$, $k_p = 0.115\ atm^{-2}$ **44.** 50

[redacted]TS AND EXPLANATIONS

1. (b) For reaction

$$\frac{[O_2]^3}{[O_3]^2} = \text{constant so, } \sqrt{K_C} = \frac{[O_2]^{3/2}}{[O_3]} = \text{constant}$$

= will be same for both the containers

2. (b) $K_p = 0.800\ atm = P_{CO_2}$ = maximum pressure of CO_2 in the container to calculate maximum volume of container the P_{CO_2} = 0.8 atm and none of P_{CO_2} = 0.8 should get converted into $CaCO_3$(s).

so, V(0.800 atm) = (10 L) (0.2 atm)
so, v = 2.5 L

3. (a) Let reaction be

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_C = \frac{[NH_3]}{[N_2][H_2]^3} = \frac{(2)^2}{\left(\frac{1}{2}\right)(3)^2} = \left(\frac{2}{3}\right)^3 = \frac{8}{27}$$

Now after distrubing equilibrium, then N2 concentration will be > 0.5 M and there will be some time taken for attainment of equilibrium hence, graphs (b) and (c) can be discarded from calculations it can be proved that the amount by which N2 should react should be less than 0.2 Hence the result.

4. (b) All the equilibrium concentrations will satisfy the equation

$$K = \frac{[NO_2]^2}{[N_2O_4]} \Rightarrow y^2 = kx$$ the required parabolic graph

5. (d) $CH_3Cl\ (aq) + OH^- \rightleftharpoons CH_3OH\ (aq) + Cl^-\ (aq)$
As equilibrium constant is very large so reaction will be almost 100% complete.

6. (b)

	$CO(g) +$	$NO_2(g) \rightleftharpoons$	$CO_2(g) +$	$NO(g)$
t = 0	1 mole	1 mole	1 mole	1 mole
Al eq.	1 – x	1 – x	1 + x	1 + x

$$CO_2 + Ba(OH)_2 \longrightarrow BaCO_3$$

$$\text{mole of } BaCO_3 = \frac{236.4}{197} = 1.2$$

So, mole of CO_2 at eq. = 1.2
or 1 + x = 1.2
x = 0.2

$$K_C = \left(\frac{1+x}{1-x}\right)^2 = \left(\frac{1.2}{0.8}\right)^2 = 2.25$$

7. (d) $2AB_2\ (g) \rightarrow 2AB\ (g) + B_2\ (g)$

Mole before dissociation	1	0	0
Mole after dissociation	(1 – x)	x	$\frac{x}{2}$

Total mole at equilibrium $(\sum n) = 1 - x + x + \frac{x}{2}$

$1 + \frac{x}{2}$

$$\text{Now, } K_p = \frac{n_{B_2} \times (n_{AB})^2}{(n_{AB_2})^2} \times \left[\frac{P}{\sum n}\right]^{\Delta n}$$

$$K_p = \frac{\frac{x}{2} \cdot (x)^2}{(1-x)^2} \times \left[\frac{p}{1+\frac{x}{2}}\right]^1$$

$$K_p = \frac{x^3 p}{2} \quad \left[\because x \text{ is small}, \therefore 1-x \text{ and } 1+\frac{x}{2} = 1\right]$$

$$x = \sqrt[3]{\frac{2K_p}{p}}$$

$$X = \left[\frac{2k_p}{p}\right]^{1/3}$$

8. (a)

	$NH_2COONH_4(s) \rightleftharpoons$	$2NH_3(g) +$	$CO_2(g)$
Initial		3P	P'

$$K_p = \left(P_{NH_3}\right)^2 \left(P_{CO_2}\right)$$

$K_p = (2P)^2\ (P)$ …… (i)
P_T(initial) = 3P

	$NH_2COONH_4(s) \rightleftharpoons$	$2NH_3(g) +$	$CO_2(g)$
Final		3P	P'

$K_p = (3p)^2\ (p')$ …… (ii)
From eq. (i) and (ii)
$(2P)^2 = (3P)^2\ (P')$

$$P' = \frac{4P}{9}$$

$$\frac{p_T(\text{New})}{p_T(\text{Old})} = \frac{3P + P'}{3P} = \frac{3P + \frac{4P}{9}}{3P} = \frac{31}{27}$$

9. (c) If CO is added 2nd equilibrium will proceed in the backward direction and concentration of Cl_2 will decrease. This Cl_2 will be further formed by the decomposition of PCl_5.

10. (a) $HgO(s) \rightleftharpoons Hg(g) + \frac{1}{2} O_2(g)$

$K_p = P_{Hg(g)} \times (PO_2)^{\frac{1}{2}}$

Total moles at equilibrium = $\frac{3x}{2}$

$P_{Hg} = \frac{x}{3x/2} = P = \frac{2}{3}P$

$PO_2 = \frac{x/2}{3x/2} P = \frac{1}{3}P$

$K_p = \frac{2}{3}P\left(\frac{1}{3}P\right)^{1/2} = \frac{2}{3^{3/2}}P^{3/2}$

11. (a) $K_c = [Cl_2] = 0.05$ mole/litre
so moles of CO_2= 6.50 × 0.05 moles = 0.3250 moles

$CaCl_3 \rightleftharpoons CaO + Cl_2$

1 mole of CO_2 = 1 mole of $CaCO_3$
0.3250 moles of CO_2 = 0.3250 moles of $CaCO_3$= 0.3250 × 100 gm of $CaCO_3$ = 32.5 gm of $CaCO_3$

12. (c) $Br_2(\ell) + CI_2(g) \rightleftharpoons 2Br\,Cl(g)$

t = 0	1	0
	(1 – x)	2x

$K_p = \frac{(P_{BrCl})^2}{P_{Cl_2}} = 1$ so, $P_{Cl_2} = (P_{BrCl})^2 = 0.01$ atm

then at equilibrium, $\frac{n_{BrCl}}{n_{Cl_2}} = \frac{0.1}{0.01} = 10 = \frac{2x}{1-x}$

so, $10 - 10x = 2x$ or $x = \frac{10}{12} = \frac{5}{6}$ moles

Moles of $Br(\ell)$ required for maintaining vapour pressure of 0.1 atm

$= 2 \times \frac{5}{6}$ moles $= \frac{10}{6}$ moles = moles of BrCl(g).

Moles required for taking part in reaction = moles of Cl_2 used up = $\frac{5}{6}$ moles.

13. (d)

	$PCI_3(g)$	$\rightleftharpoons$	$PCI_3(g)$ +	$Cl_2(g)$
t = 0	5		0	0
t = teq	5 – 5 × 0.2		5 × 0.2	5 × 0.2
	4 mole		1 mole	1 mole

Total moles at equilibrium = 4 + 1 + 1 + 1 (N_2) = 7 moles

$K_p = \frac{\left(\frac{1}{7}\times 1 \text{ atm}\right)\left(\frac{1}{7}\times 1 \text{ atm}\right)}{\left(\frac{4}{7}\times 1 \text{ atm}\right)} = \frac{1}{28}$ atm

14. (b, c) the pressure of NH_L will decrease due to addition of CO_2 (backward, shifting Le-chatelies's principle.
The pressure of CO_2 will be more than 0.1 atm.

15. (b, d) Given $K_c < 2$ therefore, in case of B and C $K_c = \frac{2\times 4}{6} = \frac{4}{3}$ and concentration of PCI_3 and Cl_2 together will decrease or increase as reaction can go in the forward or backward direction.

16. (b, c, d)

	N_2O_4	$\rightleftharpoons$	$2NO_2$
t = 0	a		0
t	a (1 – α)		2aα

vapour density = $\frac{46}{1+\alpha} = 30.67$

so, 1 + α = 1.5 = 0.5 = 50%

Total pressure = $\frac{1.5\times 1.5\times 0.082\times 300}{8.2} = 6.75$ atm

So, $K_p = \frac{4\alpha^2}{1-\alpha^2} P = 9$ atm

And for density of mixture = $\frac{138}{8.2}$ gm/L = 16.83 gm/L.

18. (a, c, d)
(a) As reaction is endothermic, therefore it will go in the forward direction hence moles of CaO will increase.
(c) With the increase or decrease of volume particle pressure of the gases will remain same.
(d) Due to the addition of inest gas at constant pressure reaction will proceede in the direct in which move number of gaseous moles are formed.

19. (b, d) 10^{-10} atm^5 = $P_{H_2O}^5$

$\Rightarrow \quad P_{H_2O} = 10^{-2}$ atm. $n = \frac{PV}{RT} = \frac{10^{-2}}{\frac{1}{12}\times 300} = 10^{-3}$

22. (d) Solubility of gas is favourable at high pressure and this process is exothermic hence solubility will be more at low temperature.

23. (c) Since density of gold decreases after melting, therefore, it is favourable at low pressure and high temperature.

25. (c) $PCI_5 \rightleftharpoons PCI_3 + CI_2$
$1-\alpha \quad \alpha \quad \alpha$

Since $\alpha = \frac{D-d}{d}$ & $Kc_1 = \frac{\alpha_1^2}{1-\alpha_1}$ & $Kc_2 = \frac{\alpha_2^2}{1-\alpha_2}$

Hence, Kp for different conditions can be calculated and kp = 0.307 and 1.19 respectively at 200°C and 250°C.

26. (a) As Kp value increases with the increase in temperature, this implies the reaction is endothermic.

27. (b) More the degree of dissociation, less is the vapour density of PCI_5.

28. (d)

	$A + B \rightleftharpoons 2C$		
at t = 0	2a	a	0
$t = t_{eq}$	2a – x	a – x	2x

$\Rightarrow 2a - x = 2x \quad \Rightarrow x = \frac{2}{3}a$

$\Rightarrow K_c = \frac{(2x)^2}{(29-x)(a-x)}$

$= \frac{4\left(\frac{2}{3}\right)^2}{\left(2-\frac{2}{3}\right)\left(1-\frac{2}{3}\right)} = \frac{4\times4}{4\times1} = 4$

29. (a)

	$A(g) + B(g) \rightleftharpoons$		$C(g) + D(g)$	
at t = 0	1	1	1	1
$t = t_{eq}$	1 + x	1 + x	1 – x	1 – x

$Q_C = \frac{(1/2)(1/2)}{(1/2)(1/2)} = 1 > K_C$

$\Rightarrow \frac{(1-x)(1-x)}{(1+x)(1+x)} = \frac{1}{4} \Rightarrow \frac{(1-x)}{(1+x)} = \frac{1}{2}$

$2 - 2x = 1 + x$

$\Rightarrow x = \frac{1}{3}$

$\therefore [C] = \frac{1-x}{2} = \frac{1}{3}M$

30. (a) **Case – I**

$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Mole before reaction	1	1	0	0
Mole at equilibrium	1 – x	1 – x	x	x

$\because x = \frac{2}{3}$

$\therefore$ Mole at equilibrium $\left(1-\frac{2}{3}\right)\left(1-\frac{2}{3}\right)\frac{2}{3}\frac{2}{3}$

$\therefore K_C = \frac{\frac{2}{3}\times\frac{2}{3}}{\frac{1}{3}\times\frac{1}{3}} = 4$

Note: Volume terms are eliminated

Case – II

$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Mole before reaction	1	1	0	0
Mole at equilibrium	(2 – x)	(2 – x)	x	x

$K_c = 4 = \frac{\frac{2}{3}\times\frac{2}{3}}{\frac{1}{3}\times\frac{1}{3}} = 4$ or $\therefore \frac{x}{(2-x)} = 2$

Or x = 1.33

31. (b) Clearly concentration of Y is not changing with the time hence it will be pure solid or liquid. Concentration of X decreasing hence it will be in reactant and Z will be in product.

32. (c) $K_c = \frac{[Z(g)]_{eq}}{[X(g)]_{eq}} = \frac{4}{6} = \frac{2}{3}$

33. (d) From the graph we can see that 4 mole/litre of Z is formed therefore 4 × 2 moles of solid will be required.

34. to 36.

$2A_2(g) \rightleftharpoons A_4(g)$
$3p - x - y \quad x/2$
$A_2 + 2C \rightleftharpoons A_2C_2$
$3p - y - x \; p - 2y \quad y - z$
$A_2C_2 \rightleftharpoons 2AC$
$y - z \quad 2z$

$\frac{P_{A_4}}{P_{A_2}^2} = K_{P_1}$

$\Rightarrow (P_{A_2})^2 = \frac{P_{A_4}}{K_{P_1}} = \frac{\frac{1}{2}}{2/81} = \frac{81}{4}$

$\Rightarrow P_{A_2} = \frac{9}{2}$ atm.

$\Rightarrow 3p - x - y = \frac{9}{2}$ … (i)

$\frac{x}{2} = \frac{1}{2}$ … (ii)

$\Rightarrow x = 1$ atm

Also given $2Z = \frac{1}{2}$ ... (iii)

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

$P_{total} = 3p - x - y + x/2 + p - 2y + y - z + 2z$
$= 4p - x/2 - 2y + z$

$= 4 \times p - \frac{1}{2} - 2 \times \frac{1}{2} + \frac{1}{4} = \frac{27}{4}$ atm.

$\Rightarrow$ p = 2 atm.

34. (c) $3p - x - y = \frac{9}{2}$

$6 - \frac{1}{2} - y = \frac{9}{2}$

y = 1 atm.

35. (d) $\frac{n_{A_2}}{n_{AC}} = \frac{P_{A_2}}{P_{AC}} = \frac{3P - x - y}{2z} = \frac{\frac{9}{2}}{1/2} = 9$

36. (b) $K_p = \frac{n_{A_2C_2}}{P_{AC}^2} = \frac{3/4}{\left(\frac{1}{2}\right)^2} = 3$

37. (a – q, s), (b – p, r), (c – q, s), (d – p,r)

38. (a – p, q, r), (b – p, q, s), (c – q, s), (d – p, q, r)

39. (a – q, s), (b – p), (c – q, s), (d – r)

40. (a – q), (b – r, s), (c – q, s), (d – p, q, r)

41. (a – r, s), (b – r), (c – q), (d – p, s)

(a) As $\Delta n > 0$, therefore, if P↑, reaction will go in the backward direction.

(b) As $\Delta < 0$, therefore, if V ↑ p ↓, reaction will go in the direction in which more number of gaseous moles are formed i.e., backward direction.

(c) As $\Delta n = 0$, hence no effect.

(d) If concentration of product is decreased reaction will go in the forward direction.

42.

	$H_2(g)$ +	$Br_2(g)$ $\rightleftharpoons$	2HBr(g)
Initial pressures	0	0	10.0 bar
	p/2	p/2	(10.0-p)

$K_p = \frac{p^2HBr}{P_{H_2} \times P_{Br_2}}$

$1.6 \times 10^5 = \frac{(10-p)^2}{(p/2)(p/2)}$

$200\ p = 10 - p$

$P = \frac{10}{201}$ bar

$P_{H_2} = p/2 = \frac{1}{2}\left(\frac{10}{201}\right)$ bar $= 2.5 \times 10^{-2}$ bar

$p_{Br_2} = p/2 = 2.5 \times 10^{-2}$ bar

$p_{HBr} = 10 - p \approx 10$ bar.

43.

	CO(g) +	$2H_2(g)$ $\rightleftharpoons$	$CH_3OH(g)$
Initial mole	0.2	a	0
Mole at equilibrium	(0.2 – 0.1)	(a – 0.2)	0.1

Now total at equilibrium are = 0.1 + a – 0.2 + 0.1 = a

Also Mole (n) $= \frac{PV}{RT} = \frac{4.92 \times 5}{0.0821 \times 600} = 0.499$

a = 0.499

$\therefore$ $[CH_3OH] = \frac{0.1}{5}$; $[CO] = \frac{0.2 - 0.1}{5} = \frac{0.1}{5}$;

$[H_2] = \frac{0.499 - 0.20}{5} = \frac{0.299}{5}$

$\therefore$ $K_c = \frac{[CO][OH]}{[CO]OH_2]^2} = \frac{0.1/5}{0.1/5 \times (0.299/5)^2}$

$= 279.64$ litre^2 mol^{-2}

$K_p = K_c (RT)\Delta^n$

$K_p = 279.64 \times (0.0821 \times 600)^{-2} = 0.115$ atm^{-2}

$K_c = 279.64$ litre^2 mol^{-2}, $k_p = 0.115$ atm^{-2}

44.

$2NH_3$ $\rightleftharpoons$	N_2 +	$3H_2$
a	0	0
a – 2x	x	3x

$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{15}{300} = \frac{P_2}{400} \Rightarrow P_2 = 20$ atm.

Now $\frac{a + 2x}{a} = \frac{30}{20}$

$2a + 4x = 3a$

$\Rightarrow$ $x = \frac{1}{4}a$.

$\therefore$ % of NH_3 decomposed $= \frac{2x}{a} \times 100 = 50\%$

50

45. $\because$ LiCl. $3NH_3$ (s) $\rightleftharpoons$ LiCl. NH_3 (s) + $2NH_3$(g) [Kp = 9 atm^2]

$\therefore$ LiCl. NH_3 (s) + $2NH_3$ (g) $\rightleftharpoons$ LiCl. $3NH_3$ (s)

Initial mole	0.1	a	0
Final mole at eq.	0	(a – 0.2)	0.1

Let initial mole of NH3 should be a to bring in completion of reaction.

At eq. $K_{P_1} = \frac{1}{(P'_{NH_3})^2}$

Or $\frac{1}{9} = \frac{1}{(P'_{NH_3})^2}$

$\therefore \quad P'_{NH_3} = 3$ atm

$\because \quad PV = nRT$

$3 \times 5 = n \times 0.0821 \times 313$

$n = 0.5837$

i.e., $(a - 0.2) = 0.5837$

$\therefore$ Initial mole of $NH_3 = a = 0.5837 + 0.2 = 0.7837$ mole

46. $3A_2(g) \rightleftharpoons A_6(g) \qquad K_p = 1.6 \text{ atm}^{-2}$

$K_p = 1.6 = \frac{P'_{A_2}}{(P_{A_2})^3}$

$P_{A_2} = \sqrt[3]{\frac{0.2}{1.6}} = 0.5$ atm

Also pressure of A_2 used for the formation of $A_6 = 0.6$ atm

For	$A_2(g)$ +	$C(g) \rightleftharpoons$	$A_2C(g)$
t = 0	2P	P	0
at eq.	$2P - P^1 - 0.6$	$P - P^1$	P^1

Also for	$3A_2(g) \rightleftharpoons$	$A_6(g)$
t = 0	2P	0
At eq.	$2P - P^1 - 0.6$	0.2

$2P - P^1 - 0.6 = 0.5$

(since P_{A_2} at eq. is 0.5 for similataneous equilibria)

Also pressure of $A_2 + C + A_2C + A_6$

$= (2P - P^1 - 0.6) + (P - P^1) + P^1 + 0.2 = 1.4$

$0.5 + P + 0.2 = 1.4$

$P = 0.7$ atm

$\therefore \quad 2P - P^1 - 0.6 = 0.5$

$P^1 = 2 \times 0.7 - 0.6 - 0.5$

$P^1 = 0.3$ atm

$\therefore \quad P_{A_2} = 0.5$ atm, $P_C = 0.7 - 0.3 = 0.4$ atm $P_{A_2C} =$ 0.3 3 atm

Also K_p for $A_2(g) + C(g) \rightleftharpoons A_2C(g)$

$K_p = \frac{P_{A_2C}}{P_{A_2} \times P_C} = \frac{0.3}{0.5 \times 0.4} = 1.5 \text{ atm}^{-1}$

SUBJECTIVE ANSWER TYPE QUESTIONS

34. In a reaction at equilibrium, 'X' mole of the reactant A decompose to give 1 mole each of C and D. It has been found that the fraction of A decomposed at equilibrium is independent of initial concentration of A. Calculate X.

Sol.

XA	$\rightleftharpoons$	D	+	C
$a(1-\alpha)$		$\frac{a\alpha}{x}$		$\frac{a\alpha}{x}$

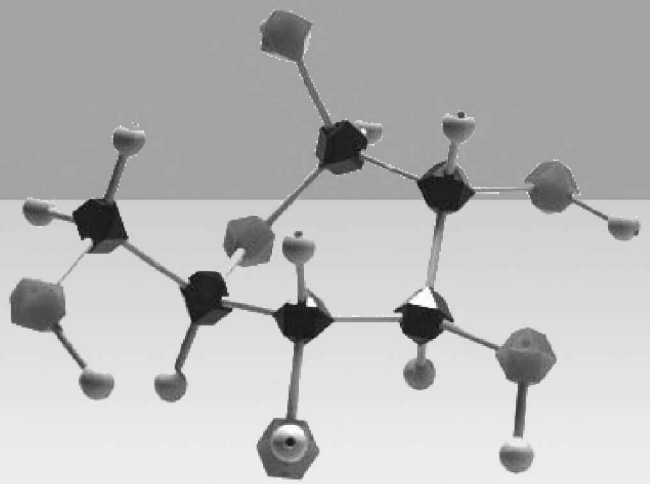
$\therefore \quad K_c = \frac{a^2\alpha^2}{V^2.x^2\left[\frac{a(1-\alpha)}{V}\right]^x} = \frac{\alpha^2.a^{2-x}}{x^2(1-\alpha)^x.V^{2-x}}$

Since α is independent of a

$\therefore \quad 2 - x = 0$

$\therefore \quad x = 2$

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CHAPTER 7

Ionic Equilibrium

ELECTROLYTE

A substance that can produce ions in the solution is known as electrolyte.

Let us consider the ionization of an electrolyte 'AB' in an aqueous solution (i.e., water as solvent)

$$\underbrace{AB\,(aq)}_{\text{Dissolved but unionized part of electrolyte}} \rightleftharpoons \underbrace{A^+(aq) + B^-(aq)}_{\text{Ions produced from the ionization of electrolyte}} \ldots\ldots\ldots\ldots \quad \underbrace{K_{in}}_{\text{Equilibrium constant known as ionization constant}}$$

[**Note** that we have considered the simplest electrolyte 'AB' it might be 'A_xB_y' type when x and y are any numbers]

Hence, $K_{in} = \dfrac{[A^+]_e[B^-]_e}{[AB]_e}$ (Suffix 'e' represents equilibrium concentration)

Now consider, C = number of moles of AB dissolved and remained before ionization per litre of solution.

X = number of moles of AB ionized till the attainment of equilibrium per litre of solution

Hence,

	$AB(aq)$	$\rightleftharpoons$	$A^+(aq)$	+	$B^-(aq)$
Initially,	C				
At equilibrium,	(C–x)		x		x

$[AB]_{eq.} = (C–x)$, $[A^+]_{eq.} = x$ and $[B^-]_{eq} = x$

We define **Degree of ionization** (some times called degree of dissociation) as the fraction of the electrolyte ionized in solution and it is represented as 'α'.

$$\alpha = \frac{n_{ionized}}{n_{taken}} = \frac{x}{C} \qquad \text{or,} \qquad x = C\alpha$$

Hence,

$$[AB]_{eq.} = C - x = C - C\alpha = C(1-\alpha)$$

$$[A^+]_{eq} = x = C\alpha = [B^-]_{eq.}$$

$$K_{in} = \frac{C\alpha C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

The value of K_{in} depends upon

(a) Nature of electrolyte
(b) Nature of solvent
(c) Temperature

Here, we always consider aqueous solution. If the temperature is fixed the K_{in} value will depend on the nature of electrolyte only.

Note that all the reactions are reversible reactions and attain equilibrium. A reversible reaction with a very large equilibrium constant can be considered to be as an irreversible reaction.

Strong Electrolytes

If the K_{in} value is too large (say 10^5) we can assume almost an irreversible or complete ionization of electrolyte at almost any practical range of concentration.

$$AB\ (aq) \xrightarrow{\sim 100\%} A^+\ (aq) + B^-\ (aq)$$

Electrolytes with such a large value of ionization constant are known as strong electrolytes. In such cases, $\alpha = 1$ at almost any concentration. So we will assume that strong electrolytes are present practically wholly as ions. A practical verification of strong elecrtolyte can be made from the high conductivities of their aqueous solution.

Weak Electrolyte

If the K_{in} value is small (say 10^{-6}), the ionization is found to be highly reversible and such electrolytes are known as weak electrolyte. At normal concentration, they are only partly dissociated into ions and the concept of equilibrium finds great use. A practical verification of weak elecrolytes can be made from the low conductivities of their aqueous solution.



Worked-out Examples

1. Are the values of 'α' for weak electrolyte always small?

Solution No, 'α' value for weak elecrolyte can be significantly large at a very low concentration of electrolytic solution (infinitely dilute solution).

Let us consider,

$$AB \rightleftharpoons A^+ + B^-$$

Initially,	C			$\alpha = \frac{x}{C}$
At Equilibrium,	C–x	x	x	x = Cα

$$K_{in} = \frac{[A]^+[B]^-}{[AB]} = \frac{x^2}{C-x}\ \frac{(C\alpha)^2}{C-C\alpha} = \frac{C\alpha^2}{1-\alpha}$$

$K_{in} \approx C\downarrow\alpha^2\uparrow$ $(\alpha << 1)$ dil $\uparrow$ conc$\downarrow$ $\alpha\uparrow$

At very high dilution even a weak electrolyte can be almost 100% ionized. So, the degree of dissociation is not a measure of strength of electrolyte.

It is the dissociation constant which determines the strength of electrolyte.

Note: Some unconventional notations have been used. '↑' represent increase of parameter and '↓' to represent the decrease of that parameter

Some abbreviations will be used as for,

Example

WA ⇒ Weak acid

SA ⇒ Strong acid

WB ⇒ Weak base

SB ⇒ Strong base

WE ⇒ Weak electrolyte

SE ⇒ Strong electrolyte

2. How can the conductivities of solution of weak electrolytes be always low?

Solution The conductivities of electrolytes solution depends upon the number of ions per unit volume of solution. The number of ions per unit volume of solution will always be small for weak electrolytes at any concentration.

3. The degree of dissociation of water at 25°C is 1.9×10^{-7}% and density is 1.0 g cm^{-3}. The ionic constant for water is: **[IIT-JEE-1995]**

(a) 1.0×10^{-14} (b) 2.0×10^{-16} (c) 1.0×10^{-16} (d) 10×10^{-8}

Solution (b) For water $[H^+] = [OH^-]$

$H_2O \rightleftharpoons H^+ + OH^-$

$(1-\alpha)\,c \quad \alpha\,c \quad \alpha\,c$

$\alpha = 1.9 \times 10^{-7}$; Density of water $= \frac{1.0g}{cm^3}$

$\therefore\ c = \frac{1}{18} \times 1000 = 55.56$ moles/L

$\therefore\ [H^+] = 55.56 \times 1.9 \times 10^{-9} = 1.055 \times 10^{-7}$

$\therefore\ K_w = [H^+]\,[OH^-] = (1.055 \times 10^{-7})^2$

4. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The percentage dissociation of Na_2SO_4 is: **[IIT-JEE-2004]**

(a) 25% (b) 50% (c) 75% (d) 85%

Solution (c) $\underset{(0.004-x)}{Na_2SO_4} \rightleftharpoons 2\underset{2x}{Na^+} + \underset{x}{SO_4^{2-}}$

Since both solutions are isotonic, therefore, $0.004 + 2x = 0.01$;- $= 3 \times 10^{-3}$

% Dissociation $= (3 \times 10^{-3}/0.004) \times 100 = 75$

Auto Dissociation of Water

Water is considered to be as a solvent in this chapter.

At equilibrium,

$$\underset{\text{weak electrolyte}}{H_2O} \rightleftharpoons H^+ + OH^- \qquad \underset{\text{deg ree of dissociation}}{\alpha} = \frac{x}{c}\frac{(\text{n reactd})}{(\text{n taken})}$$

At equilibrium, $(C-x)$ x x $x = C\alpha$

$$\underset{\substack{\text{(ionization cons tan t}\\ \text{of water)}}}{K_{in}} = \frac{[H^+]\,[OH^-]}{[H_2O]} = \frac{x^2}{C-x} = \frac{C^2\alpha^2}{C-C\alpha} = \frac{C\alpha^2}{1-\alpha} = (C\alpha^2) \quad [\alpha << 1 \text{ at } 25^oC]$$

Since water is a weak electrolyte and is poorly ionized (degree of dissociation is 1.8×10^{-9} at 25°C), concentration of water does not change, thus the concentration of undissociated water is nearly constant and is 55.55 mole litre^{-1}

Note If it is acidic or basic solution in the aqueous medium, K_w remains the same. (Concentration of H^+ and OH^- ions will have to adjust).

$$\frac{1000\,g/dm^{-3}}{18\,g/mol^{-1}} = 55.55\ M$$

Thus, we can write $K_{in} = \dfrac{[H^+][OH^-]}{\text{cons tan t}}$

$\therefore \quad [H^+][OH^-] = K_{in} \times \text{constant}$

or $K_w = K_{in} \times \text{constant} = [H^+]\,[OH^-]$

$= C\alpha^2 = (55.55 \times 1.8 \times 10^{-9})^2$

$K_w = 10^{-14}$ at 25°C

[where K_w = ionic product of water]

Effect of Temperature on K_w

$$H_2O \rightleftharpoons H^+ + OH^-$$

('endothermic' reaction since bonds are broken)

(According to Le-Chatelier's principle) On increasing temperature, the product formation will be favoured. Thus, K_w increases with increase in temperature. On increasing temperature concentration of H^+ and OH^- ions will increases.

The variation of K_w can be expressed as follows:

$$\log \frac{K_{w1}}{K_{w2}} = \frac{\Delta H}{2.3003 \times R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$



Worked-out Examples

5. Calculate the pH of pure water at 35°C. Given, enthalpy of dissociation of water is 350.88 KJ.

Solution $\log \frac{K_{w35}}{K_{w25}} = \frac{350.88 \times 10^3}{2.3003 \times R}\left[\frac{1}{298} - \frac{1}{308}\right]$

$= K_{w(35°C)} = 10^{-12}$

$[H^+] = 10^{-6}$

$\therefore$ PH = 6

6. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be ..... **[IIT-JEE-1984]**

Solution amphoteric;

pH and pOH

The negative logarithm (to the base 10) of the concentration in moles per litre of hydroxynium ions or hydrogen ions in a solution is called the pH of that solution.

pH scale of hydrogen ion concentration which is used to represent very low concentration. of H^+ (very dilute solution).

i.e., $pH = -\log_{10}[H_3O^+] = -\log_{10}[H^+]$

Actually,

$pH = -\log a_{H}^{+}$ (Where a_{H}^{+} is the activity of H^+ ions).

Activity of H^+ ions is the concentration of free H^+ ions in a solution. By free, we mean those that are at a large distance from the other ion so as not to experience its pull. We can infer from this that in dilute solutions, the activity of an ion is same as its concentration, since more number of solvent molecules would separate the two ions. For concentrated solutions, the activity would be much less than the concentration itself.

Therefore, the earlier given expression of pH can be modified for dilute solutions as, $pH = -\log [H^+]$. This assumption can only be made when the solution is very much dilute, i.e., $[H^+] \leq 1M$. For higher concentration of H^+ ions, one needs to calculate the activity experimentally and then calculate the pH.

Note:

$x\uparrow \quad \log x\uparrow \quad -\log x\downarrow \qquad [H^+]\uparrow \quad pH\downarrow$

- If value of x increases then $\log_{10} x$ also increases $\Rightarrow -\log_{10} x$ decreases $\Rightarrow$ px decreases
- $[H^+]\uparrow$ pH $\downarrow$

The greater the concentration of hydrogen ions, the lesser is the pH.

$pOH = -\log_{10}[OH^-]$

$K_w = 10^{-14} = [H^+]\,[OH^-]$ If pK_w = constant then pH + pOH = constant thus when pH will increase pOH will decrease

$\log_{10} K_w = \log_{10} ([H^+]\,[OH^-])$

$\log_{10} K_w = \log_{10}[H^+] + \log_{10}[OH^-]$

$$-\log_{10} K_w = -\log_{10}[H^+] - \log_{10}[OH^-]$$

$$pK_w = pH + pOH$$

At 25°C $pH + pOH = 14$

For neutral solution $[H^+] = [OH^-]$

Hence, $K_w = [H^+]^2 = [OH^-]^2$ for neutral solution.

Neutral solution: $pH = 7$ $pOH = 7$

Acidic solution: $[H^+] > [OH^-]$, $pOH > pH$, $pOH + pH = 14$ (At 25°C), $pH < 7$

Alkaline solution: $[OH^-] > [H^+]$, $pH > 7$

Pure water (when nothing is dissolved in it) is neutral at any temperature.

Note: $K_w \uparrow$ $= [H^+]^2 \uparrow$ $= [OH^-]^2 \uparrow$ $[H^+] = [OH^-]$



Worked-out Examples

7. The K_w value at 35°C is 10^{-12} if the pH of a solution at 35°C is 6.2 classify it as acidic or basic or neutral solution.

$K_w = 10^{-12}$ At 35°C

$pH = 6.2$ Acidic or Basic?

Solution $K_w = [H^+]^2$

$= 10^{-12}$

$H^+ = 10^{-6}$

$pH = 6$ Neutrality scale $\begin{cases} pH > 6 & \text{Basic} \\ pH < 6 & \text{Acidic} \end{cases}$

Thus, pH = 6.2 represents basic solution at this temperature and K_w value at this temperature is given.

The scale of neutrality changes with the change in temperature

Here, we have found out the neutrality scale because temperature is given we take 25°C as the standard temperature and pH = 7 to taken as neutrality scale.

See the following numerical to understand the theory based application.

Note the following log values, which will be frequently used in the question.

$\log_{10}2 = 0.3$ $\log_{10}3 = 0.48$ $\log_{10}5 = 0.69$

$\log_{10}7 = 0.84$ $\log_{10}11 = 1.04$

See the following numerical examples to understand how we can calculate pH of different types of solutions:

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

pH of Strong Acids and Bases

Case I: pH of Strong acid

8. Calculate pH of

(a) 0.01 M HCl

(b) 0.0005 M H2SO4

Solution (a) Since K_w value is not given, it is a strong electrolyte.

$$HCl \longrightarrow \underset{\underset{0.01M}{\downarrow}}{H^+} + Cl^-$$

$[H^+] = 10^{-2}$ M $\Rightarrow$ pH = **2**

(b) $H_2SO_4 \longrightarrow 2H^+$

0.0005 M $\quad$ 0.0005×2

$[H^+] = 0.001$ M

$[H^+] = 10^{-3}$ M, $\quad$ pH = **3**

Case II: pH of Strong Base

9. Calculate pH of

(a) 0.1 NaOH $\quad$ (b) 0.001 $Ba(OH)_2$ $\quad$ (c) 0.02 M Sr $(OH)_2$

Solution (a) $\underset{0.1\ M}{NaOH} \longrightarrow Na^+ + \underset{0.1M}{OH^-}$

$[OH^-] = 0.1\ M = 10^{-1}$ M

pOH = 1

pH = 14 – 1= **13**

(b) $Ba(OH)_2 \longrightarrow Ba^{2+} + \underset{0.002\ M}{2(OH)^-}$

pOH = 3 – (log 2) $10^{-3} \times 2$

pOH = 3 – 0.3 = 2.7, $\quad$ pH = (14 – 2.7) = **11.3**

(c) $Sr(OH)_2 \longrightarrow 2(OH)^-$

$0.02 \times 2 = 0.04\ M = 4 \times 10^{-2}$

pOH = $-\log (4 \times 10^{-2}) = -\log (2^2 \times 10^{-2}$

$= -\log_{10} 2^2 - \log_{10} 10^{-2} = -2 \log_{10} 2 + 2\log_{10}10 = 2 - 2\log_{10}2$

$= 2 - 2 \times (0.3) \quad = 2 - 0.6 = 1.4 \quad$ pH = 14 – 1.4 = 12.6

Case III: pH of mixture of strong acids

10. Calculate pH of following mixtures.

(a) 200 ml 0.01 M HCl + 400 ml 0.01 M H_2SO_4

(b) 400 ml 0.01 M HCl + 600 ml 0.01 M H_2SO_4

Solution (a) 200 ml 0.01 M HCl + 400 ml 0.01 M H_2SO_4

$\underbrace{\quad\quad}$ $\quad$ $\underbrace{\quad\quad}$

~ 2 mm HCl + 4 mm of H_2SO_4

~ 2 mm H^+ $\quad$ or 8 mm of H^+

Total H^+ ions = 10 mm
Total volume = 600 ml

Molarity or Conc. of $H^+ = \frac{10}{600} = \frac{1}{60}$ M $= \frac{1}{6} \times 10^{-1}$

pH = 1 + log 6
= 1 + log (3 × 2)
= 1 + log 3 + log2
= 1 + 0.48 + 0.3
pH = **1.78**

(b) 400 ml 0.01 M HCl + 600 ml 0.01 M H_2SO_4

~ 4 mm of H^+ ~ 6 mm

~ 12 mm of H^+

Total H^+ = 16 mm
Total V = 1000 ml
Total mm of $H^+ = 16 \times 10^{-3}$
Total mm of $H^+ = 2^4 \times 10^{-3}$
pH = 3 – 4 log 2
= 3 – 4 (0.3)
= 3 – 1.2
pH = 1.8

Case IV: pH of mixture of strong bases

11. Calculate the pH of following mixture.
(a) 100 ml 0.01 M NaOH + 200 ml 0.01M $Ba(OH)_2$

Solution (a) 100 ml 0.01 M NaOH + 200 ml 0.01M $Ba(OH)_2$
$OH^- \equiv 1$ mm $OH^- = 2 \times 2 = 4$ mm
Total $OH^- = 1 + 4 = 5$ mm
Total volume = 100 + 200 = 300 ml

$[OH^-] = \frac{5\,\text{mm}}{300\,\text{ml}} = \frac{1}{60}$ M

pOH = 1 + log 6 = 1.78, pH = **12.22**

Case V: pH of mixture of strong Acid and Strong Base:

Note: If strong acid and strong base react with each other in equivalent amount then the resulting solution will be neutral.

12. Calculate the pH of following mixture.
(a) 200 ml 0.1 M HCl + 100 ml 0.2 M NaOH
(b) 400 ml 0.1 M HCl + 100 ml 0.2 M NaOH
(c) 400 ml 0.1 M HCl + 400 ml 0.2 M NaOH

Solution (a) 200 ml 0.1 M HCl + 100 ml 0.2 M NaOH
≡ 20 mm of HCl ≡ 20 mm NaOH
≡ 20 mm of H^+ ions ≡ 20 mm of OH^- ions

Solution is **neutral** because $[H^+] = [OH^-]$

Thus the pH of the mixture is **7**.

(b) 400 ml 0.1 M HCl + 100 ml 0.2 M NaOH

$H^+ \equiv 40$ mm $OH^- = 20$ mm

number of mm of H^+ in excess = 20 mm

Total volume = 500 ml

Concentration of H^+ in resulting solution $= \frac{20}{500} = \frac{1}{25}\ M = \frac{1}{5^2} M$

$$pH = -\log_{10}\left(\frac{1}{5^2}\right)$$

$$= +2 \log_{10} 5$$

$$= 2 \times 0.69 = \mathbf{1.38}$$

(c) 400 ml 0.1 M HCl + 400 ml 0.2 M NaOH

$\equiv 40$ mm $\equiv 80$ mm

Excess OH^- ions = 40 mm

Total volume = 800 ml

$$\text{Molarity} = \frac{40}{800} = 0.5 \times 10^{-1} = \frac{1}{2} \times 10^{-1} = 2^{-1} \times 10^{-1}$$

$$pOH = 1 - \log_{10}(2^{-1})$$

$$= 1 + \log_{10} 2 = 1 + 0.3 = 1.3$$

$$pH = 14 - 1.3 = \mathbf{12.7}$$

Case VI: pH of Weak Monobasic Acid

$HA \rightleftharpoons H^+ + A^-$ ..... $K_a \rightarrow$ dissociation constant

Initially,	C	–	–	
At equilibrium,	C–x	x	x	
	C(1–α)	Cα	Cα	$(\alpha = \frac{x}{C},\ x = C\alpha)$

$$K_{a\ \text{constant}} = \frac{x^2}{C - x} = \frac{(C\alpha)^2}{C - C\alpha} = \frac{C \downarrow \alpha^2 \uparrow}{1 - \alpha \uparrow}$$

The α value of a weak acid can have different magnitude at different temperature. α value of a strong acid is 100% very high so does not alter.

If $\alpha << 1$. Then $1 - \alpha \approx 1$

$$K_a = C\uparrow\alpha^2\downarrow$$

As the concentration increases, α decreases to keep constant the value of K_a at given temperature

Note: The greater the K_a value the more is the acidic strength.

$$pK_a = -\log_{10} K_a$$

If $K_a \uparrow$ then $-\log_{10} K_a \downarrow$ and $pK_a \downarrow$

- The lesser the pK_A value the more is the strength of the acid.
- K_A is constant for a particular acid at constant temperature.

13. Which of the following solutions will have pH close to 1.0? **[IIT-JEE-1992]**

(a) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH

(b) 55 ml of (M/10) HCl+ 45 ml of (M/10) NaOH

(c) 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH

(d) 75 ml of (M/5) HCl+ 25 ml of (M/5) NaOH

Solution (d) 100 ml of HCl will completely neutralize 100 ml of NaOH. So (a) is not possible, (c) will become a basic solution, (d) is the correct option.

25 ml HCl neutralizes 25 ml NaOH

Remaining solution contains 50 ml of $\frac{M}{5}$ HCl

Which becomes 100 ml of $\frac{M}{10}$ HCl (as the total solution becomes 100 ml)

$$\therefore \quad pH = -\log[H^+] = -\log\left[\frac{1}{10}\right] = 1$$

14. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution? **[IIT-JEE-2005]**

(a) 8×10^{-2} M (b) 8×10^{-11} M

(c) 1.6×10^{-11} M (d) 8×10^{-5} M

Solution (b) $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+Cl^-$

0.1	0.08	0
0.02	0	0.08

As it is a basic buffer solution.

$$pOH = pK_b + \log\frac{0.08}{0.02} = -\log 5 \times 10^{-4} + \log 4 = 3.30 + 0.602 = 3.902$$

$pH = 14 - 3.902 = 10.09$; $[H^+] = 7.99 \times 10^{-11} \approx 8 \times 10^{-11}$ M

15. Which of the following statements(s) is (are) correct? **[IIT-JEE-1998]**

(a) The pH of 1.0×10^{-8} M solution of HCl is 8.

(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}.

(c) Autoprotolysis constant of water increases with temperature.

(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = (1/2)pK_a.

Solution (b, c) pH of 1×10^{-8} M is below to 7.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

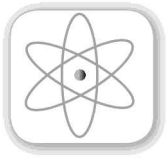
K (Auto protolysis constant of water i.e., ionic product of water) increases with temperature.

For half neutralisation of a weak acid by a weak base, $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

[Salt] = [Acid],

$pH = pK_a$

OSTWALD'S DILUTION LAW



When dilution increases, concentration decreases and α increase to keep the value of K_a constant with dilution the degree of dissociation of weak electrolyte increases.

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} \Rightarrow [H^+] = \sqrt{K_a C} \quad \text{..... } (\alpha << 1)$$

The above equation is not valid for very dilute solution of weak electrolyte (as 'α' will be significant

Solving Procedure:

- K_a and C are given,

  Calculate approximate value of α from $\alpha = \sqrt{\frac{Ka}{C}}$

  (i) Suppose α comes ≥ 0.1 (greater than 0.1 or equal to)

  $$K_a = \frac{C\alpha^2}{1-\alpha} \quad 0 < \alpha < 1$$

  solve α

  $H^+ = C\alpha$

  (ii) Suppose α comes < 0.1

  $[H^+] = \sqrt{K_a C}$



Worked-out Examples

16. Calculate pH of

(a) 1 M CH_3COOH ($K_a = 10^{-6}$)

(b) 10^{-5} M CH_3COOH

Solution (a) $H^+ \rightarrow 1$ M approx $\alpha = 10^{-3}$ $\alpha << 1$

$$H^+ = \sqrt{K_a C} = \sqrt{10^{-6}} = 10^{-3} \quad pH = 3$$

(b) H+ = 10–5 M $\alpha = \sqrt{\frac{10^{-6}}{10^{-5}}} = \sqrt{10^{-1}} = 0.1$

$$K_a = \frac{10^{-5}\alpha^2}{1-\alpha}$$

$$10^{-6} = \frac{10^{-5}\alpha^2}{1-\alpha}$$

Quadratic equation: $10\alpha^2 + \alpha - 1 = 0$ ($\alpha \simeq$ Solving this equation we get, 0.27)

$[H^+] = C\alpha = 10^{-5} \times 0.27 = 3^3 \times 10^{-7}$

$= 7 - 3\log_{10}3 = 7 - 3\,(0.48) = 5.56$

17. The pH of a monobasic weak acid ($K_a = 10^{-5}$) is 5. Calculate degree of dissociation.

Solution pH = 5

$[H^+] = 10^{-5} = C\alpha$ since approximate $\alpha = 1$

$C\alpha = 10^{-5}$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{(C\alpha)(\alpha)}{(1-\alpha)} = \frac{10^{-5}\alpha}{1-\alpha} = 10^{-5}$$

$\Rightarrow \alpha = 1-\alpha$ $\quad 2\alpha = 1$

$\alpha = 0.5$ $\quad$ 50% dissociation

18. Calculate pH of 0.1M HCOOH ($Ka = 10^{-5}$). To what volume should 1 litre solution be diluted to double pH.

Solution (a) $C = 10^{-1}$ $\quad$ approximate $\alpha = \frac{10^{-5}}{10^{-1}} = 10^{-4} << 1$.

$$K = \frac{C\alpha^2}{1-\alpha} \qquad H^+ = \sqrt{K_a C} = \sqrt{10^{-5} \times 10^{-1}} \quad pH = 3$$

(b) $V_1 = 1L$ $\quad V_2 = ?$

$pH = 3$ $\quad pH = 6$

$K_a = C\downarrow\alpha^2\uparrow = (C\alpha)\,\alpha = [H^+]\downarrow\,\alpha\uparrow$

When $C\downarrow \Rightarrow \alpha\uparrow \rightarrow H^+\downarrow \Rightarrow pH\uparrow$

Thus on dilution pH increases. On dilution C as well as α both will change.

$[H^+] = 10^{-6}\,M = C_2\alpha_2$ $\quad C_2\alpha_2 = 10^{-6}$

$$K_a = \frac{C_2\alpha_2^2}{1-\alpha_2} \qquad C_2 = \frac{10^{-6} \times 11}{10}\,M$$

$$10^{-5} = \frac{10^{-6}\alpha_2}{1-\alpha_2} \qquad C_2 = 1.1 \times 10^{-6}\,M$$

$$\alpha_2 = \frac{10}{11}$$ $\Rightarrow$ At high dilution α is appreciable

C_2 = concentration before ionization

$C_1V_1 = C_2V_2 \rightarrow$ (concentration of undissociated acid assuming no ionization)

$(0.1\ (1L) = (1.1 \times 10^{-6})\ V_2$

$$V_2 = \frac{10^{+5}}{1.1}\ \text{litre}$$

Note: Better method to increase pH would be to add alkali instead of adding 10^5 L water.

Case VII: pH of Weak Monoacidic Base

$$BOH \rightleftharpoons B^+ + OH^\ominus$$

Initially,	C	–	–	$K_a = [H^+]$
At equilibrium,	C–x	x	x	$K_b = [OH^-]$
	C(1–α)	Cα	Cα	

19. Calculate the pH of

(a) 0.1 M NH_3 $\quad K_b(NH_3) = 10^{-5}$

(b) 10^{-5} M NH_3

$NH_3 + H_2O \longrightarrow NH_4OH$

(Ammonia and Ammonium hydroxide are assumed to be same.)

Solution (a) 0.1 M NH_3 $\quad \alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{10^{-5}}{10^{-1}}} = 10^{-2} << 1$

$[OH^-] = 10^{-1}$

$[OH^-] = \sqrt{K_b C} = \sqrt{10^{-5} \times 10^{-1}}$ $\quad$ pOH = 3 $\quad$ **pH = 11**

(b) $[OH^-] = 10^{-5}$ $\quad \alpha = \sqrt{\frac{10^{-5}}{10^{-5}}} = 1 > 0.1$

$$K_b = \left(\frac{C\alpha^2}{1-\alpha}\right)$$

$$10^{-5} = \frac{10^{-5}\alpha^2}{1-\alpha} \Rightarrow 1 - \alpha = \alpha^2 \quad \Rightarrow \alpha^2 + \alpha - 1 = 0$$

$-1 + \alpha + \alpha^2 = 0 \Rightarrow$ Solving we get $\alpha \approx 0.6$

$[OH^-] = C\alpha = 10^{-5} \times 0.6 = 6 \times 10^{-6}$ $\quad$ pOH = 6 – log 6

= 6 – 0.78 = 5.22

pH =14 – 5.22 = **8.78**

Case VIII: pH of very dilute solution of strong acid and strong base (Special case)

When we add 10^{-7} M HCl in water, the $[H^+]$ from HCl would be10^{-7} M. But pH is the negative logarithm of the total H^+ ion concentration of a solution and not that part which comes from only HCl. Therefore, we need to add the concentration of H^+ ions coming from water also. This can be done in two ways.

The statement given above that **"the addition of an ion to an equilibrium, having the same ion makes the equilibrium reaction move in a direction to consume that ion"** is called the common ion effect. This implies that water would dissociate less in the presence of HCl. Let the amount to which water dissociates be x′ in the presence of 10^{-7} M HCl.

$$\therefore \quad H_2O \quad \rightleftharpoons \quad H^+ + OH^-$$

At equilibrium: $\quad x' + 10^{-7} \quad x'$

$$[H^+]\,[OH^-] = 10^{-14}$$

$$\Rightarrow (x' + 10^{-7})\,(x') = 10^{-14}$$

Calculating for x′, we get $x' = 0.618 \times 10^{-7}$ M.

One can clearly see the common ion effect in action. Water which was dissociating to give 10^{-7}M H^+ ions, has now experienced the common ion effect and has finally yielded 0.618×10^{-7} M H^+ ions.

Therefore, $[H^+]_T = 10^{-7} + 0.618 \times 10^{-7}$

$= 1.618 \times 10^{-7}$ M

$\therefore \quad$ pH $= -\log(1.618 \times 10^{-7}) = 6.7910$

Now, lets answer the question as to why we take the H^+ ions of water into account for calculating the pH of 10^{-7} M HCl while we never considered it for calculating the pH of 10^{-6}M, 10^{-5}M, 10^{-4}M, 10^{-3}M, 10^{-2}M and 10^{-1}M HCl. It can be seen that the H^+ ions from water have decreased due to the common ion effect. Greater the concentration of the common ion added, greater will be the effect. Therefore, for concentrations higher than 10^{-6}M (and inclusive of 10^{-6}M), the H^+ from water will be even less than 0.618×10^{-7} M and would be so small in comparison to the $[H^+]$ from HCl, that we can ignore the

contribution from it. So, finally we conclude that H^+ ions of water needs to be considered only if an acid is present such that $[H^+]_{acid} < 10^{-6}M$.

Case IX: pH of Mixture of Weak Acids:

$$HA \rightleftharpoons H^+ + A^\ominus$$

Initial	C_1	0	0
equilibrium,	$C_1(1-\alpha_1)$	$(C_1\alpha_1 + C_2\alpha_2)$	$C_1\alpha_1$

$$HA \rightleftharpoons H^+ + A^- \Rightarrow$$

Initial	C_1	0	0
equilibrium,	$C_1(1-\alpha_1)$	$(C_1\alpha_1 + C_2\alpha_2)$	$C_1\alpha_1$

$$HB \rightleftharpoons H^+ + B^\ominus$$

Initial	C_2	–	–
equilibrium,	$C_2(1-\alpha_2)$	$(C_1\alpha_1 + C_2\alpha_2)$	$C_2\alpha_2$

$$HB \rightleftharpoons H^+ + B^- \Rightarrow (C_2)\ C_2(1-\alpha_2) \qquad C_2\alpha_2$$

Initial	C_2	0	0
equilibrium,	$C_2(1-\alpha_2)$	$(C_2\alpha_2$	$C_2\alpha_2$
		$+ C_1\alpha_1)$	
		↓	
		common ion	

Here 'C_1' and 'C_2' are the concentrations of acids *after mixing* of K_1 and K_2 are the ka values of the acids, we can write,

$$K_1 = \frac{C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)}\ C_1\alpha_1 \qquad \ldots\ldots (1)$$

$$K_2 = \frac{(C_1\alpha_1 + C_2\alpha_2)C_2\alpha_2}{C_2(1-\alpha_2)} \qquad \ldots\ldots (2)$$

Since the common ion H^+ is on the product side, the degree of dissociation of the weak acids will be supressed,

From 1 $\quad K_1C_1 = (C_1\alpha_1 + C_2\alpha_2)\ C_1\alpha_1\ \alpha_1 << 1 >> \alpha_2 \Rightarrow (1-\alpha_1) \approx 1$

From 2 $\quad K_2C_2 = (C_2\alpha_2 + C_1\alpha_1)\ (C_2\alpha_2) \quad \Rightarrow \quad (1-\alpha_2) \approx 1$

Adding we get

$$K_1C_1 + K_2C_2 = (C_1\alpha_1 + C_2\alpha_2)^2 = [H^+]^2$$

$$H^+ = \sqrt{K_1C_1 + K_2C_2}$$

We will directly use this equation to solve numerical problems.

20. 200 ml 1 M CH_3COOH ($K_a = 10^{-6}$) + 200 ml 0.1 M HCOOH (Ka = 10^{-5}).

(a) Calculate pH of the mixture. Also calculate $[CH_3COO^-]$ and $[HCOO^-]$.

Solution $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$HCO_2H \rightleftharpoons HCOO^- + H^+$

≡ 200 mm (x) ≡ 20 mm (y)

After mixing total volume = 400 ml, $C_1 = \frac{200}{400}$ M $C_2 = \frac{20}{400}$ M

After mixing: $H^+ \sqrt{K_1C_1 + K_2C_2}$

$$= \sqrt{10^{-6} \times \frac{200}{400} + 10^{-5} \times \frac{20}{400}} \text{ M}$$

$$= \sqrt{10^{-6} \times 0.5 + 0.05 \times 10^{-5}}$$

$$= \sqrt{10^{-6} \times 0.5 + 0.5 \times 10^{-6}} = \sqrt{10^{-6} \times 1}$$

$$= 10^{-3} \text{ M}$$

pH = 3

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH] \rightarrow \text{after mixing}}, \quad [CH_3COO^-] = \frac{[10^{-6}][0.5]}{[10^{-3}]} = \mathbf{0.5 \times 10^{-3} M}$$

$$K_2 = \frac{[HCOO^-][H^+]}{[HCOOH]} \qquad [HCOO]^- = \frac{[10^{-5}][10^{-3}]}{[0.05]} = \mathbf{0.5 \times 10^{-3} M}$$

Case X: pH of Mixture of Monoacidic Weak Bases

C_1 and C_2 are concentrations of weak bases after mixing. $[OH^-] = \sqrt{K_1C_1 + K_2C_2}$

K_1 and K_2 are K_b values.

Dibasic and Polybasic Acids

21. Calculate the hydronium ion concentration and the sulphide ion concentration of a 0.100 M solution of H_2S.

Solution The second step in the ionization process is the only source of sulphide ions, but neither the hydronium ion concentration nor the HS^- concentration is significantly changed by this step. Thus, $[H_3O^+]$ and $[HS^-]$ can be calculated from K_1 only.

$$K_1 = \frac{[H_3O^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7}$$

Let $[H_3O^+] = x$ then $[HS^-] = x$ and $[H_2S] = 0.100 - x \approx 0.100$

$$\frac{x^2}{0.100} = 1.0 \times 10^{-7} \quad \text{so} \quad x = 1.0 \times 10^{-4} = [H_3O^+] = [HS^-]$$

The sulphide ion concentration is calculated by use of K_2 and the values of $[H_3O^+]$ and $[HS^-]$ just determined.

$$K_2 = \frac{[H_3O^+][S^{2-}]}{[HS^-]} = 1.0 \times 10^{-14}$$

so $[H_3O^+] = [HS^-] = 1.0 \times 10^{-4}$

$$K_2 = \frac{(1.0 \times 10^{-4})[S^{2-}]}{(1.0 \times 10^{-4})} = 1.0 \times 10^{-14}$$

so $[S^{2-}] = 1.0 \times 10^{-14}$

The quantity of additional hydronium ion produced and the quantity of hydrogen sulphide ion used up in the second ionization step are each equal to the quantity of sulphide ion produced and

are small compared to the quantities of H_3O^+ and HS^- produced in the first step. As was previously stated, the second ionization does not change the hydronium ion concentration or the hydrogen sulphide ion concentration significantl .

22. Determine the $[S^{2-}]$ in a saturated H_2S solution to which enough HCl has been added to produce a $[H^+]$ of 2×10^{-4}.

Solution $K_1K_2 = \dfrac{[H^+]^2[S^{2-}]}{[H_2S]} = \dfrac{(2\times10^{-4})^2[S^{2-}]}{0.10} = 1.0\times10^{-21}$ so $[S^{2-}] = \dfrac{1.0\times10^{-22}}{4\times10^{-8}} = 2.5\times10^{-15}$

Warning: Do not use the K_1K_2 form of the equation unless you have an independent method of calculating $[H^+]$ or $[S^{2-}]$.

23. Calculate the values of the equilibrium constants for the reactions with water of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} as bases. Comparing the relative values of the two equilibrium constants of $H_2PO_4^-$ with water, deduce whether solutions of this ion in water are acidic or basic. Deduce whether solutions of HPO_4^{2-} are acidic or basic.

Solution $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$ $\quad K_h = \dfrac{K_w}{K_1} = \dfrac{1.0\times10^{-14}}{7.1\times10^{-3}} = 1.4\times10^{-12}$

$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ $\quad K_h' = \dfrac{K_w}{K_2} = \dfrac{1.0\times10^{-14}}{6.3\times10^{-8}} = 1.6\times10^{-7}$

$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$ $\quad K_h'' = \dfrac{K_w}{K_3} = \dfrac{1.0\times10^{-14}}{4.5\times10^{-13}} = 2.2\times10^{-2}$

$H_2PO_4^-$ can react with water to yield HPO_4^{2-} and H_3O^+, with a constant 6.3×10^{-8}. Its reaction with water to yield H_3PO_4 and OH^- has a much smaller equilibrium constant, 1.4×10^{-12}, and so this ion in water solution is acidic. Comparison of the constants for HPO_4^{2-} (4.5×10^{-13} as an acid, 1.6×10^{-7} as a base) leads to the conclusion that this ion in solution is basic.

24. Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$, and $[PO_4^{3-}]$ in 0.0100 M H_3PO_4.

Solution Begin by assuming that H^+ comes principally from the first stage of dissociation, and that the concentration of any anion formed by one stage of an ionization is not appreciably lowered by the succeeding stage of ionization.

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $\quad K_1 = 7.1 \times 10^{-3}$

Let $[H^+] = [H_2PO_4^-] = x$. Then $[H_3PO_4] = 0.0100 - x$, and

$$\frac{x^2}{0.0100 - x} = 7.1\times10^{-3} \qquad \text{or} \qquad x = 0.0056$$

Next take the above value for $[H^+]$ and $[H_2PO_4^-]$ to solve for $[HPO_4^{2-}]$.

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ $\quad K_2 = 6.3 \times 10^{-8}$

$$[HPO_4^{2-}] = \frac{K_2[H_2PO_4^-]}{[H^+]} = \frac{(6.3\times10^{-8})(0.0056)}{0.0056} = 6.3\times10^{-8}$$

Check of assumption: The relative extent of the second dissociation $(6.3 \times 10^{-8})/(5.6 \times 10^{-3})$ is indeed small. Next, take the above values for $[H^+]$ and $[HPO_4^{2-}]$ to solve for $[PO_4^{3-}]$.

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ $\quad K_3 = 4.5 \times 10^{-13}$

$$[PO_4^{3-}] = \frac{K_3[HPO_4^{2-}]}{[H^+]} = \frac{(4.5\times10^{-13})(6.3\times10^{-8})}{5.6\times10^{-3}} = 5.1\times10^{-18}$$

Check of assumptions: (1) x is indeed small compared with 0.10. (2) For the above values of $[H^+]$ and $[HS^-]$, the extent of the second dissociation is given by,

25. Calculate the H^+ concentration of 0.10 M H_2S solution.

Solution Most of the H^+ results from the primary ionization: $H_2S \rightleftharpoons H^+ + HS^-$.
Let $x = [H^+] = [HS^-]$. Then $[H_2S] = 0.10 - x \approx 0.10$.

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} \quad \text{or} \quad 1.0 \times 10^{-7} = \frac{x^2}{0.10} \quad \text{or} \quad x = 1.0 \times 10^{-4}$$

Check of assumptions: (1) x is indeed small compared with 0.10. (2) For the above values of $[H^+]$ and $[HS^-]$, the extent of the second dissociation is given by,

$$[S^{2-}] = \frac{K_2[HS^-]}{[H^+]} = \frac{(1.0 \times 10^{-14})(1.0 \times 10^{-4})}{1.0 \times 10^{-4}} = 1.0 \times 10^{-14}$$

The second dissociation is so limited that it does not appreciably lower $[HS^-]$ or raise $[H^+]$ as calculated from the first dissociation only. In general, the concentration of the conjugate base resulting from the second dissociation is numerically equal to K_2, whenever the extent of the second dissociation is less than 5%.

Conjugate Acid and Base

Acids are proton donors. Bases are proton acceptors or OH^- donor in aqueous medium. The relation between conjugate acid and conjugate base can be expressed as follows.

$$\text{HA (conjugate acid of } A^-) \underset{+H^{\oplus}}{\overset{-H^{\oplus}}{\rightleftharpoons}} A^- \text{ (conjugate base of acid HA)}$$

$$X^- \xrightarrow{+H^+} HX$$

base Conjugate Acid of X^-

$$XH \xrightarrow{-H^+} X^-$$

Acid Conjugate Base of HX

$$H_2O \xrightarrow{-H^+} OH^- \xrightarrow{-H^+} O^{2-}$$

Conjugate base of OH^-

↓

Conjugate
base of water
and conjugate acid of O^{2-}

Conjugate acid and conjugate base differ in one proton only.

$$HA \rightleftharpoons H^+ + A^- \quad \ldots\ldots\ldots\ldots\ldots\ldots K_a(HA)$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \quad \ldots\ldots\ldots\ldots\ldots K_b(A^-)$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \ldots\ldots\ldots\ldots\ldots K_w$$

$$K_w = K_a(HA)\ K_b(A^-)$$

If acid is strong, its conjugate base will be weak and vice versa.



Worked-out Examples

26. The conjugate base of HSO_4^- in aqueous solution is..... **[IIT-JEE-1982]**

Solution SO_4^{2-}

27. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid. **[IIT-JEE-1992]**

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterises the conjugate acid-base pairs is

(a) (HCl, CH_3COOH) and ($CH_3COOH_2^+$, Cl^-)

(b) (HCl, CH_3COOH_3) and (CH_3COOH, Cl^-)

(c) (CH_3COOH_3, HCl) and (Ch CH_3COOH)

(d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

Solution (d) Since, HCl is stronger than CH_3COOH and acts as acid. On the other hand, CN^- is a stronger base than $CH_3COOH_2^+$ and is the conjugate base of HCl.

$$\underset{acid_1}{HCl} + \underset{base_2}{CH_3COOH} \rightleftharpoons \underset{base_3}{Cl^-} + \underset{acid_4}{CH_3COOH_2^+}$$

28. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order. **[IIT-JEE-1996]**

ClOH (l), BrOH(II), IOH(III)

(a) I>II>III (b) II>l>III (c) III>II>l (d) I> III> II

Solution (a) Among oxyacids of the same type formed by different elements, acidic nature increases with increasing electronegativity. In general, the strength of oxyacids decreases as we go down the family in the periodic table.

HOCl (I) > HOBr(II) > HOI (III)

29. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in waters temperature is **[IIT-JEE-1997]**

(a) 1.74×10^{-5} (b) 3.52×10^{-3} (c) 6.75×10^{-4} (d) 5.38×10^{-2}

Solution (c) $HF + H_2O \xrightarrow{K_a} H_3O^+ + F^-$

$$K_a = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

$$HF + H_2O \xrightarrow{K_b} H_3O^+ + F^-$$

$$K_b = \frac{[HF][H_2O]}{[F^-][H_2O]}$$

$$K_a \times K_b = [H_3O^+][OH^-] = K_w = 10^{-14}$$

Given, pKb = 10.83

Kb =1.48 × 10–11

$$K_a = \frac{10^{-14}}{1.48 \times 10^{-11}} = 6.75 \times 10^{-4}$$

SALT HYDROLYSIS

When a salt is dissolved in water, it dissociates into its constituent ions i.e., cation and anion. Now these ions react with water to form acid and base.

$$\underset{\text{(Most Salts are ionic crystals)}}{AB(s)} \xrightarrow[\text{completely dissolved}]{H_2O} AB(aq) \xrightarrow[\text{ionization}]{100\%} \underset{\text{salt undergoes 100\% ionization.}}{A^+(aq) + B^-(aq)}$$

Hydrolysis takes place only after dissolution and complete ionization of salt

$$A^+ + H_2O \rightleftharpoons AOH + H^+$$

$$B^- + H_2O \rightleftharpoons BH + OH^-$$

Both can hydrolyse or any one of them can hydrolyse.

The cleavage of water by cation or anion of the salt is called salt hydrolysis.

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Types of Hydrolyses

(A) Salt of strong acid + strong base

$$\underset{\text{Strong base}}{NaOH} + \underset{\text{Strong Acid}}{HCl} \rightarrow \overset{+}{N}a\overset{-}{C}l + H_2O$$

$Na^+ \rightarrow$ Cation from strong base

$Cl^- \rightarrow$ Anion from strong acid

The cation of the salt is derived from base and the anion is derived from the acid.

Salts of strong acids and strong bases **do not hydrolyse**. For example, when potassium chloride is dissolved in water, its ions, K^+ and. Cl^-, have no tendency to react with water. This is because the possible products of such interactions, namely, KOH and HCl are themselves almost completely dissociated. Consequently, there is no change in the concentration of H^+ or OH^- ions and the solution continues to remain neutral.

(B) Salt of weak acid and strong base

$$CH_3COOH + NaOH \rightleftharpoons CH_3CO\overset{-}{O}Na^+ + H_2O$$

The hydrolysis of salt of a weak acid and a strong base forms an alkaine solution, i.e., its pH **will be greater than 7.** This process is known as **anionic hydrolysis**. Example of these types of salts are CH_3COONa, NaCN, Na_2CO_3, Na_3PO_4, etc.

$$CH_3COO^- + H_2O(l) \longrightarrow CH_3COOH + OH^- \ldots\ldots\ldots\ldots$$

Initial	C	0	0
equilibrium,	C–X	X	X

$K_a(CH_3COOH) \times K_b(CH_3COO^-) = K_W$

$K_b(CH_3COO^-) = \dfrac{K_W}{Ka(CH_3COOH)} = K_h$ hydrolytic constant

$K_h = \dfrac{Kw}{Ka}$

$K_h = \dfrac{x^2}{C - x}$

$K_h = \dfrac{C\alpha^2}{1 - \alpha}$

$K_h = C\alpha^2,\ \alpha = \sqrt{\dfrac{K_h}{C}}$

$K_h = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{10^{-6}} \approx 10^{-8}$ [Assuming

$K_a(CH_3COOH) = 10^{-6}$]

So dissociation is very less

Solving procedure: K_a (weak acid) → Given and 'e' is given

↓

$K_h = \dfrac{K_w}{K_a}$ Check $\alpha = \sqrt{\dfrac{K_h}{C}}$

If $\alpha \geq 0.1$	If $\alpha < 0.1$
(very rare)	$[OH^-] = \sqrt{K_h C}$
$K_h = \dfrac{C\alpha^2}{1-\alpha}$ solve for α	or
Then, $[OH^-] = C\alpha$	$pH = 7 + \dfrac{1}{2} pK_a + \dfrac{1}{2} \log_{10} C$

(C = concentration of ion in moles per litre undergoing hydrolysis.)

(This equation is applicable when $\alpha \ll 1$)



Worked-out Examples

30. Calculate the pH of 0.005 M $Ba(CH_3COO)_2$. Also calculate the degree of hydrolysis. Given: $K_a(CH_3COOH) = 10^{-6}$

Solution It must have been a salt of weak acid and strong base because K_a value is given.

$0.005 \times 2 = 0.001 \leftarrow CH_3COO^-$

$\left(\sqrt{\dfrac{K_h}{C}} = \alpha \quad \sqrt{\dfrac{10^{-8}}{10^{-2}}} = 10^{-3}\right)$

Since, α is < 0.1

$K_h = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{10^{-6}} = 10^{-8}$

Thus, $[OH^-] = \sqrt{K_h C} = \sqrt{10^{-8} \times 10^{-2}} = 10^{-5}$

$pOH = 5 \qquad pH = \mathbf{9}$

Another method $\quad pH = 7 + \frac{1}{2} pKa + \frac{1}{2} \log_{10} C$

$$7 + \frac{6}{2} + \frac{1}{2} \log_{10} 10^{-2}$$

$$7 + 3 - 1 = 10 - 1 = \mathbf{9}$$

31. The K_a value for CH_3COOH is 10^{-6}. Calculate the equilibrium constant of the following reaction

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

$$\underset{WA}{CH_3COOH} + Na^+ + \underset{SB}{OH^-} \rightleftharpoons \underset{SE}{CH_3COO^-} + Na^+ + H_2O$$

Salts undergo 100% ionization.

$$\begin{cases} CH_3COOH & CH_3COOH^- + H^+ \\ NaOH \longrightarrow & Na^+ + OH^- \end{cases} \quad H_2O$$

Contribute

- Regardless the nature of acid and base we can assume that the neutralization will proceed to completion.
- The pH will be governed by salt hydrolysis when we have **only** salt in water.

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O \} \text{ Hydrolysis}$$

Salt hydrolysis is the reverse reaction of neutralization.

$$K_{eq} = \frac{1}{K_h} = \frac{1}{\frac{K_w}{K_a}} = \frac{10^{-6}}{10^{-14}} = 10^8$$

32. 200 ml of 0.1 M CH_3COOH (WA) + 100 ml of 0.2 M NaOH (SB). Calculate pH_{mix} $K_a = 10^{-6}$.

Solution First of all, write the reaction and analyse the nature of reaction.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

20mm 20 mm – – (complete neutralization)

– – 20 mm"

At equivalence point, we have only salt in water. So pH will be governed by salt hydrolysis.

Equivalence point

At Eq. Pt. entire acid and base will be consumed and pH will be governed by salt hydrolysis.

$$[CH_3COO^-] = [C] = \frac{20}{300} = \frac{1}{15}$$

$$[OH^-] = \sqrt{K_h C} = \sqrt{10^{-8} \times \frac{1}{15}} = 10^{-4} \times 15^{-\frac{1}{2}}$$

$$4 + \frac{1}{2}(\log 5 + \log 3) = 4 + 0.59 = 4.59 \Rightarrow p$$

Alternatively,

$$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log_{10}C$$

$$pH = 7 + \frac{6}{2} - \frac{1}{2}[\log 5 + \log 3]$$

$$= 10 - \frac{1}{2}[0.7 + 0.48]$$

$$= 10 - 0.59$$

$$= 9.4$$

(C) Salt of weak base and strong acid (PH < 7)

$$NH_4OH + HCl \longrightarrow \overset{+}{N}H_4\,Cl^- + H_2O$$

WB SA WB : SA

The hydrolysis of salt of a strong acid and a weak base forms an acidic solution i.e., its pH will be less than 7. This process is known as cationic hydrolysis. Example of these type of salts are NH_4Cl, $FeCl_3$, $CuSO_4$, etc.

$$\underset{(C)\ (aq)}{NH_4Cl} \xrightarrow{100\%} \underset{(C)}{NH_4^+} + Cl^-$$

$$\underset{(C)}{NH_4^+} + H_2O \longrightarrow NH_4OH + H^+$$

$C(1-\alpha)$ $C\alpha$ $C\alpha$

$[H^+] = C\alpha$ α = degree (extent) of hydrolysis

$$K_h = \frac{K_w}{K_b} \approx C\alpha^2 \text{ when } \alpha << 1$$

$$\alpha = \sqrt{\frac{K_H}{C}} \qquad H^+ = \sqrt{K_H C} \text{ or } pOH = 7 + \frac{1}{2}pK_b + \frac{1}{2}\log_{10}C$$

$(\alpha << 1)$



Worked-out Examples

33. Calculate the pH of 0.005 M $(NH_4)_2SO_4$. $K_b(NH_3) = 10^{-5}$

Solution $0.05 \times 2 = 0.1 = 10^{-1}$

$$K_h = \frac{K_W}{K_B} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$\alpha = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$$

$$H^+ = \sqrt{10^{-9} \times 10^{-1}} = 10^{-5} \qquad pH = 5$$

34. 20 ml 0.1 NH_4OH + 40 ml 0.05 M HCl. Calculate pH of the solution produced on mixing ($K_b(NH_3)$ = 10^{-5}

Solution $\underset{2\text{ mm}}{\overset{WB}{NH_4OH}} + \underset{2\text{ mm}}{\overset{SA}{HCl}} \longrightarrow \underset{-}{NH_4Cl} + \underset{-}{H_2O}$

Make sure, acid and base are totally consumed then only salt hydrolysis will govern the pH value.

$NH_4^+ + H_2O \longrightarrow \underset{2\text{ mm}}{NH_4OH} \quad H^+$

$K_h = \frac{K_W}{K_B} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$ $[NH_4^+]$ = Constant = $\frac{2}{60}$ $\frac{1}{3} \times 10^{-1}$

$[OH^-] = \sqrt{K_h C} = \sqrt{10^{-9} \times \frac{1}{3} \times 10^{-1}} = 10^{-5} \times \sqrt{\frac{1}{3}}$

$$\begin{cases} 10^{-5} \times \frac{1^{\frac{1}{2}}}{3} = \frac{10^{-5}}{1.732} \\ 10^{-5} \times 3^{-\frac{1}{2}} \end{cases}$$

$pOH = 7 + \frac{1}{2} pK_B + \frac{1}{2} \log_{10} C$

$= 7 + \frac{5}{2} - \frac{1}{2}(1 + 0.48)$

$= (9.5 - 0.74)$

$= 8.76$

pH= **5.24**

$pH = 5 + \frac{1}{2} \log 3 = 5 + 0.24 = 5.24$

(D) Salt of weak acid and weak base

$$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$$

In this case, the products of hydrolysis are both weak and hence would be almost undissociated. This process involves anionic hydrolysis as well as cationic hydrolysis.

Range of pH cannot be predicted, depends on individual strength of acid or base. The pH due to salt hydrolysis of this type of salt has been discussed latter in the chapter.



Worked-out Examples

35. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 6.1 M solution of NaX is **[IIT-JEE-2004]**

(a) 0.0001% (b) 0.01% (c) 0.1% (d) 0.15%

Solution (b) $\sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}}$ =10–4; Hence, % hydrolysis = 10– × 1 00 = 0.01

36. The pH of 0.1 M solution of the following salts increases in the order. **[IIT-JEE-1999]**

(a) $NaCl < NH_4Cl < NaCN < HCl$ (b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$ (d) $HCl < NaCl < NaCN < NH_4Cl$

Solution (b) The characteristics of the given solutions are:

NaCl	neutral solution	
NH_4Cl	slightly acidic due to the reaction	$NH_4 + H_2O \rightleftharpoons NH_4OH + H^+$
NaCN	slightly alkaline due to the reaction	$CN^- + H_2O \rightleftharpoons HCN + OH^-$
HCl	highly acidic	

The pH of the solution will follow the order highly acidic < slightly acidic < neutral < slightly alkaline i.e., $HCl > NH_4Cl > NaCl > NaCN$

(a) The given reaction will be exothermic in nature due to the formation of three X-Y bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species. Hence, the reaction will be affected by both temperature and pressure. The use of catalyst does not affect the equilibrium concentrations of the species in the chemical reaction.

37. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is **[IIT-2009]**

Solution 8 $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$

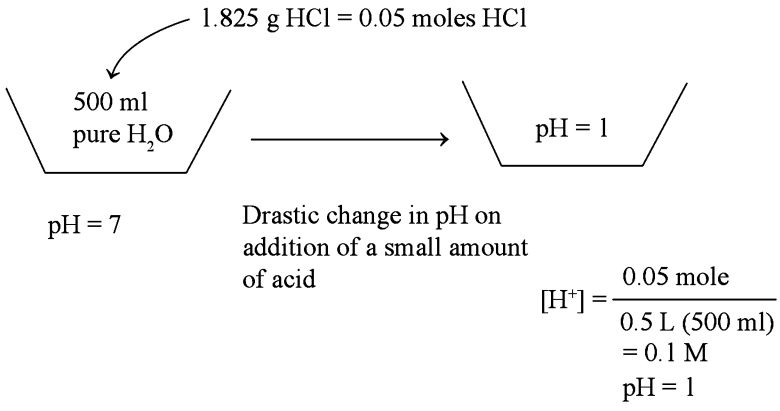
$= 7 + \frac{1}{2} \times 4 + \frac{1}{2}\log 0.01$

$= 8$

Buffer Solution



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry



When a very small amount of strong acid or strong base is added to a normal solution, there is a large change in the pH value.

A solution which can resist a large change in pH value upon the addition of small amount of strong acid or strong base is called a **buffer solution**.

Buffer solution can be classified as

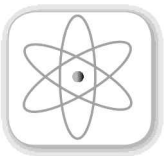
(i) Single Buffer
↓
Salt of weak acid and weak base

(i) Mixed Buffer
↙ ↘
Acidic Buffer | Basic Buffer

Hence, there are three types of buffer solutions:

(i) weak acid–salt buffer
(ii) weak base–salt buffer and
(iii) salt buffer

BUFFER OF A WEAK ACID AND ITS SALT WITH A STRONG BASE



It is possible to prepare a buffer solution by the addition of a weak acid and a salt of the acid with a strong base.

We shall explain the buffer action by the following example. Let us consider a buffer solution made up of CH_3COOH and CH_3COONa. The weak acid dissociates to a very small extent more so due to the common ion effect of its salt.

$$CH_3COOH \quad CH_3COO^- + H^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

Now let us assume that a buffer solution contains 20 moles of CH_3COOH and 20 moles of CH_3COONa. The salt being a strong electrolyte would completely dissociate while the acid would be hardly dissociated. We assume that the amount of CH_3COO^- is 20 moles as the contribution from CH_3COOH would be negligible. We also assume that the amount of CH_3COOH to be 20 moles as it would be very weakly dissociated. Therefore, the solution contains 20 moles of CH_3COOH and 20 moles of CH_3COO^- ions.

Let us now add 10 moles of H^+ ions to this solution. These 10 moles of H^+ ions would react with the 20 moles of CH_3COO^- ions to produce 10 moles of CH_3COOH. (This is because the reaction of CH_3COOH to give CH_3COO^- ions and H^+ ions has an equilibrium constant value of approximately 10^{-5}. Therefore, the reverse reaction, that is the reaction of CH_3COO^- ions to combine with H^+ ions to give CH_3COOH would have an equilibrium constant of approximately 10^5. So this reaction can be assumed to be complete). These 10 moles of CH_3COOH formed would ionize weakly because it is a weak acid. Moreover, due to the common ion effect of CH_3COO^- ion (10 moles, left over), it would ionize even less. So the amount of H^+ ion produced back is much less than the 10 moles that were added. So effectively, 10 moles of H^+ ions were consumed and an amount much less than that is produced back which causes an insignificant change in pH of the buffer solution.

Let us add 10 moles of OH^- ions to the same buffer solution containing 20 moles of CH_3COOH and 20 moles of CH_3COO^- ions. These 10 moles of OH^- ions added would be consumed by the 10 moles of CH_3COOH to produce 10 moles of CH_3COO^- ions ($CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$. This is because the reverse reaction is the hydrolysis of CH_3COO^- ions which has an equilibrium constant of $\frac{K_w}{K_a}$ $\approx 10^{-9}$. So the forward reaction's equilibrium constant would be 10^9, which implies that the reaction is practically complete). The 10 moles of CH_3COO^- ions produced would be hydrolysed weakly (due to a very low K value of 10^{-9}). On top of that, the presence of 10 moles of CH_3COOH would further hamper

the hydrolysis process and therefore, the OH^- ion produced is much less than the amount that was added. This causes a minor change in pH.

For a buffer to act as a good buffer the amount of CH_3COOH and CH_3COO^- ion should be high.

The pH of a buffer can be calculated as follows.

Since acetic acid is in equilibrium,

$$\frac{[H^+]\ [CH_3COO^-]}{[CH_3COOH]} = K_a$$

$$\Rightarrow \frac{[H^+][\text{Conjugate base}]}{[\text{Acid}]} = K_a \Rightarrow [H^+] = K_a \ \frac{[\text{Acid}]}{[\text{Conjugate base}]}$$

$$\Rightarrow \log [H^+] \ = \log K_a + \log \ \frac{[\text{Acid}]}{[\text{Conjugate base}]}$$

$$-\log [H^+] = -\log K_a + \log \ \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$\Rightarrow pH = pK_a + \log \ \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

This equation is called Henderson – Hasselbalch equation.

pH will not change on dilution. [Ratio of concentration will remain same]

$$pH = pKa + \log_{10}\left(\frac{\text{no. of mm of conjugate base (salt)}}{\text{no. of mm of acid}}\right)$$

When a weak dibasic acid is taken then the pH at half neutralisation is given by a special formula which is derived by balancing charge and mass of reactants and products. For example, at half neutralization of H_2CO_3 by NaOH, the pH is given by,

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$$

Where K_{a_1} and K_{a_2} are 1st and 2nd dissociation constant of H_2CO_3.



Worked-out Examples

38. pK (HCOOH) = 5 $\underset{\text{(formic acid)}}{HCOOH}$ 20 ml 0.1 M + 40 ml 0.1 M $\underset{\text{(Sodium format)}}{HCOONa}$

Calculate pH of the solution produced after mixing.

Solution (a) $\underset{2\,mm}{HCOOH}$ $\underset{4\,mm}{HCOONa}$

Total mm = 6 Total V. = 60 ml $C\,3(H^+) = \frac{6}{60} = 10^{-1}$ $^{HCOO^-}$

$$pH = pKa + \log_{10}\left(\frac{\text{no. of mm of conjugate base}}{\text{no. of mm of acid}}\right)$$

$$= 5 + \log_{10}\left(\frac{4}{2}\right) = 5 + \log_{10}2 = 5 + 0.3 = 5.3$$

39. Calculate the pH of the solution after mixing.

(40 ml 0.1 M $Ba(HCOO)_2$ + 20 ml 0.1 M HCOOH)

Solution ≡ 8 mm of $HCOO^-$

≡ 2 mm of HCOOH

$$pH = 5 + \log\left(\frac{8}{2}\right) = 5 + \log_{10} 4$$

$$= 5 + 2\,(0.3) = 5.6$$

40. Calculate pH of solution produced after mixing.

(30 ml 0.1 M CH_3COOH + 10 ml 0.1 M NaOH) $K_a = (CH_3COOH) = 10^{-6}$

Solution

CH_3COOH + NaOH	⟶	CH_3COONa + H_2O	
3 mm	1 mm	–	–
2 mm	–	1mm	
↓	totally		
left	consumed		

- Number of meq of weak acid number of meq of strong base added then nature of solution should be acidic buffer.

$$pH = pKa + \log_{10}\left(\frac{Cs}{Ca}\right) = 6 + \log_{10}\left(\frac{1}{2}\right) = 6–0.3 = 5.7$$

41. A weak monobasic acid is made to react with NaOH. When 15 ml 0.1
(20 ml 0.1 M) NaOH is added, the pH of the solution is 6.48. Calculate the K_a value of the weak acid.

Solution

Weak Acid + NaOH	⟶	Salt of W.A. + H_2O
2 mm	1.5 mm	1.5 mm
0.5 mm left	–	formed

$$K_a = \frac{K_W}{K_B} \qquad pH = pKa + \log_{10}\left(\frac{C_S}{C_A}\right)$$

$$6.48 = pKa + \log_{10}\left(\frac{1.5}{0.5}\right)$$

$6.48 – \log 3 = pKa$

$6.48 – 0.48 = pKa$

$pKa = 6$

$Ka = 10^{-6}$

After the addition of NaOH, the solution formed will be an acidic buffer solution.

42. Calculate pH of solution.

Given $K_a = 10^{-6}$

(i) 10 ml of NaOH is added to 20 ml weak monobasic acid

(ii) 20 ml of NaOH is added to 20 ml weak monobasic acid

(iii) 30 ml of NaOH is added to 20 ml of 0.1 M monobasic weak acid

Solution Acidic Buffer

(i) $\underset{\substack{2\,mm\\1\,mm\,left.}}{Acid} + \underset{1\,mm}{NaOH} \longrightarrow \underset{1mm}{Salt} + H_2O$

$$pH = 6 + \log_{10}\left(\frac{1}{1}\right) = 6$$

(ii) Salt Hydrolysis

$$\underset{\substack{(WA)\\2\,mm\\-}}{Acid} + \underset{\substack{(SB)\\2mm\\-}}{NaOH} \longrightarrow \underset{\substack{-\\2\,mm}}{Salt} + \underset{-}{H_2O}$$

When 20 ml NaOH is added the equivalence pt. of titration is attained. The pH at equilibrium point is governed by salt hydrolysis.

$$K_h = \frac{10^{-14}}{10^{-6}} = 10^{-8} = \frac{2}{40} = \frac{1}{20} = 2^{-1} \times 10^{-1}$$

$$[H^+] = \sqrt{10^{-8} \times 10^{-1} \times 2^{-1}}$$

$$pH = 7 + \frac{6}{2} + \frac{1}{2}\log\frac{1}{20}$$

$$= 10 - \frac{1}{2}(1.3)$$

$$= 10 - 0.65$$

$$= 9.35$$

(iii) $\underset{2\,mm}{Acid} + \overset{SB}{\underset{\substack{3\,mm\\1\,mm}}{NaOH}} \longrightarrow \overset{Salt}{\underset{2mm}{Salt}} + H_2O$

In salt hydrolysis, large deviations from pH = 7 do not take place.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$NaOH \longrightarrow Na^+ + OH^-$$

In presence of the strong base, the salt hydrolysis will be suppressed to a greater extent. We neglect the salt hydrolysis and pH is governed by presence of excess strong base.

$$\underset{excess}{[NaOH]} = [OH]^- = \frac{1mm}{50(\text{total volume})} = 50^{-\frac{1}{2}}$$

$$pOH = 1.69 = + \frac{1}{2}(\log 5 + \log 10)$$

$$pH = 14 - 1.69 = 12.31 = \frac{1}{2}(0.69 + 1) = 1.69$$

43. 2.5 mL of $\frac{2}{5}$ weak monoacidic base ($K_b = 1 \times 10^{-12}$) at 25°C is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalences point is ($K_w = 1 \times 10^{-14}$ at 25°C) **[IIT-2008]**

(a) 3.7×10^{-13} M (b) 3.2×10^{-7} M

(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M

Solution (d) 2.5 ml, $\frac{2}{5}$ M BOH + $\frac{2}{15}$ M HCl, Vml

At equivalence point

$$M_1V_1 = M_2V_2$$

$$2.5 \times \frac{2}{5} = V \times \frac{2}{15}$$

$$V = 2.5 \times \frac{2}{5} \times \frac{2}{15} = 7.5 \text{ ml}$$

Number of moles of BCl formed = 1×10^{-3}

Total volume = (2.5 + 7.5)ml = 10ml = 10×10^{-3}L

$$[BCl] = \frac{1}{10} = 0.1\,M$$

$$BCl \rightleftharpoons B^+ + Cl^-$$

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$C(1-h) \quad Ch \quad Ch$$

$$K_h = \frac{Ch^2}{(1-h)} = \frac{K_w}{K_b}$$

$$\frac{0.1h^2}{1-h} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

$$\text{or } \frac{h^2}{1-h} = \frac{1}{10} \text{ or } h = 0.27$$

So $[H^+] = Ch = 0.1 \times 0.27 = 2.7 \times 10^{-2}$ M

44. A weak monobasic acid is titrated against NaOH. The pH of solution are 4 and 5 after the addition of 20 ml and 40 ml NaOH respectively. Calculate the volume of NaOH required to reach equivalence point.

1. Acid + $\underset{\substack{20\,ml\\ pH=4\\ OH^-=10^{-4}}}{NaOH}$ 2. Acid + $\underset{\substack{40\,ml\\ pH=5\\ OH^-=10^{-5}}}{NaOH}$

At equilibrium point, number of mm of NaOH = Number of mm of acid.

Solution V = Volume of NaOH (in ml) required to reach the equivalence point

Since the salt formed at equivalence point will be of weak acid and stong base the pH must be more than 7. On addition of 40 ml NaOH pH is 5 so more volume of NaOH to reach equilibrium point should be added so as to make pH > 7. Thus, V > 40 ml

M = Molarity of NaOH (MV) mm

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

The number of mm of acid taken initially, number of mm of NaOH added till equilibrium point

(MV) mm of weak Acid were taken initially.

NaOH → (20 m) mm

$$\text{Buffer solution} \begin{cases} CH_3COOH & +NaOH & \longrightarrow & CH_3COONa + H_2O \\ (MV)mm & (20M)mm & & \\ (MV - 20M) & - & & 20\ M \end{cases}$$

$$pH = pKa + \log_{10}\left(\frac{.20M}{MV - 20M}\right)$$

$$4 = pKa + \log_{10}\left(\frac{20}{V - 20}\right) \quad \ldots..1$$

$$\text{Similarly, } 5 = pKa + \log_{10}\left(\frac{40}{V - 40}\right) \quad \ldots.2$$

$(2 - 1)$

$$1 = \log_{10}\left(\frac{20}{V - 20}\right).\left(\frac{40}{V - 40}\right) \times \left(\frac{V - 20}{20}\right)$$

$$\log_{10} 10 = \log_{10}\left(2.\frac{V - 20}{V - 40}\right)$$

$$2\left(\frac{V - 20}{V - 40}\right) = 10$$

$$V - 20 = 5V - 200$$

$$4V = 180$$

$$V = 45\ ml$$

Basic Buffer Solution

Weak base +Salt of (that WB + SA)

Example (i) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ chloride

$NH_4Cl \xrightarrow{100\%} NH_4^+ + Cl^-$

We assume that ammonium ion is mainly contributed by salt because dissolution of WB is almost negligible due to common ion effect.

Case I: H^+ added

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ Amount of OH^-

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

100% ionized

$$\underset{\text{base}}{NH_4OH} + \underset{\text{acid}}{H^+} \rightleftharpoons \underset{\text{salt}}{NH_4^+} + H_2O$$

$OH^- + H^+ \rightleftharpoons H_2O$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O \qquad K_{eq} = \frac{1}{K_h}$

Case II OH^- added

pH should increase but in the buffer solution, it will not change much.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$NH_4^+ + OH^- \longrightarrow NH_4OH \qquad K_{eq} = \frac{1}{K_B}$$

pH:

(i) The NH_4^+ ion is mainly contributed by the salt. The ammonium ion from the base can be neglected because

→ Base is weak

→ Due to Comon Ion effect $C_b - x \approx C_b$ $\quad C_S \approx x + C_S$ neglected $\quad x$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

Cs Cs

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{(C_S + x)[OH^-]}{(C_b - x)} = \frac{C_S[OH^-]}{C_b}$$

$$pOH = pK_b + \log_{10}\left(\frac{|\,C_S}{C_b}\right) \text{ concentration of corresponding acid}$$

$$pOH = pK_b + \log_{10}\left[\frac{\text{conjugate acid}}{\text{weak base}}\right]$$

Since the ratio of concentration is independent of volume, the pH does not change on dilution.



Worked-out Examples

45. Calculate pH of [0.01 M NH_3 + 0.001 M $(NH_4)_2SO_4$] $\quad K_a(NH_4^+) = 10^{-8}$

Solution $pOH = \underset{(NH_3)}{pK_b} + \log_{10}\left(\frac{C_S}{C_b}\right) \qquad pK_b = pK_w - pK_a$

$$= 6 + \log_{10}\left(\frac{10^{-3} \times 2}{10^{-2}}\right) = 6 + \log(2 \times 10^{-1}) = 5 + \log 2 = 5.3$$

$pH = 14 - 5.3 = 8.7$

46. [30 ml 0.1 M weak monoacidic base + 10 ml of 0.1 N HCl]
Find pH mixture $\quad pK_b$ (base) = 5

Solution

Base	+	HCl	⟶	Salt	+	Water
30 ml 0.1 M mm = 3		10 ml 0.1 N meq. = 1 mm = 1		-		

2 mm left – 1mm formed

- After mixing, basic buffer solution is formed.

$$pOH = pK_b + \log_{10}\left(\frac{C_s}{C_b}\right)$$

$$= 5 + \log_{10}\left(\frac{1}{2}\right)$$

$$= 5 - 0.3 = 4.7 \quad pH = 9.3$$

47. Calculate pH of the mixture [20 ml 0.02 M NH_4Cl + 10 ml 0.01M NaOH] $pK_b = NH_4OH = 5$

$$\underset{0.4mm}{NH_4Cl}\ (Salt) + \underset{0.1\ mm}{NaOH} \longrightarrow \underset{0.1\ mm}{NaCl} + \underset{0.1\ mm}{NH_4OH}\ (weak\ base)$$

0.3 mm left

$$pOH = pK_b + \log_{10}\left(\frac{C_s}{C_b}\right) = 5 + \log_{10}\left(\frac{0.3}{0.1}\right) = 5 + \log 3$$

$$= 5 + 0.48$$

$pOH = 5.48$ $pH = 8.52$

48. Weak Monoacidic Base BOH (30 ml 0.1 M) is titrated against HCl. When 20 ml of0.1 M HCl is added the pH of the mixture is 8.7, Calculate pH at equivalence point.

$$\underset{1mm}{\overset{3\ mm}{BOH}}\ (weak\ base) + \underset{-}{\overset{2mm}{HCl}} \longrightarrow \underset{2mm}{\overset{-}{BCl}}\ (salt) + \underset{-}{H_2O}$$

$$pOH = pK_b + \log_{10}\left(\frac{Cs}{C_b}\right)$$

$$5.3 = pK_b + \log_{10}(2)$$

$$5.3 = pK_b + 0.3$$

$$pK_b = 5.3 - 0.3$$

$$= 5$$

$$K_b = 10^{-5}$$

At equivalence point pH will be governed by salt hydrolysis.

10 ml more of HCl will have to be added to make volume = 30 ml (to make 3 mm so as to completely react with weak base.)

Total volume = 60 ml

at equivalence point

$$[NH_4Cl] = \frac{3mm}{60} = \frac{1}{20}\ M = C = [NH_4^{\oplus}]$$

$$pOH = 7 + \frac{1}{2}\ pK_b + \frac{1}{2}\ \log C$$

$$= 7 + \frac{1}{2}(5) - \frac{1}{2}(1.3) + \log_{10}\left(\frac{1}{20}\right)$$

$pOH = 9.5 - 0.65$

$pH = 14 - 9.5 + 0.65 = 5.15$

49. A buffer solution can be prepared from a mixture of **[IIT-JEE-1999]**

(a) sodium acetate and acetic acid in water

(b) sodium acetate and hydrochloric acid in water

(c) ammonia and ammonium chloride in water
(d) ammonia and sodium hydroxide in water

Solution (a, c) A buffer solution is prepared by mixing a weak acid/base with salt of its conjugate base/acid.

Buffer Action

50. 0.02 moles of NaOH is added to a buffer solution
(a) Containing 1L (0.1 M CH_3COOH + 0.1 M CH_3COONa)
(b) Containing 1 L (0.01 M CH_3COOH + 0.01 M CH_3COONa)
Calculate the change in pH in each case. Neglect the volume of NaOH added. K_a (CH_3COOH) = 10^{-6}

Solution (a) Number of moles of weak acid and salt = 0.1 m

Initially $pH = pKa + \log_{10}\left(\frac{C_s}{C_a}\right)$

$pH = 6$

$$\underset{(0.1-0.02)}{\overset{0.1\text{ mole}}{CH_3COOH}} + \underset{-}{\overset{0.02\text{ moles}}{NaOH}} \longrightarrow \underset{(0.1+0.02)}{\overset{0.1\text{ mole}}{CH_3COONa}}$$

0.08 mole totally consume $\longrightarrow$ 0.12

$$pH = pK_a + \log_{10}\left(\frac{3}{2}\right)\ \frac{0.12}{0.08} = pKa + 0.18 \qquad \text{Change} = 0.18$$

(b) $$\underset{x}{\overset{0.01\text{ m}}{CH_3COOH}} + \underset{0.01\text{mole}}{\overset{0.002\text{ m}}{NaOH}} \longrightarrow \underset{0.02\text{mole}}{\overset{0.01\text{ m}}{CH_3COONa}}$$

Since strong base is present along with the salt, hydrolysis can be neglected and pH will be governed by excess strong base present.

In this case, the change in pH is significant because the amount of base added is beyond the buffer capacity of the solution.

$[OH^-] = 0.01$

$pOH = 2$

$pH = 12$

Change in pH (Increase) = 6

51. 0.1 mole of HCl is added to
(a) 1L (1 M NH_4OH + 1M NH_4Cl)
(b) 1L (0.01 M NH_4OH + 0.01 M NH_4Cl)
Calculate change in pH in each case. K_B (NH_3) = 10^{-5}

Solution (a) $$\underset{0.9\text{ mole}}{\overset{1.\text{ mole}}{NH_4OH}} + \underset{-}{\overset{0.1.\text{ mole}}{HCl}} \longrightarrow \underset{1.1\text{ mole}}{\overset{1.\text{ mole}}{NH_4Cl}}$$

Initially, $pOH_i = pK_B + \log\left(\frac{C_s}{C_b}\right)$

Finally, $pOH_f = pK_B + \log_{10}\left(\frac{C_s}{C_b}\right)$

$pOH = 5 \qquad = 5 + \log_{10}\left(\frac{1.1}{0.9}\right)$

pH = 14–5 = 9 $= 5 + \log_{10} 11 - 2 \log_{10} 3$

$= 5 + 1.04 - 2\ (0.48)$

$= 6.04 - 0.96$

$= 5.08$

$pH_f = 8.92$

Change $= 0.08$

- in pH (The volume change on addition of HCl can be neglected.)

(b) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

0.01		0.1	0.01
–		0.09	0.02

The pH will be governed by excess amount of strong acid.

$pH = -\log_{10} [H^+]$

$= -\log_{10} [9 \times 10^{-2}]$

$= -\log_{10} 9 + 2$

$= 2 - 2\ (\log_{10} 3)$

$= 2 - 0.96$

pH = 1.04

Amount of the strong acid added is beyond the buffer capacity of the solution. Hence, the change in pH is significant.

Buffer Capacity

It is the number of mols of H^+ ion or OH^- ion that should be added to 1 litre of a buffer solution so as to change the pH by unity.

$$\beta = \frac{dPH}{dn}\ (\text{change in pH}) \quad \frac{\partial n}{\partial (pH)}$$

Buffer capacity of a solution is defined in terms of buffer index which is the change in the concentration of Buffer acid (or base) required for change of it's pH value by one, keeping ($C_{salt} + C_{acid}$) or ($C_{base} + C_{salt}$) constant.

Let there be a buffer solution of volume 1 litre with 'x' mole of acid and 'S' moles of 'salt'.

$$pH = pK_a + \log_{10} \frac{S}{x - S}$$

$$pH = pK_a + \frac{1}{2.303} \log_e \frac{S}{x - S}$$

$$\frac{\partial (pH)}{\partial S} = \frac{1}{2.303}\left[\frac{x - S + S}{S(x - S)}\right]$$

$$\frac{\partial S}{\partial (pH)} = \frac{1}{2.303}\left[\frac{S(x - S)}{x}\right]$$

Maximum value of Buffer Index

$$B.I = \frac{1}{2.303}\frac{S(x-S)}{x}$$

$$\frac{d}{dS}(B.I) = \frac{1}{2.303}\left[\frac{1}{x}[x-2s]\right]$$

For maximum value of buffer index,

$$\frac{d}{dS}(B.I) = 0$$

After solving, S = x/2

Thus $\frac{[Salt]}{[Acid]} = \frac{S}{x-S} = \frac{x/2}{x-x/2} = 1$

Hence maximum value of Buffer index occurs when, $\frac{[Salt]}{[Acid]} = 1$

For buffer capacity to be maximum $= \frac{[conjugate\ base]}{[acid]} = 1$

Worked-out Examples

52. 0.1 mole of HCl added to 1 L of buffer solution.

Change in pH = 0.1. Calculate buffer capacity.

Solution $\beta = \frac{n}{\Delta pH} = 1$

53. 0.1 mole of NaOH added to 250 ml of buffer solution. Change in pH = 0.2 units. Calculate buffer capacity.

Solution 250 ml $\longrightarrow$ 0.1 mole

1000 ml $\longrightarrow$ $\frac{0.1}{250} \times 1000 = 0.4$ mole

$\beta = \frac{\Delta n}{\Delta pH} = \frac{0.4}{0.2} = 2$

SALT BUFFER

Salt of Weak Acid and Weak Base

The fundamental principle behind a buffer action is the fact that on adding an acid the system consumes the H^+ ion added to produce a weak acid and on adding a base, it consumes the OH^- ion added to produce a weak base. This ensures that H^+ or OH^- ion added is consumed and the weak acid or the weak base produced gives less H^+ or OH^- ion as they are weak.

Based on this principle, a solution of a salt of a weak acid and weak base is also called as a buffer. Let us take the example of CH_3COONH_4. It dissociates as, $CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$. When H^+

ion is added, CH_3COO^- ion consumes it to give CH_3COOH. When OH^- ion is added, NH_4^+ ion consumes it to give NH_4OH. Hence it acts as a buffer.

Let the weak acid be CH_3COOH and the weak base be NH_4OH. Therefore, the salt is CH_3COONH_4.

The salt completely dissociates.

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

The ions get hydrolysed according to the reaction.

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons NH_4OH + CH_3COOH$$

Initial,	C	C	0	0
At equilibrium,	C(1–α)	C(1–α)	Cα	Cα

$$K_h = \frac{[NH_4OH]\,[CH_3COOH]}{[NH_4^+]\,[CH_3COO^-]}$$

Multiplying and dividing by H^+ and OH^- and rearranging,

$$K_h = \frac{[NH_4OH]\,[CH_3COOH]\,[H^+]\,[OH^-]}{[NH_4^+]\,[CH_3COO^-]\,[H^+]\,[OH^-]}$$

$$\Rightarrow \quad \frac{[H^+]\,[OH^-]}{\dfrac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} \times \dfrac{[NH_4^+]\,[OH^-]}{[NH_4OH]}} \Rightarrow \frac{K_w}{K_aK_b}$$

$$\therefore \quad K_h = \frac{K_w}{K_aK_b}$$

Substituting the concentration terms,

$$K_h = \frac{K_w}{K_aK_b} = \frac{C\alpha \times C\alpha}{C\,(1-\alpha)\,C\,(1-\alpha)} = \frac{(C\alpha)^2}{[C\,(1-\alpha)]^2} = \frac{\alpha^2}{(1-\alpha)^2}$$

$$\therefore \quad \frac{\alpha}{1-\alpha} = \sqrt{\frac{K_w}{K_aK_b}}$$

There is an important issue that needs clarification before we move on further. In this case, we can see that both the ions (i.e., cation and anion) get hydrolyzed to produce a weak acid and a weak base (hence, we cannot predict whether the solution is acidic, basic or neutral). We have considered the degree of hydrolysis of both the ions to be the same. Now we present an explanation as to why this is incorrect and then state reasons for the validity of this assumption.

Actually the hydrolysis reaction given earlier,

$$CH_3COO^- + NH_4^+ + H_2O \;\; CH_3COOH + NH_4OH$$

is made up of the following three reactions,

$$CH_3COO^- + H_2O \;\; CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \;\; NH_4OH + H^+$$

$$H^+ + OH^- \;\; H_2O$$

If we add these three reactions, the net reaction is the one stated previously. This suggests that both CH_3COO^- and NH_4^+ get hydrolysed independently and their hydrolysis depends on: (i) Their initial

concentration and (ii) the value of K_h which is $\frac{K_w}{K_a}$ for CH_3COO^- and $\frac{K_w}{K_b}$ for NH_4^+. Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore, unless and until the value of $\frac{K_w}{K_a}$ and $\frac{K_w}{K_b}$ or K_a and K_b is same, the degree of hydrolysis of the ions cannot be same.

To explain why this assumption is valid, we need to now look at the third reaction, i.e., combination of H^+ and OH^- ions. It is obvious that this reaction happens only because one reaction produced H^+ ion and the other produced OH^- ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. You will notice that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason, if for any reason a reaction is made to occur to a greater extent by the consumption of any one product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore, we conclude that firstl , the hydrolysis of both the ions occurs more in the presence of each other (due to the consumption of the product ions) than in each other's absence. Secondly, the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of K_h) is affected more than the one whose K_h is greater. Hence we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

Now, to calculate the pH of this solution, we need to understand one more principle. Let us assume that we have an aqueous solution of CH_3COOH. Let us also assume that we do not know whether CH_3COO^- and H^+ are in the solution or not (even though H^+ would be there since the solution is aqueous). We can see that the Q_a for the reaction,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \text{ is zero (if we assume no } CH_3COO^- \text{ or } H^+)$$

$\therefore$ $Q_a < K_a$. The reaction would therefore move forward to reach equilibrium. The same is true when CH_3COO^- and H^+ are present without CH_3COOH. Hence, we conclude that "Any equilibrium that can exist (i.e., when all reactants and/or all products are present) will exist (except when pure solids or liquids are not present, in which case this statement will not be true)".

As can be seen in the hydrolysis reaction,

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons NH_4OH + CH_3COOH,$$

CH_3COOH is present in the solution. This implies that the equilibrium between CH_3COOH, CH_3COO^- and H^+ can exist and therefore would exist.

$$\therefore \quad CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

In fact, the equilibrium between NH_4OH, NH_4^+ and OH^- also exists.

Now, we calculate the pH of the solution as,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$C\alpha \qquad\qquad C(1-\alpha)$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{C(1-\alpha)(H^+)}{C\alpha}$$

$$\therefore \quad [H^+] = K_a \times \left(\frac{\alpha}{1-\alpha}\right)$$

Substituting $\frac{\alpha}{1-\alpha}$ as $\sqrt{\frac{K_W}{K_aK_b}}$

$$[H^+] = K_a \times \left(\frac{\alpha}{1-\alpha}\right)$$

$$= K_a \times \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w K_a}{K_b}}$$

or $$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$



Worked-out Example

54. Calculate (a) pH (b) Degree of hydrolysis (c) hydrolytic constant for 0.1 M CH_3COONH_4 [$K_a(CH_3COOH) = 10^{-6}$]

$K_b\ (NH_4OH) = 10^{-5}$

Solution (a) $pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b = 7 + \frac{1}{2}(6) - \frac{1}{2}(5) = 7.5$

(b) $Kh = \frac{\alpha^2}{(1-\alpha)^2} = \frac{K_w}{K_a K_b} = \frac{10^{-14}}{10^{-6}\ 10^{-5}} = 10^{-3}$

Solving we get

$\alpha \approx 0.03$

(c) Hydrolytic constant = 10^{-3} [Calculated earlier]

(Kh)

Solubility Product (K_{sp})

It is defined only for sparingly soluble salt



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

$$\text{Example } AgCl(s) \rightleftharpoons AgCl(aq) \xrightarrow[\text{ionization}]{100\%} Ag^+(aq) + Cl^-(aq)$$

[A sparingly soluble salt forms a dilute solution. So even a weak electrolyte when dissolved, will dissociate completely. 100% ionized according to ostwald's dilution Law.]

$$AgCl(s) \rightleftharpoons AgCl(aq) \xrightarrow[\text{ionization}]{100\%} Ag^+ + Cl^-(aq)$$

Here AgCl(aq) does not exist. Hence the equilibrium can be represented as:

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$ ..... K_{sp}

Here, K_{sp} is called solubility product

$K_{sp} = [Ag^+][Cl^-]$

Expression of K_{sp} interms of solubility 'S' (in moles L–1) for $A_x B_y$ type salt

$$A_xB_y(s) \rightleftharpoons A_xB_y(aq) \xrightarrow{100\%} xA^{y+} + yB^{x-}$$
$$S \text{ mol } L^{-1} \qquad Sx \qquad Sy$$

K_{sp} is defined for saturated solution only which is the equilibrium constant of the above equilibrium

$[A^{y+}] = Sx$ $A_xB_y \rightleftharpoons xA^{y-} + yB^{x-}$ ..... equilibrium

$[B^{x-}] = Sy$

$K_{sp} = [A^{y+}]^x[B^{x-}]^y = (Sx)^x (Sy)^y$

$= x^x y^y S^{x+y}$ ..... for AxBy type salt solubility of A_xB_y is saturated aqueous solution in moles per litre

Example, (i) for A_2B or AB_2 salt

$K_{sp} = 4S^3$

(ii) for AB type salt $K_{sp} = S^2$



Worked-out Examples

Type I: Solubility in Pure Water

55. Calculate the concentration of AgCl (g/ml) in the saturated solution at 25°C.

$K_{sp} = 10^{-10}$ Ag = 108 Cl = 35.5

Solution $K_{sp} = S^2$

$S = 10^{-5}$ moles of AgCl in moles/litre

$\equiv 10^{-8}$ moles of AgCl in moles/ml

$\equiv 143.5 \times 10^{-8}$ g/ml

$\equiv 1.435 \times 10^{-6}$ g/ml

Type II: Solubility in Solution Containing Common Ions

56. Calculate solubility of Ag_2SO_4 in (i) water (ii) 0.1 M $AgNO_3$

$K_{sp} = 4 \times 10^{-15}$ (iii) 0.1 M Na_2SO_4

Solution (a) $K_{sp} = 4s^3$

$4 \times 10^{-15} = 4S^3$

$S^3 = \dfrac{10^{-15}}{4}$ $S = 10^{-5}$

Solubility in pure water = 10^{-5} moles per litre

(b) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$

$(2S_1 + 0.1) \quad S_1$

We have to take the total concentration of $Ag^{\oplus}$ ion (common ion) in the expression of K_{sp}

$AgNO_3(aq) \longrightarrow Ag^+(0.1M) + NO_3^-$

Because of common ion present, the solubility will decrease and the equilibrium will shift towards reactant side.

$S_1 < 10^{-5}$ (Because solubility has now decreased)

$K_{sp} = 4 \times 10^{-15} = (2S_1 + 0.1)^2 S_1$

$= 4S_1^3$ ..... $(S < 10^{-15})$

$\approx (0.1)^2 S_1$

$S_1 \approx 4 \times 10^{-13}$ M

(c) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+ + SO_4^{2-}$

$2S_2 \quad (0.1 + S_2)$

$Na_2SO_4(aq) \longrightarrow 2Na^+ + SO_4^{2-}$

$(0.1)M \quad (2 \times 0.1)M \quad (0.1)M$

Solubility is assumed to be maximum solubility, minimum solubility has no limit.

$K_{sp} = 4 \times 10^{-15} = (2S_2)^2 (0.1 + S_2)$

$4 \times 10^{-15} = (4 S_2^2) (0.1 + S_2) \quad S_2 < 10^{-5}$

$10^{-15} \approx S_2^2 \times 0.1$

$S_2 \approx 10^{-7}$

Solubility in water > solubility in Na_2SO_4 > solubility in $AgNO_3$

The solubility in silver nitrate ($AgNO_3$) is less than the solubility in Na_2SO_4. It is because common ion effect is more pronounced for Ag^+ ion (as it is produced in larger amount)

Type III: Solubility in Alkaline Solution

57. Calculate solubility of $Ca(OH)_2$ [$K_{sp} = 4 \times 10^{-12}$] in
(i) water (ii) alkaline solution pH = 13

Solution (i) $4 \times 10^{-12} = 4S^3$

$S = 10^{-4}$ M

(ii) $K_{sp} = 4 \times 10^{-12}$

Now $S < 10^{-4}$ (because of common ion effect)

In alkaline solution, pOH = 1 $\Rightarrow$ [$OH^\ominus$] = 0.1 M

$Ca(OH)_2 \longrightarrow 2OH^- + Ca^{2+} \quad (S_1 + 0.1)$

pOH = 1 $\quad [OH^-] = 0.1$ M

$K_{sp} \approx (0.1 + 2S_1)^2 S_1$

$\approx S_1(0.1)^2$

$S_1 = 4 \times 10^{-10}$ M

Type IV: Solubility of Two Sparingly Soluble Salt in The Same Solvent (Simultaneous Solubility)

58. Calculate the simultaneous solubility of $SrSO_4$ and $BaSO_4$.

$K_{sp}(SrSO_4) = 10^{-13}$

$K_{sp}(BaSO_4) = 6 \times 10^{-14}$

Solution $SrSO_4(s) \rightleftharpoons Sr^{2+} + SO_4^{2-}$

$S_1 \quad (S_1 + S_2)$

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$S_2 \quad (S_1 + S_2)$

$(S_1)(S_1 + S_2) = 10^{-13}$ .....(1)

$S_2(S_1 + S_2) = 6 \times 10^{-14}$ .....(2)

Solving equation (1) and (2) we get

Hence we get $S_1 = \frac{1}{4} \times 10^{-6}$

$S_1 = 0.25 \times 10^{-6}$

Type V: Solubility in Buffer Solution

59. Calculate the solubility of CH_3COOAg ($K_{sp} = 10^{-10}$) in a buffer solution of pH = 5,

$K_a(CH_3COOH) = 10^{-5}$

Solution $CH_3COO\,Ag \xrightarrow{100\%} \underset{(S-x)}{CH_3COO^-} + \underset{S}{Ag^+}\ H^+ = 10^{-5} + x \approx 10^{-5}$

$\Downarrow$

$\underset{(S-x)}{CH_3COO^-} + \underset{(10^{-5}-x)}{H^+} \approx \underset{10^{-5}M}{\longrightarrow} \underset{x}{CH_3COOH}$ ..... $\frac{1}{K_a}$ from base AgOH $\Rightarrow$strong base

Since, the product CH_3COO^- (acetate ion) is consumed by H^+, the solubility equilibrium will shift towards product side. Hence the solubility will be more than the solubility in water.

[Solubility in water = 10^{-5} M Here solubility will be more than 10^{-5}M]

$K_{sp} = (S-x)\,S$ 1

$\frac{1}{K_a} = \frac{x}{(10^{-5})(S-x)}$ 2

Multiplying, $\frac{K_{sp}}{K_a} = \frac{Sx}{10^{-5}}$

$\Rightarrow \quad \frac{10^{-10}}{10^{-5}} = \frac{Sx}{10^{-5}}$

$Sx = 10^{-10}$

$K_{sp} = S^2 - Sx$

$10^{-10} = S^2 - 10^{-10}$

$S^2 = 2 \times 10^{-10}$

$S = \sqrt{2 \times 10^{-10}}$ M

$S = \sqrt{2} \times 10^{-5}$ M

$= 1.414 \times 10^{-5}$ M (mol L^{-1})

60. Prove that the solubility of CH_3COOAg in a buffer solution of pH = x (x < 7) is

$$S = \sqrt{K_{sp}\left(1+\frac{10^{-pH}}{K_a}\right)}.$$

Solution

$$CH_3COOAg(s) \rightleftharpoons \underset{(S-x)}{CH_3COO^-} + \underset{S}{Ag^+} \quad \ldots\ldots\ldots\ldots K_{sp}$$

[The concentration of $H^{\oplus}$ can be assumed to be constant as the solution is a buffer solution]

$$\underset{(S-x)}{CH_3COO^-} + \underset{10^{-x}}{H^+} \rightleftharpoons \underset{x}{CH_3COOH} \quad \ldots\ldots\ldots\ldots \frac{1}{K_a}$$

$$K_{sp} = (S-x)\,(S)$$

$$\frac{1}{K_a} = \frac{(x)}{(10^{-pH})(S-x)}$$

$$\frac{K_{sp}}{K_a} = \frac{Sx}{10^{-pH}} \qquad Sx = \frac{K_{sp}}{K_a} \times 10^{-pH}$$

$$K_{sp} = \frac{Sx}{10^{-pH}}.K_a$$

$$K_{sp} = S^2 - Sx$$

$$K_{sp} + Sx - S^2$$

$$S = \sqrt{K_{sp} + Sx}$$

$$= \sqrt{K_{sp} + \frac{K_{sp}}{K_a} \times 10^{-pH}}$$

$$S = \sqrt{K_{sp}\left(\frac{1+10^{-pH}}{K_a}\right)}$$

Hence, Solubility increases with the decrease in pH and solubility increases as K_a decreases.

(v) Solubility of CH_3COOAg in an buffer solution of pH = 9

Following the same logic as given in the earlier section,

$$CH_3COOAg\,(s) \rightleftharpoons CH_3COO^-\,(aq) + Ag^+\,(aq)$$

At equilibrium, $\qquad x''-y'' \qquad\qquad x''$

$$CH_3COO^-(aq) + H_2O \rightleftharpoons CH_3COOH + OH^-$$

At equilibrium, $\qquad x''-y'' \qquad\qquad y'' \qquad\qquad 10^{-5}$

Where x'' 'M is the solubility of the salt and y'' the extent to which it is hydrolysed.

$\therefore\ (x''-y'')\,x'' = K_{sp}$

$$\frac{y'' \times 10^{-5}}{(x''-y'')} = \frac{K_w}{K_a}$$

Knowing, K_{sp} and K_a, the solubility can be calculated.

(vi) Solubility of AgCl in an aqueous solution containing NH_3.

Let the amount of NH_3 initially be 'a' M. If the solubility of the salt is *x* moles/*l*, then

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

At equilibrium, $x - y$ x

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$
$$x-y \quad a-2y \quad y$$

Where y is the amount of Ag^+ which has reacted with NH_3.

$\therefore\ (x-y)\,x = K_{sp}$

$$\frac{y}{(x-y)(a-2y)^2} = K_f \text{ (formation constant of } Ag(NH_3)_2^+)$$

Knowing K_{sp} and K_f, the solubility can be calculated.

Preciptiation

Insoluble solids are called precipitates, **(the solution over any precipitate must be saturated.)**

$$AgCl(S) \rightleftharpoons Ag^+ + Cl^-$$

$K_{sp} = [Ag^+][Cl^-]$ ..... at equilibrium

$\Downarrow$

Equilibrium constant

(Reaction Quotient) = K_{in} (ionic product)

Ionic product (K_{in}) has the same expression to that of solubility product but the reaction may or may not be at equilibrium.

Infect K_{in} is the reaction quotient whereas, K_{sp} is the equilibrium constant.

Case I: If $K_{in} < K_{sp}$

$\therefore$ Solution is unsaturated

Hence, more solute can be dissolved till the ionic product K_{in} equals K_{sp}.

Case II $K_{in} = K_{sp}$

Solution is saturated.

Case III $K_{in} > K_{sp}$ $\Rightarrow$ Unstable condition

When ionic product exceeds solubility, product precipitation takes place by union of ions. This precipitation will continue till ionic product equals K_{sp}.



Worked-out Example

61. Given K_{sp} (AgCl) = 10^{-10}

If we mixup (500 ml 2×10^{-5} M NaCl + 500 ml 3×10^{-5} M $AgNO_3$) predict whether AgCl will precipitate or not.

If precipitation occurs calculate the amount of precipitate.

Solution $NaCl(aq) + AgNO_3(aq) \longrightarrow AgCl\downarrow + NaNO_3(aq)$

$[Cl^-] = 10^{-5}$ M (concentration will be half due to doubling the volume.)

$[Ag^+] = 1.5 \times 10^{-5}$ M

$$K_{in} = 1.5 \times 10^{-5} \times 10^{-5}$$

(ionic product) $= 1.5 \times 10^{-10}$

$\Downarrow$

This is more than the K_{sp} of AgCl, thus precipitation will take place.

Let us Calculate the amount of AgCl(s) precipitated.

$Ag^+ + Cl^- \longrightarrow AgCl(s)$..... K_{eq}

This reaction is reverse to dissolution process

So $K_{eq} = \frac{1}{10^{-10}} = 10^{10}$

Thus, forward reaction will go to completion.

1.5×10^{-2} mm	10^{-2} mm		
Ag^+ +	Cl^-	$\longrightarrow$	AgCl(s)
$(1.5 \times 10^{-2} - x)$	$(10^{-2} - x)$	x mm	mass of AgCl precipitated
mm	mm		$= [(x \times 10^{-3})\ (143.5)]$g.
in 10^3 ml	in 10^3 ml		moles

$$[Ag^+] = \frac{(1.5 \times 10^{-2} - x)}{10^3}$$

$\Downarrow$

concentration of Ag^+ left in the solution

$$[Cl^-]_{left} = \left[\frac{10^{-2} - x}{10^3}\right] \qquad [Ag^+]_{left}[Cl^-]_{left} = K_{sp} \qquad \frac{(1.5 \times 10^{-2} - x)}{10^3}\frac{(10^{-2} - x)}{10^3} = 10^{-10}$$

Hence, we can calculate 'x' and find out the amount of AgCl precipitated.



Worked-out Examples

62. 200 ml, $(2 \times 10^{-7}$ M) NaBr + 200 ml $(2 \times 10^{-7}$ M) $AgNO_3$

Calculate mass of AgBr precipitated. K_{sp} (AgBr) = 10^{-12}

Solution $\underset{\substack{2\times10^{-7}\text{ M}\\200\text{ ml}}}{NaBr} + \underset{\substack{2\times10^{-7}\text{ M}\\200\text{ ml}}}{AgNO_3} \longrightarrow AgBr + NaNO_3$

$[Ag^+] = 10^{-7}$

$[Br^-] = 10^{-7}$

$K_{in} = 10^{-14}$

$K_{sp} = 10^{-12}$

So no precipitation will occur.

63. 200 ml; 2×10^{-5} M NaBr + 200 ml 2×10^{-5} M $AgNO_3$

Will there be precipitation. If yes, calculate the amount of AgBr precipitated.

Solution $[Ag^+] = 10^{-5}$

$[Br^-] = 10^{-5}$

$K_{in} = 10^{-10} > 10^{-12}$

So precipitation of AgBr will occur as ionic product is more than K_{sp}.

$Ag^+ + Br^- \longrightarrow AgBr$ (almost completion because $K_{eq} = \frac{1}{K_{sp}} = 10^{12}$ very high)

10^{-5} 10^{-5} –

$(10^{-5}-x)$ $(10^{-5}-x)$ x

mm mm

$$K_{in} = \frac{(10^{-5}-x)}{400}\frac{(10^{-5}-x)}{400} = 10^{-12}$$

Solving the equation we get, $x = 36 \times 10^{-4}$ M

Mass of AgBr = $(36 \times 10^{-4} \times 10^{-3} \times 188) = 6.768 \times 10^{-4}$ g

64. The solubility of A_2X_3 is y mol dm^{-3}. It solubility product is **[IIT-JEE-1997]**

(a) $6y^4$ (b) $64y^4$ (c) $36y^5$ (d) $108y^5$

Solution (d) $A_2X_3 \rightleftharpoons 2A^{3+} + 3X^{2-}$

$2y \quad 3y$

$K_{sp} = [A^{3+}]^2 [X^{2-}] = (2y)^2 (3y)^2$ or $K_{sp} = 108\, y^5$

65. For a sparingly soluble salt $A_p B_q$, the relationship of its solubility product (L_s) with its solubility (S) is **[IIT-JEE-2001]**

(a) Ls = Sp+q.pP.qq (b) Ls = Sp+q.pq.qp (c) ls = Spq.pp.qq (d) Ls = Spq.(p q)p+q

Solution (a) $A_pB_q(s) \rightleftharpoons pA^{+q} + qB^{-p}$ $L_S = (pS)^p.(qS)^q = \overset{pS}{p^p}.q^q.\overset{qS}{S^{(p+q)}}$

66. Solubility product constants (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively, solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order: **[IIT-2008]**

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

Solution (d) S_1 = solubility of MX

S_2 = solubility of MX_2

S_3 = solubility of M_3X

$\therefore \quad S_1^2 = 4 \times 10^{-4}$ or $S_1 = 2 \times 10^{-4}$ (M) $\quad 4\, S_2^1 = 32 \times 10^{-15}$

Or $S_2^3 = 2^3 \times 10^{-15}$ or $S_2 = 2 \times 10^{-5}$ (M)

$M_3X(S) \rightleftharpoons 3M^+ + X^{3-}$

$3S_3 \quad S_3$

$27S_3^4 = 27 \times 10^{-16}$

$S_3 = 10^{-4}$ (M)

67. Solid Ba $(NO_3)_2$ is gradually dissolbed in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{so} for Ba $CO_3 = 5.1 \times 10^{-9}$). **[AIEEE-2009]**

(a) 4.1×10^{-5} M (b) 5.1×10^{-5} M (c) 8.1×10^{-8} M (d) 8.1×10^{-7} M

Solution (b) $Ba(NO_3)_2 + CaCO_3 \rightarrow BaCO_3 + 2NaNO_3$

Here $[CO_3^{-2}] = [Na_2CO_3] = 10^{-4}$M

$$K_{so} = [Ba^{+2}][CO_3^{-2}] \Rightarrow 5.1\times10^{-9} = [Bah^{2+}](10^{-4}) \Rightarrow [Ba^{+2}] = 5.1\times10^{-5}$$

At this value, just precipitation starts.

Formation of Complex Ions

The solubility of an ionic compound increases dramatically if the solution contains a Lewis base that can form a coordinate covalent bond to the metal cation. Silver chloride, for example, is insoluble in water and in acid, but it dissolves in an excess of aqueous ammonia, forming the complex ion $Ag(NH_3)_2^+$. A complex ion is an ion that contains a metal cation bonded to one or more small molecules or ions, such as NH_3, CN^-, or OH^-. In accord with Le Chatelier's principle, ammonia shifts the solubility equilibrium to the right by tying up the Ag^+ ion in the form of the complex ion:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

The stability of a complex ion is measured by its formation constant K^f (or stability constant), the equilibrium constant for formation of the complex ion from the hydrated metal cation. For example, K_f for $Ag(NH_3)_2^+$ is the equilibrium constant for the reaction of $Ag^+(aq)$ with $NH_3(aq)$:

$$Ag^+(aq) + 2NH_3(aq) \rightleftarrows Ag(NH_3)_{2^+}(aq)$$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7 \qquad \text{At } 25°C$$

The large value of K_f for $Ag(NH_3)_2^+$ means that the complex ion is quite stable, and nearly all the Ag^+ ion in an aqueous ammonia solution is therefore present in the form of the complex ion.

The net reaction for dissolution of AgCl in aqueous ammonia is the sum of the equations for the dissolution of AgCl in water and the reaction of Ag^+ with $NH_3(aq)$ to give $Ag(NH_3)_2^+$:

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq)$$

$$\text{Net: } AgCl(s) + 2NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

Its equilibrium constant, K is the product of the equilibrium constants for the reactions added:

$$K = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = (K_{sp})(K_f) = (1.8 \times 10^{-10})\,(1.7 \times 10^7) = 3.1 \times 10^{-3}$$

Because K is much larger than K_{sp} the solubility equilibrium for AgCl in the presence of ammonia lies much farther to the right than it does in the absence of ammonia.

Silver chloride is insoluble in water (left) but dissolves on addition of an excess of aqueous ammonia (right). The increase in the solubility of AgCl on addition of ammonia is shown graphically in figure. In general, the solubility of an ionic compound increases when the metal cation is tied up in the form of a complex ion. The quantitative effect of complex formation on the solubility of AgCl is explored in Example.

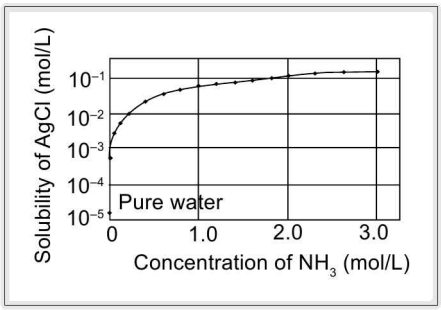


Fig. 7.1

The solubility of AgCl in aqueous ammonia at 25°C increases with increasing ammonia concentration owing to formation of the complex ion $Ag(NH_3)_2^+$. Note that the solubility is plotted on a logarithmic scale.

Worked-out Example

68. What are the concentrations of Ag^+ and $Ag(NH_3)_2^+$ in a solution prepared by adding 0.10 mol of $AgNO_3$ to 1.0 L of 3.0 M NH_3?

Solution Because K_f for $Ag(NH_3)_2^+$ is large, nearly all the Ag^+ from $AgN0_3$ will be converted to $Ag(NH_3)_2^+$:

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \quad K_f = 1.7 \times 10^7$$

To calculate the concentrations, it is convenient to introduce the fiction of 100% conversion of Ag^+ to $Ag(NH_3)_2^+$ followed by a tiny amount of back-reaction [dissociation of $Ag(NH_3)_2^+$] to give a small equilibrium concentration of Ag^+. Conversion of 0.10 mol/L of Ag^+ to $Ag(NH_3)_2^+$ consumes 0.20 mol/L of NH_3. Assuming 100% conversion to $Ag(NH_3)_2^+$, the following concentrations are obtained:

$$[Ag^+] = OM \quad [Ag(NH_3)_2^+] = 0.10\ M$$
$$[NH_3] = 3.0–0.20 = 2.8\ M$$

Dissociation of x mol/L of $Ag(NH_3)_2^+$ in the back-reaction produces x mol/L of Ag^+ and 2x mol/L of NH_3. Therefore, the equilibrium concentrations (in mol/L) are

$$[Ag(NH_3)_2^+] = 0.10 - x$$
$$[Ag^+] = x$$
$$[NH_3] = 2.8 + 2x$$

Let's summarize our reasoning in a table under the balanced equation:

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

Initial cone (M)	0.10	3.0	0
After 100% reaction (M)	0	2.8	0.10
Equilibrium cone (M)	x	2.8 + 2x	0.10 –x

Substituting the equilibrium concentrations into the expression for K_f and making the approximation that x is negligible compared with 0.10 (and with 2.8) gives

$$K_f = 1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{0.10 - x}{(x)(2.8 + 2x)^2} \approx \frac{0.10}{(x)(2.8)^2}$$

$$[Ag^+] = x = \frac{0.10}{(1.7 \times 10^7)(2.8)^2} = 7.5 \times 10^{-10}\ M$$

$$[Ag(NH_3)_2^+] = 0.10–x = 0.10–(7.5 \times 10^{-10}) = 0.10\ M$$

Note that nearly all the Ag^+ is in the form of the complex ion.

SEPARATION OF IONS BY SELECTIVE PRECIPITATION

A convenient method for separating a mixture of ions in a solution is to add a reagent that will precipitate some of the ions but not others. The anions SO_4^{2-} and Cl^-, for example, can be separated by addition of a solution of $Ba(NO_3)_2$. Insoluble $BaSO_4$ precipitates, but Cl^- remains in solution because $BaCl_2$ is soluble. Similarly, the cations Ag^+ and Zn^{2+} can be separated by addition of dilute HCl. Silver chloride, AgCl, precipitates, but Zn^{2+} stays in solution because $ZnCl_2$ is soluble.

In the next section, we will see that mixtures of metal cations, M^{2+}, can be separated into two groups by selective precipitation of metal sulphides, MS. For example, Pb^{2+}, Cu^{2+}, and Hg^{2+}, which form very insoluble sulphides, can be separated from Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, which form more soluble sulphides. The separation is carried out in an acidic solution and makes use of the following solubility equilibrium:

$$MS(s) + 2H_3O^+(aq) \rightleftarrows M^{2+}(aq) + H_2S(aq) + 2H_2O(l)$$

The equilibrium constant for this reaction, called the solubility product in acid, is given the symbol K_{spa}:

$$K_{spa} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2}$$

The separation depends on adjusting the H_3O^+ concentration so that the reaction quotient Q_c exceeds K_{spa} for the very insoluble sulphides but not for the more soluble ones (Table).*

Solubility Products in Acid (K_{spa}) at 25°C for Metal Sulphides

MS	K_{spa}
MnS	3×10^{10}
FeS	6×10^{2}
CoS	3
NiS	8×10^{-1}
ZnS	3×10^{-2}
PbS	3×10^{-7}
CuS	6×10^{-16}
HgS	2×10^{-32}

In a typical experiment, the M^{2+} concentrations are about 0.01 M, and the H_3O^+ concentration is adjusted to about 0.3 M by adding HCl. The solution is then saturated with H_2S gas, which gives an H_2S concentration of about 0.10 M. Substituting these concentrations into the equilibrium constant expression, we find that the reaction quotient $_c$ is 1×10^{-2}:

$$Q_c = \frac{[M^{2+}]_t[H_2S]_t}{[H_3O^+]_t^2} = \frac{(0.01)(0.10)}{(0.3)^2} = 1 \times 10^{-2}$$

This value of Q_c exceeds K_{spa} for PbS, CuS, and HgS change number but does not exceed K_{spa} for MnS, FeS, CoS, NiS, or ZnS. As a result, PbS, CuS, and HgS precipitate under these acidic conditions, but Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} remain in solution.

Qualitative Analysis

Qualitative analysis is a procedure for identifying the ions present in an unknown solution. The ions are identified by specific chemical tests, but because one ion can interfere with the test for another, the ions must first be separated. In the traditional scheme of analysis for metal cations, some 20 cations are separated initially into five groups by selective precipitation.

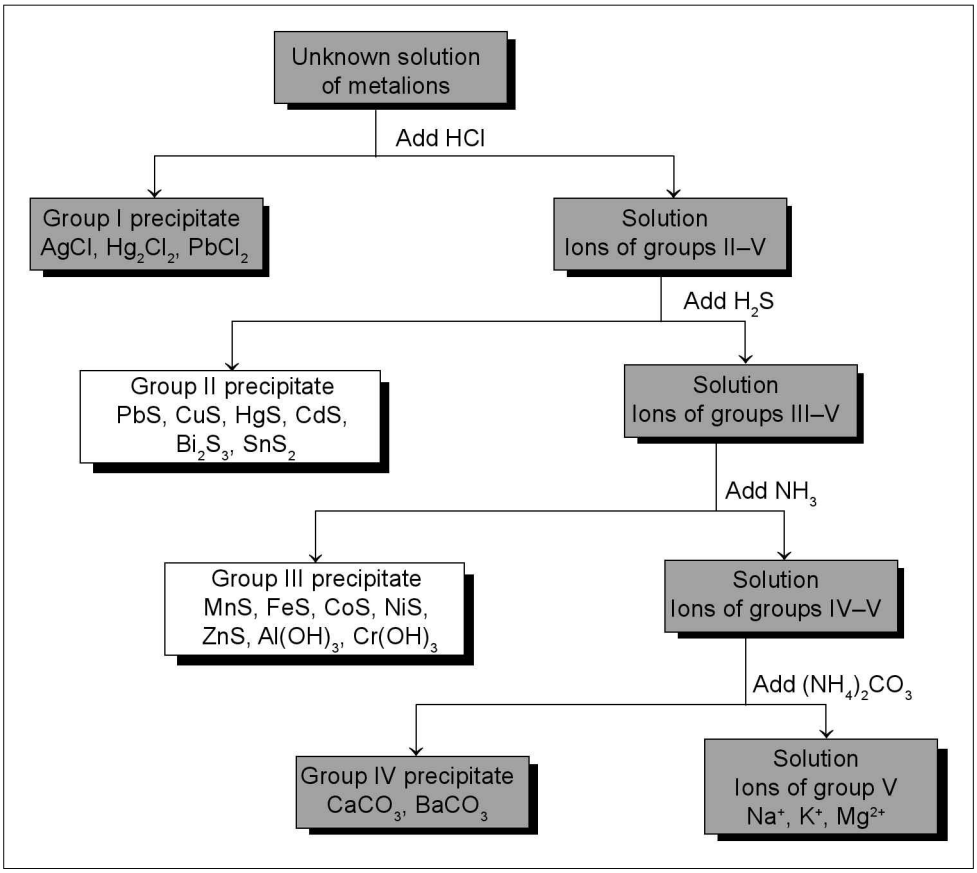


Fig. 7.2

Group I: Ag^+, Hg_2^{2+}, and Pb^{2+} When aqueous HCl is added to the unknown solution, the cations of group I precipitate as insoluble chlorides—AgCl, Hg_2Cl_2, and $PbCl_2$. The cations of groups II-V, which form soluble chlorides, remain in solution. A small amount of the Pb^{2+} also remains in solution because $PbCl_2$ is slightly soluble.

Group II: Pb^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Bi^{3+}, and Sn^{4+} After the insoluble chlorides have been removed, the solution is treated with H_2S to precipitate the cations of group II as insoluble sulphide—PbS, CuS, HgS, CdS, Bi_2S_3, and SnS_2. Because the solution is strongly acidic at this point ($[H_3O^+] = 0.3$ M), only the most insoluble sulphide precipitate. The acid-insoluble sulphide are then removed from the solution.

Group III: Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, and Cr^{3+} At this point, aqueous NH_3 is added, neutralizing the acidic solution and giving an NH_4^+-NH_3 buffer that is slightly basic (pH–8). The decrease in $[H_3O^+]$ shifts the metal sulphide solubility equilibrium to the left, thus precipitating the 2+ cations of group III as insoluble sulphide—MnS, FeS, CoS, NiS, and ZnS. The 3+ cations precipitate from the basic solution, not as sulphide, but as insoluble hydroxides—$Al(OH)_3$ and $Cr(OH)_3$.

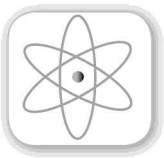
Group IV: Ca^{2+} and Ba^{2+} After the base-insoluble sulphide and the insoluble hydroxides have been removed, the solution is treated with $(NH_4)_2CO_3$ to precipitate the cations of group IV as insoluble carbonates—$CaCO_3$ and $BaCO_3$. Magnesium carbonate does not precipitate at this point because $[CO_3^{2-}]$ in the NH_4^+-NH_3 buffer is maintained at a low value.

Group V: Na^+, K^+, and Mg^{2+} The only ions remaining in solution at this point are those whose chlorides, sulphide, and carbonates are soluble under conditions of the previous reactions. Magnesium ion is separated and identified by addition of a solution of $(NH_4)_2HPO_4$; if Mg^{2+} is present, a white precipitate of $Mg(NH_4)PO_4$ forms. The alkali metal ions are usually identified by the characteristic colours that they impart to a Bunsen flame

Once the cations have been separated into groups, further separations and specific tests are carried out to determine the presence or absence of the ions in each group. In group I, for example, lead can be separated from silver and mercury by treating the precipitate with hot water. The more soluble $PbCl_2$ dissolves, but the less soluble AgCl and Hg_2Cl_2 do not. To test for Pb^{2+}, the solid chlorides are removed, and the solution is treated with a solution of K_2CrO_4. If Pb^{2+} is present, a yellow precipitate of $PbCrO_4$ forms.

Detailed procedures for separating and identifying all the ions can be found in general chemistry laboratory manuals. Although modern methods of metal-ion analysis employ sophisticated analytical instruments, qualitative analysis is still included in many general chemistry laboratory courses because it is an excellent vehicle for developing laboratory skills and for learning about acid-base, solubility, and complex-ion equilibria.

INDICATORS



It is a substance that changes its colour near the equivalence point of any titration.

Indicators are very weak organic acids or bases.

An acid and base indicator is a substance which changes its colour within limits with variation in pH of the solution to which it is added. Indicators, in general are either organic weak acid or weak bases with a characteristics of having different colours in the ionized and unionized form. Example, phenophthalein is a weak acid (ionized form is pink and unionized form is colourless).

Acidic Indicator Action (Example HPh)

HPh (Phenolpthalein) is a colourless weak acid

$$\underset{\text{Colurless}}{HPh} \rightleftharpoons H^+ + \underset{\text{(Pink)}}{Ph^-}$$

$$K_{IN} = \frac{[H^+][Ph^-]}{[HPh]}$$

If the solution is acidic, the H^+ by the acid increases and since K_{in} is constant and it does not depend upon the concentration so HPb also increases mean equilibrium will shift towards left means solution remain colourless. By addition of alkali, OH^- will be furnished and that OH^- will combines with H^+ of HPh to form water and equilibrium will moves towards right and therefore solution becomes pink. Thus, HPh appears colourless in acidic and pink in alkaline solution pH range of HPh is (8.3 –10).

$$pH = pK_{In} + \log\frac{[In^-]}{[HIn]}$$

The colour of the indicator changes from colour A to colour B at a particular point known as end point of indicator. At this point means (at this point half of indicator is in the acid form and half in the form of its conjugate form and $pH = pK_{in}$ at the end point.

Indication (Basic) Action of MeOH (Methyl Orange)

When MeOH is dissolved in water and undergoes dissociation to a small extent. The undissociated molecules are yellow while dissociated Me^+ are red in colour.

$$\underset{\text{yello}}{MeOH} \rightleftharpoons \underset{\text{red}}{Me^+} + \underset{\text{colourless}}{OH^-}$$

If the solution is acidic, the H^+ furnished by the acid combines with OH^- ions furnished by the indicators to form undissociated water. This shifts the equilibrium towards right giving red coloured solution.

Therefore in acid solution, this indicator gives red colour. In the presence of alkali, OH^- increases and due to common ion effect the dissociation of MeOH surpress means equilibrium will shifts towards left. Hence, the solution in alkaline medium remains yellow in colour.

Colour of solution depends upon relative amount of ionized form to unionized form (ratio of Me^+/ MeOH).

In general, pH range of indicator lies between $pK_a \pm 1$.

Case I: $pH = pK_{In} - 1$

$$\text{Means } \frac{In^-}{[HIn]} = 0.1 = 10\%$$

Percentage ionization of indicator would be,

$$\frac{In^-}{[In^-]+[HIn]} \times 100\% = \frac{0.10\ HIn}{0.10\ HIn + (HIn)} \times 100\%$$

$$= \frac{1}{11} \times 100 = 9.1\%$$

In fact, $pH = pK_{In} - 1$ is the maximum pH upto which the solution has a distinct colour characteristic of HIn. At pH smaller than this value, more of the indicator is present in the unionized form.

Thus, at pH $pK_{in} - 1$, the solution has a colour characteristic of HIn.

Case II: at $pH = pK_{In} + 1$

$$\text{Mean } \frac{[In^-]}{[HIn]} = 10$$

Percentage of ionization of indicator is

$$\frac{[In^-]}{[In^-]+[HIn]} \times 100\% = \frac{10\ [HIn]}{10\ [HIn]+[HIn]} \times 100\% = \frac{1000}{11} = 91\%$$

Thus, most of the indicator is present in the ionized form and solution gets the characteristic. Infact $pH = pK_{In} + 1$ is the minimum pH upto which the solution has a distinct characteristic colour. At pH greater than this value, still more of the indicator is present in the ionized form. Thus, the solution has a colour characteristic of In^-.



Worked-out Examples

69. An indicator is a weak acid and pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the centre of the hydrogen ion concentrations corresponding to the given pH range, calculate the ionization constant of the indicator.

Solution $pH = -\log [H_3O^+]$, or $\log [H_3O^+] = -pH$

$\therefore$ $[H_3O^+]$ = antilog of (–pH)

for pH = 3.1 $[H_3O^+]_1$ = antilog of (–3.1) = antilog of

for pH = 4.5 $[H_3O^+]_2$ = antilog of (–4.5) = antilog of

Since neutral point lies at the centre of the hydrogen ion concentration in the given pH range, hence $[H_3O^+]$ at the neutral point.

$$[H_3O^+] = \frac{[H_3O^+]_I + [H_3O^+]}{2}$$

$$= \frac{7.94\times10^{-4} + 3.16\times10^{-5}}{2} = 4.13\times10^{-4}\ M$$

Let the indicator be HIn behaving as weak acid, then

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$ [ionization constant of indicator is K_{In}]

$= [H_3O^+]$ {since at neutral point $[In^-] = [HIn]$} $= 4.13 \times 10^{-4}$.

70. Calculate the pH at which an acid indicator with $K_a = 1\ \ 10^{-5}$ changes colour when the indicator concentration is 10^{-3} M. Also report the pH at which coloured ion is 80% present.

Solution $pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$

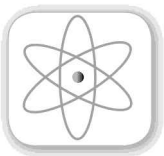
For colour change, $\frac{[In^-]}{[HIn]} = 1$

$\therefore$ $pH = pK_{In} = -\log (1\times10^{-5}) = 5$

now, $[In^-] = 80$, $[HIn] = 20$

$\therefore$ $pH = 5 + \log\frac{80}{20} = 5.6$

PRACTICAL APPLICATION OF THE THEORY OF ACTION OF INDICATOR



The colour change is due to ionization of the acid-base indicator. The unionized form has different colour than the ionized form.

The ionization of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionization is very much low in acids due to common H^+ ions while it is fairly ionized in alkalies. Similarly, if the indicator is a weak base, its ionization is large in acids and low in alkalies due to common OH^- ions.

Considering two important indicators, phenophthalein (a weak acid) and methyl orange (a weak base), Ostwald theory can be illustrated as follows:

Phenolphthalein

It can be represented as HPh. It ionizes in solution to a small extent as:

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons H^+ + \underset{\text{Pink}}{Ph^-}$$

Applying law of mass action,

$$K = \frac{[H^+][Ph^-]}{[HPh]}$$

The undissociated molecules of phenolphthalein are colourless while Ph^- ions are pink in colour. In presence of an acid, the ionization of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of

alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

$$\underset{\text{'Acid form'}}{HIn} + H_2O \rightleftharpoons H_3^+O + \underset{\text{'Base form'}}{In^-}$$

Conjugate acid-base pair

$$K_{In} = \frac{[In^-][H_3^+O]}{[HIn]}; K_{In} = \text{ Ionization constant of indicator, } [H_3^+O] = K_{In} \times \frac{[HIn]}{[In^-]}$$

$$pH = -\log_{10}\ [H_3^+O] = -\log_{10}[KIn] - \log_{10}\frac{[HIn]}{[In^-]}$$

$$pH = pK_{In} + \log_{10}\frac{[In^-]}{[HIn]} \text{ (Handerson equation for indicator)}$$

At equivalence point;

$$[In^-] = [HIn] \text{ and } pH = pK_{In}$$

Methyl Orange

It is a weak base and can be represented as MeOH. It is ionized in solution to give Me^+ and OH^- ions.

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + OH^-$$

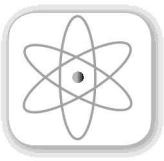
Applying the law of mass action,

$$K = \frac{[Me^+][OH^-]}{[MeOH]}$$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH^- ions increases in the solution and the equilibrium shifts to left hand side (due to common ion effect), i.e., the ionization of MeOH is practically negligible. Thus, the solution acquires the colour of unionized methyl orange molecules, i.e., yellow.

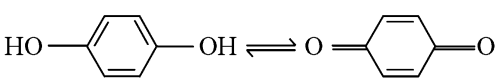
This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

QUINONOID THEORY



According to this theory:

The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

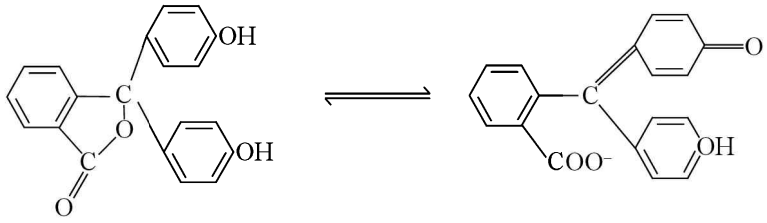


The two forms have different colours. The colour change is due to the interconversion of one tautomeric form into other.

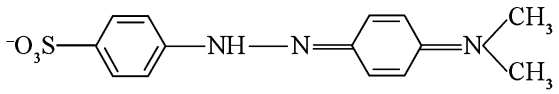
One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during titration the medium changes from acidic to alkaline or vice versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.

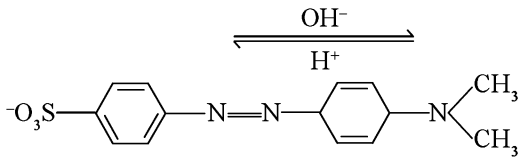
Phenolphthalein has benzenoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The colour of benzenoid form is yellow while that of quinonoid form is red.



Quinonoid form — Acidic solution (red)



Choice of Indicator

The pH at the equivalence point is governed by salt hydrolysis and pH changes sharply at equivalence point.

Condition: The pH at the equivalence point should remain within the pH range of indicator.



Worked-out Example

71. Anacidic indicator changes colour from 75% red (acidic form) to 75% blue (basic form). Calculate change in pH.

Solution Initially,

$$\frac{[In^{\ominus}]}{[HIn]} = \frac{25}{75} = \frac{1}{3} \Rightarrow pH_i = pK_{in} + \log\left(\frac{1}{3}\right)$$

$$pH_f = pK_{in} + \log_{10}\left(\frac{75}{25}\right) = pK_{in} + \log_{10}3$$

Hence, change in pH

$$\Delta pH = pH_f - pH_i$$

$$= 2\log_{10}3 = 0.96$$

ONE CORRECT OPTION TYPE QUESTIONS

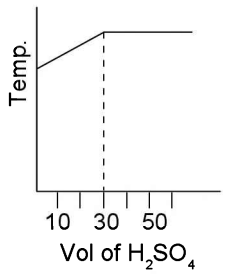
1. On adding 20 mL of N/10 NaOH solution to 10 ml of N/10 HCl, the resulting solution will
(a) Turn blue litmus red
(b) Turn phenolphthalein solution pink
(c) Turn methyl orange red
(d) Will have no effect on red or blue litmus solutions.

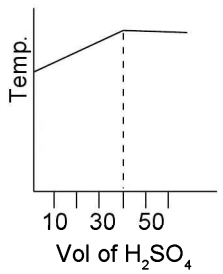
2. HCOOH and CH_3COOH solutions have equal pH. If K_1/K_2 is 4, their molar concentration ratio will be
(a) 2 (b) 0.5
(c) 4 (d) 0.25.

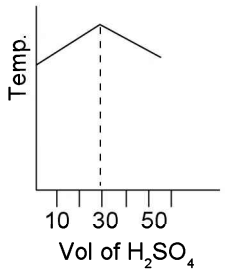
3. An indicator is a weak acid and *p*H range of its colour is 3.1 to 4.5. If the neutral points of the indicator lies on the centre of the hydrogen ion concentration corresponding to given *p*H range, then what is the ionization constant of the indicator?
(a) 4.11×10^{-4} M (b) 4.0
(c) 7.0 (d) 5.0.

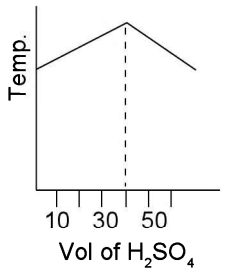
4. A weak base (BOH) with $K_b = 10^{-5}$ is titrated with a strong acid HCl. At 3/4th of the equivalent point, *pH* of the solution is
(a) 5 + log 3 (b) 5 – log 3
(c) 9 + log 3 (d) 8.523.

5. In an experiment to determine the enthalpy of neutralization of sodium hydroxide with sulphuric acid, 50 cm^3 of 0.4 *M* sodium hydroxide were titrated thermometrically with 0.25 *M* sulphuric acid. Which of the following plots give the correct representation?

(a)


(b)


(c)


(d)


6. Percentage ionisation of a weak monobasic acid can be calculated by using the formula
(a) $100\sqrt{\frac{K_a}{C}}$ (b) $\frac{100}{1+10^{(pK_a - pH)}}$
(c) Both (a) and (b) (d) None of these

7. The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is releated to ratio of the concentrations of the conjugated acid (HIn) and base (In) forms of the indicator by the expression.
(a) $\log \frac{[In^-]}{[HIn]} = pH - pH_{In}$
(b) $\log \frac{[In^-]}{[HIn]} = pK_{In} - pH$
(c) $\log \frac{[HIn]}{[In^-]} = pK_{In} - Ph$
(d) $\log \frac{[HIn]}{[In^-]} = pH - pK_{In}$

8. For an aqueous solution to be neutral it must have
(a) pH = 7 (b) $[H^+]=[OH^-]$
(c) $[H^+] = \sqrt{K_w}$ (d) $[H^+] < [OH^-]$

9. 10^{-2} mole of NaOH was added to 10 litre of water. The pH will change by
(a) 4 (b) 3
(c) 11 (d) 7

10. 2 g NaOH is added to 100ml $\left(\frac{M}{20}\right)$ H_2SO_4 solution and the resulting solution is obtained by addition of 900 ml H_2O, then what will be the pH of the solution?
(a) 12.6 (b) 1.4
(c) 10.6 (d) 2.4

11. A 50 ml solution of pH = 1 is mixed with a 50 ml solution of pH = 2. The pH of the mixture will be nearly
(a) 0.76 (b) 1.26
(c) 1.76 (d) 2.26

12. How much volume of pure water needs to be added to 1mL of 0.1M solution of a weak mono basic acid ($K_a = 10^{-5}$) so as to increase its pH by one unit?
(a) 1000 mL (b) 99 mL
(c) 500 mL (d) 999 mL

13. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0 \times 10^{-5}$)?
(a) 4 (b) 2
(c) 6 (d) 1

14. The pH at which an acid indicator with $K_a = 1 \times 10^{-5}$ changes colour when the indicator concentration is 1×10^{-3} *M*, is
(a) 4 (b) 5
(c) 6 (d) 3

15. 50 mL of *2 N* acetic acid mixed with 10 mL of 1 N sodium acetate solution will have an approximate pH of ($K_a = 10^{-5}$)
(a) 4 (b) 5
(c) 6 (d) 7

16. How much volume of pure water needs to be added to 1ml of 0.1M solution of a weak mono basic acid ($K_a = 10^{-5}$) so as to increase its pH by one unit?
(a) 1000 ml (b) 99 ml
(c) 500 ml (d) 999 ml

17. pKa for NH_4^+ ion is 8.24 at 100°C. A solution of 0.2M NH_4OH and a solution of 0.1M HCI are mixed together in equivolume proportion. The pH of the resulting mixture at 100°C ($K_w = 10^{-12}$) will be
(a) 8.24 (b) 10.24
(c) 3.76 (d) 77

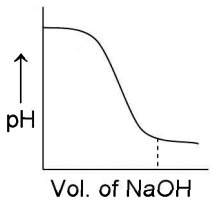
18. 100 mL of a solution of a strong acid HA of pH = 1 was mixed with 200 ml of a solution of the same acid of pH = 2. The pH of the mixture will be approximately.
(a) 1.50 (b) 1.67
(c) 1.40 (d) 3.0

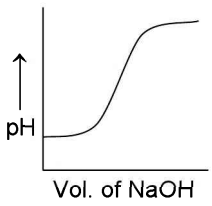
19. The K_{sp} of MS is 3.6×10^{-6}. To a 0.1 M solution of M^{2+} ion, H_2S gas is passed. The sulphide ion concentration of the solution is 2.2×10^{-8} mole L^{-1}. In order that MS may precipitate, what is needed?
(a) HCI to be added into the solution
(b) NH_4Cl(s) to be added followed by NH_4OH into solution
(c) NH_4Cl(s) to be added
(d) Nothing is needed MS will precipitate under the conditions specified

20. A hand book states that the solubility of RNH_2(g) in water at 1 atm and 25°C is 22.41 volumes of RNH_2 (g) per volume of water. (pK_a of $RNH_2 = 4$) Find the max. pOH that can be attained by dissolving RNH_2 in water.
(a) 1 (b) 2
(c) 4 (d) 6

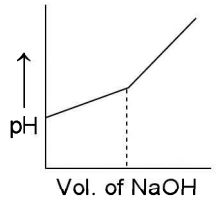
21. 6.0 g weak acid HA (mol. wt. = 60 g/mol.) is dissolved in water and formed $10m^3$ solution. If $K_{a(HA)} = 10^{-9}$, then pOH of solution is: [Given: log 4 = 0.6]
(a) 6.7
(b) greater than 6.7 and less than 7.0
(c) greater than 7.0 and less than 7.3
(d) greater than 7.3

22. Which one of the following curves represents the graph of pH during the titration of NaOH and HCl(aq.)?

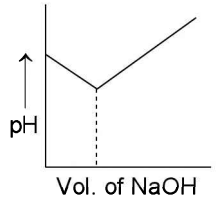
(a)


(b)


(c)



(d)



23. A 1 litre solution containing NH_4C1 and NH_4OH has hydroxide ion concentration of 10^{-6} mol/litre. Which of the following hydroxides could be precipitated when the solution is added to 1 litre solution of 0.1 M metal ions?

(I) $Ba(OH)_2$ ($K_{sp} = 5 \times 10^{-3}$)

(II) $Ni(OH)_2$ ($K_{sp} = 1.6 \times 10^{-16}$)

(III) $Mn(OH)_2$ ($K_{sp} = 2 \times 10^{-13}$)

(IV) $Fe(OH)_2$ ($K_{sp} = 8 \times 10^{-16}$)

(a) I, II, IV (b) IV

(c) II and IV (d) II, III, IV

24. What mass of Agl will dissolve in 1.0 L of 1.0 M NH_3? Neglect change in cone, of NH_3. [Given: K_{sp} (Agl) = 1.5×10^{-16}; $K_f [Ag(NH_3)_2^+] = 1.6 \times 10^7$]; (At. wt. Ag =108; I = 127)

(a) 4.9×10^{-5} g (b) 0.0056 g

(c) 0.035 g (d) 0.011 g

25. Equilibrium constants of T_2O (T or $_1H^3$ is an isotope of $_1H^1$) and H_2O are different at 298 K. Let at 298 K pure T_2O has pT (like pH) is 7.62. The pT of a solution prepared by adding 10 mL of 0.2 M TCl to 15 mL of 0.25 M NaOT is:

(a) 2 – log7 (b) 14 + log 7

(c) 13.24 – log 7 (d) 13.24 + log7

26. Liquid NH_3 ionises to a slight extent. At a certain temp, it's self ionization constant $K_{SIC(NH_3)} = 10^{-30}$. The number of NH_4^+ ions are present per 100 cm^3 of pure liquid are:

(a) 10^{-15} (b) 6.022×10^8

(c) 6.022×10^7 (d) 6.022×10^6

27. Calculate the ratio of $HCOO^-$ and F^- in a mixture of 0.2 M HCOOH ($K_a = 2 \times 10^{-4}$) and 0.1 M HF ($K_a = 6.6 \times 10^{-4}$).

(a) 1 : 6.6 (b) 1 : 3.3

(c) 2 : 3.3 (d) 3.3 : 2

28. If first dissociation of $X(OH)_3$ is 100% where as second dissociation is 50% and third dissociation is negligible then the pH of 4×10^{-3} M $X(OH)_3$ is

(a) 11.78 (b) 10.78

(c) 2.5 (d) 2.22

29. Calcium lactate is a salt of weak organic acid and strong base represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.6 mole in 2 litre solution. pOH of solution is 5.60. If 90% dissociation of the salt takes place then what is pK_a of lactic acid?

(a) 2.8 – log (0.54) (b) 2.8 + log (0.54)

(c) 2.8 + log (0.27) (d) None of these

30. A 1.025 g sample containing a weak acid HX (mol. wt. =82) is dissolved in 60 mL water and titrated with 0.25 M NaOH. When half of the acid was neutralised the pH was found to be 5.0 and at the equivalence point the pH is 9.0. Calculate weight percentage of HX in sample.

(a) 50% (b) 75%

(c) 80% (d) None of these

31. Solubility of AgCl in water, 0.01M $CaCl_2$, 0.01M NaCl and 0.05M $AgNO_3$ are S_1, S_2, S_3 and S_4 respectively then

(a) $S_1 > S_2 > S_3 > S_4$ (b) $S_1 > S_3 > S_2 > S_4$

(c) $S_1 > S_2 = S_3 > S_4$ (d) $S_1 > S_3 > S_4 < S_2$

32. A solution of weak acid HA was titrated with base NaOH. The equivalent point was reached when 40 ml of 0.1 M NaOH has been added. Now 20 ml of 0.1 M HCl were added to titrated solution, the pH was found to be 5.0. What will be the pH of the solution obtained by mixing 20 ml of 0.2 M NaOH and 20 ml of 0.2 M HA?

(a) 7 (b) 9

(c) 11 (d) None of these

33. In the titration of a solution of a weak acid HA and NaOH, the pH is 5.0 after 10 mL of NaOH solution has been added and 5.60 after 20 mL NaOH has been added. What is the value of pK_a for *HA?*

(a) 5.15 (b) 5.3

(c) 5.6 (d) None of these

34. 10 mL of 0.1 M tribasic acid H_3A is titrated with 0.1 M NaOH solution. What is the ratio of $\frac{[H_3A]}{[A^{3-}]}$ at 2nd equivalence point? [Given: $K_{a_1} = 10^{-3}$, $K_{a_2} = 10^{-8}$, $K_{a_3} = 10^{-12}$]

(a) $\simeq 10^{-4}$ (b) $\simeq 10^{+4}$

(c) $\simeq 10^{-7}$ (d) $\simeq 10^{+6}$

35. A solution of 0.1 M in Cl^- and 10^{-4} M CrO_4^{-2}. If solid $AgNO_3$ is gradually added to this solution, what will be the concentration of Cl^- when Ag_2CrO_4 begins to precipitate?
[K_{sp} (AgCl) = 10^{-10} M^2; K_{sp} (Ag_2CrO_4) = 10^{-12} M^3]
(a) 10^{-6} M (b) 10^{-4} M
(c) 10^{-5} M (d) 10^{-9} M

36. The simultaneous solubility of AgCN (K_{sp} = 2.5 × 10^{-6}) and AgCl (K_{sp} = 1.6 × 10^{-10}) in 1.0 M NH_3(aq.) are respectively:
[Given: $K_f[Ag(NH_3)_2^+] = 10^7$]
(a) 0.037, 5.78 × 10^{-8} (b) 5.78 × 10^{-8}, 0.037
(c) 0.04, 6.25 × 10^{-8} (d) 1.58 × 10^{-3}, 1.26 × 10^{-5}

37. What is [Ag^+] in a solution made by dissolving both Ag_2CrO_4 and $Ag_2C_2O_4$ until saturation is reached with respect to both salts?
[K_{sp} ($Ag_2C_2O_4$) = 2 × 10^{-11},
K_{sp} (Ag_2CrO_4) = 2 × 10^{-12}]
(a) 2.80 × 10^{-4} (b) 7.6 × 10^{-5}
(c) 6.63 × 10^{-6} (d) 3.52 × 10^{-4}

38. The pH of a monobasic weak acid HA (pK_a = 5) is 5. Its degree of dissociation is
(a) 1 (b) 0.1
(c) 0.5 (d) 0.25

39. The K_a (dissociation constant) of weak monobasic acid is 10^{-6}. The equilibrium constant for its reaction with NaOH (neutralization)
(a) 10^6 (b) 10^{-8}
(c) 10^{-6} (d) 10^8

40. The equilibrium constant for the following reaction at 25°C is

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$$

[Given: $K_1(H_2S) = 10^{-7}$ and $K_2(H_2S) = 10^{-14}$]
(a) 10^{-7} (b) 10^{-14}
(c) 1 (d) 10^7

41. The hydrolysis constant for $ZnCl_2$ will be
(a) $K_h = \frac{K_w}{K_b}$ (b) $K_h = \frac{K_w^2}{K_b}$
(c) $K_h = \frac{K_w^2}{K_b^2}$ (d) $K_h = \frac{K_b}{K_w^2}$
Where K_b is effective dissociation constant of base Zn^{++}

42. 0.01 mol of $AgNO_3$ is gradually added to 1 litre of a solution, which is 0.1 M in Na_2CrO_4 and 0.005 M in $NaIO_3$. If K_{sp} values of Ag_2CrO_4 and $AgIO_3$ are 10^{-8} and 10^{-13} respectively, the precipitate(s) i.e., formed first is
(a) $AgIO_3$
(b) Ag_2CrO_4
(c) Both $AgIO_3$ and Ag_2CrO_4
(d) Cannot be predicted

43. If pK_b for CN^- at 25°C is 4.7, the pH of 0.5 M aqueous NaCN solution is ($\log_{10}2$=0.3)
(a) 12 (b) 10
(c) 11.5 (d) 11

44. 20 ml 0.5 M HCl is added to 80 ml 0.1 M NH_4Cl solution. The pH of the resulting mixture
(a) 2 (b) 1
(c) 7 (d) 0.74

45. The pH of 0.05 M $(NH_4)_2SO_4$ (Given: $K_b(NH_3)$ = 10^{-5}; $\log_{10}5$ = 0.69)
(a) 6 (b) 5
(c) 5.2 (d) 4

46. The pH of the mixture of (40 ml 0.1 M $Ba(HCOO)_2$ + 20 ml 0.1 M HCOOH) is
($\log_{10}2$ = 0.3)
Given pK_a (HCO_2H) = 5 (Hypothetical values are given to simplify calculation part)
(a) 5.6 (b) 5.3
(c) 5 (d) 6

47. Consider the following reaction:

$$BaF_2(s) + Na_2C_2O_4(aq) \rightleftharpoons BaC_2O_4 + 2NaF$$

$K_{sp}(BaF_2) = X$ $K_{sp}(BaC_2O_4) = Y$
The expression of equilibrium constant of the following reaction in terms of X and Y:
(a) X/Y (b) Y/X
(c) XY (d) X^2/Y^2

48. An acidic indicator HIn (K_{in} = 10^{-6}) ionises as $HIn \rightleftharpoons H^+ + In^-$. The acid colour predominates over the basic colour when HIn is at least 10 times more concentrated than In^- ion. On the other hand basic colour predominates over the acid colour when the In^- ion is at least 5 times more concentrated than HIn. Hence pH range of the indicator is
(a) 5.0 – 6.7 (b) 7.0 – 8.7
(c) 5.3 – 7.0 (d) 7.0 – 8.1

49. pH of a mixture of 1M benzoic acid (pKa = 4.20) and 1M C_6H_5COONa is 4.5. In 300 ml buffer, benzoic acid is [log 2 = 0.3]
(a) 200 ml (b) 150 ml
(c) 100 ml (d) 50 ml

50. 0.01 mol of $AgNO_3$ is gradually added to 1 litre of a solution, which is 0.1 M in Na_2CrO_4 and 0.005 M in $NaIO_3$. If K_{sp} values of Ag_2CrO_4 and $AgIO_3$ are 10^{-8} and 10^{-13} respectively, the precipitate(s) i.e., formed first is

(a) $AgIO_3$

(b) Ag_2CrO_4

(c) Both $AgIO_3$ and Ag_2CrO_4

(d) Cannot be predicted

51. If pK_b for CN^- at 25°C is 4.7, the pH of 0.5 M aqueous NaCN solution is $(\log_{10}2=0.3)$

(a) 12 (b) 10

(c) 11.5 (d) 11

ANSWER KEYS

1. (b)	**2.** (d)	**3.** (a)	**4.** (d)	**5.** (b)	**6.** (c)	**7.** (a)	**8.** (b)	**9.** (a)	**10.** (a)
11. (b)	**12.** (b)	**13.** (b)	**14.** (b)	**15.** (a)	**16.** (b)	**17.** (a)	**18.** (c)	**19.** (b)	**20.** (b)
21. (c)	**22.** (b)	**23.** (c)	**24.** (d)	**25.** (d)	**26.** (c)	**27.** (c)	**28.** (a)	**29.** (a)	**30.** (c)
31. (b)	**32.** (b)	**33.** (b)	**34.** (c)	**35.** (a)	**36.** (a)	**37.** (d)	**38.** (c)	**39.** (d)	**40.** (c)
41. (b)	**42.** (a)	**43.** (c)	**44.** (b)	**45.** (b)	**46.** (a)	**47.** (a)	**48.** (a)	**49.** (c)	**50.** (a)
51. (c)									

HINTS AND EXPLANATIONS

1. The resulting solution is basic in nature. Phenolphthalein is colourless in acidic solution and pink in basic solution.

2. $HCOOH \rightleftharpoons HCOO^- + H^+$

$$K_1 = \frac{[HCOO^-][H^+]}{[HCOOH]} = \frac{[H^+]^2}{[HCOOH]}$$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_2 = [H^+]^2/[CH_3COOH]$

$$\therefore \quad \frac{K_1}{K_2} = \frac{[CH_3COOH]}{[HCOOH]} = 4$$

$$\text{or} \quad \frac{[HCOOH]}{[CH_3COOH]} = \frac{1}{4} = 0.25.$$

3. $pH = 3.1 = -\log [H^+]$

$[H^+] = 7.9 \times 10^{-4}$ M

$pH = 4.5$

Similarly $[H^+] = 3.2 \times 10^{-5}$ M

$\therefore$ Average of the two hydrogen ion concentrations is $= \dfrac{7.9\times10^{-4} + 3.2\times10^{-5}}{2}$

$= 4.11 \times 10^{-4}$ M

At this position, $[HIn] = [In^-]$

$$\therefore \quad pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$$

$$\Rightarrow \quad pH = pK_{In}$$

$\Rightarrow [H^+] = K_{In} = 4.11 \times 10^{-4}$ M

4. For basic buffer

$$pOH = pK_a + \log \frac{[Salt]}{[Base]}$$

$\because$ $BOH + HCl \longrightarrow BCl + H_2O$

6 = 0 a meq 3a/4m 0 0

At t = 0, at 3/4 th, a/4 $\frac{3a}{4}$ m eg 0 0

equivalence point

At t = t, $\frac{a}{A}$ 0 3a/4 $\quad \therefore$ $pOH = pK_b + \log \dfrac{\frac{3a}{4}/V_T}{\frac{a}{4}/V_T}$

$pOH = pK_b + \log 3 = 5 + \log 3$

$\therefore$ $pH = 14 - 5 - \log 3 = 9 - \log 3 = 8.523$

5. (b) Meq. of H_2SO_4 needed for 20 Meq. of NaOH = 20

Thus, volumes of H_2SO_4 needed = V_{mL}

or $V \times 0.25 \times 2 = 20$ $\quad \therefore$ $V = 40$ mL

Also, temperature increase during neutralization and becomes constant after neutralization.

6. (c) $HA \rightleftharpoons H^+ + A^-$

Initial, C

At equilibrium, $C(1-\alpha)$ $C\alpha$ $C\alpha$

$$K_a = \frac{[H^+][A^-]}{[HA]} \approx C\alpha^2$$

$[1-\alpha \approx 1]$

$$\alpha = \sqrt{\frac{K_a}{C}} \text{ and } C = \frac{K_a}{\alpha^2}$$

$$\%\alpha = 100\sqrt{\frac{K_a}{C}}$$

If α is not very small

$$K_a = \frac{C\alpha^2}{1-\alpha} \qquad K_a = \frac{[H^+]\alpha}{1-\alpha}$$

$$\frac{1-\alpha}{\alpha} = \frac{H^+}{K_a} \qquad \frac{1}{\alpha} - 1 = \frac{H^+}{K_a}$$

$$\frac{1}{\alpha} = \frac{H^+}{K_a} + 1 \qquad \frac{1}{\alpha} = \frac{10^{-pH}}{10^{-pK_a}} + 1$$

$$\frac{1}{\alpha} = 10^{pK_a - pH} + 1 \qquad \alpha = \frac{1}{10^{pK_a - pH} + 1}$$

$$\therefore \quad \%\alpha = \frac{100}{10^{pK_a - pH} + 1}$$

7. (a) $HIn \rightleftharpoons H^+ + In^-$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

$$-\log K_{In} = -\log [H^+] - \log \frac{[In^-]}{[HIn]}$$

$$pK_{In} = pK_a - \log \frac{[In^-]}{[HIn]} \qquad \log \frac{[In^-]}{[HIn]} = pH - pK_{In}$$

8. (b) For neutral solution $[H^+]$ always must be equal to $[OH^-]$

$\therefore$ (b)

9. (a) Old pH = 7

New $[OH^-] = 10^{-2} \times \frac{1}{10} = 10^{-3}$

New pH = 11

Change in pH = 4

$\therefore$ (a)

10. (a) m eq. of NaOH taken $= \frac{2}{40} \times 1000 = 50$

m eq. of H_2SO_4 taken $= 100 \times \frac{1}{20} \times 2 = 10$

$$[OH^-] = \frac{50-10}{1000} = \frac{40}{1000} = 4 \times 10^{-2}$$

$pOH = 2 - \log 4 = 2 - 0.6 = 1.4$

$\therefore$ $pH = 14 - pOH = 14 - 1.4 = 12.6$

11. (b)

12. (b) $pH = \frac{1}{2}[pK_a - \log C]$

Before dilution: $pH = \frac{1}{2}[5+1] = 3$.

After dilution $4 = \frac{1}{2}[5 - \log C]$

$\therefore$ $\log C = -3$, or $C = 10^{-3}$ M

That is, molarity will have to be decreased 100 times or dilution has to be increased 100 times. So, approximately 99 ml of water needs to be added.

$\therefore$ (b)

13. (b) The two conditions when colour of indicator will be visible are derived by,

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

(i) $pH = 5 + \log 10 = 6$

(ii) $pH = 5 + \log 0.1 = 4$

Thus, minimum change in pH = 2.

14. (b) For indicator dissociation equilibrium; being an acid

$$\underset{\text{Colour A}}{HIn} \rightleftharpoons \underset{\text{Colour B}}{H^+ + In^-}$$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

The mid point of the colour range of an indicator HIn is the point at which $[In^-] = [HIn]$.

$\therefore$ $K_{In} = [H^+] = 1 \times 10^{-5}$

$\therefore$ $[H^+] = 1 \times 10^{-5}$

or pH = 5.

15. (a) Meq. of acetic acid $= 50 \times 2 = 100$

Meq. of $CH_3COONa = 10 \times 1 = 10$

$$pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

or $pH = -\log 10^{-5} + \log \frac{10}{100} = 4.$

16. (b) $pH = \frac{1}{2}[pK_a - \log C]$

Before dilution: $pH = \frac{1}{2}[5+1] = 3$

After dilution $4 = \frac{1}{2}[5 - \log C]$

$\therefore$ $\log C = -3$, or $C = 10^{-3}$ M

That is, molarity will have to be decreased 100 times or dilution has to be increased 100 times. So, approximately 99 ml of water needs to be added.

$\therefore$ (b)

17. $\frac{[salt]}{[base]} = 1$ pK_b (NH_4OH)

$= pK_w - pK_a (NH_4^+)$

$= 12 - 8.24 = 3.76$

$\therefore$ The mixture will be basic buffer.

$pOH = 3.76 + \log 1 = 3.76$

$pH = 12 - 3.76 = 8.24$

18. (c) $pH = 1$ $\therefore$ $[HA] = 10^{-1}$ M $\therefore$ 100 mL $\equiv$ 10 millimole

$pH = 2$ $\therefore$ $[HA] = 10^{-2}$ $\therefore$ 200 mL $\equiv$ 2 millimole

300 mL $\equiv \frac{12}{300}$ millimole

$\therefore$ The resulting mixture will be $\frac{12}{300}$ M

$pH = -\log [H^+] = -\log \frac{12}{300} = 1.40$ $\therefore$ (c)

19. Condition of precipitation of MS: $[M^{++}][S^{=}] > Ksp$. But $[M^{++}][S^{=}] = 0.1 \times 2.2 \times 10^{-8}$

$= 2.2 \times 10^{-9}$ I which is less than Ksp. So, MS will not precipitate.

$$H_2S \rightleftharpoons 2H^+ + S^{=}$$

Upon addition of HCI, the ionisation of H_2S will be suppressed by common ion effect. The concentration of S^{2-} ion will decrease. But for precipitation of MS we need to increase S^{2-} ion concentration This can be achieved by adding NH_4OH. OH^- ions produced by the partial ionisation of NH_4OH will combine with H^+ ions to form freebly ionised molecules of water. This would lead to decrease in H^+ ion concentration and hence increase in the degree of dissociation of H_2S.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

20. (b) $n_{RNH_2(g)} = \frac{1 \times 22.41}{0.0821 \times 273} = 1$

$[RNH_2(aq.)] = \frac{n_{RNH_2}}{\text{Volume of solution}} = 1$

α is negligible with respect to 1

so $pOH = \frac{1}{2}[pK_b - \log C] = 2$

21. (c) $[HA] = \frac{\left(\frac{6}{60}\right)}{1000} \Rightarrow 10^{-5}$ M $\alpha = \frac{\sqrt{10^{-9}}}{10^{-5}}$

$\Rightarrow$ 0.01 (negligible with respect to 1)

$\therefore$ $[H^+] = \sqrt{10^{-9} \times 10^{-5}}$

$\Rightarrow \sqrt{10^{-14}}$

$\Rightarrow 10^{-7}$ M, $\because [H^+] < 10^{-6}$ M

So we should consider $[H^+]$ from $H_2O \Rightarrow [H^+]_{total}$ $= 2 \times 10^{-7}$ without considering common ion effect

pH = 6.7, so pOH = 7.3 but due to C.I. effect H^+ from H_2O will be less

so $pH > 6.7$ $\therefore$ pOH of solution exists between 7.0 and 7.3

23. (c) When 1 litre each solution are mixed $[OH^-] = 10^{-6}$ M (Buffer solution)

$M^{n+} = 0.05$ M For $Q = [0.5][10^{-6}]^2 = 5 \times 10^{-14}$

$Q > K_{sp}$ for Fe^{2+} and Ni^{2+}

So $Fe(OH)_2$ and $Ni(OH)_2$ are ppt.

24. (d) Due to higher value of K_f, mostly Ag^+ converted into complex.

$AgI(s) \rightleftharpoons Ag^+(aq.) + I^-(aq.)$; K_{sp}

$Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.)$; K_f

Overall reaction is,

$AgI(s) + 2NH_3(aq.) \rightleftharpoons$
$Ag(NH_3)_2^+(aq.) + I^-(aq.)$

$K_{eq} = K_{sp} \cdot K_f$ $K_{sp} \cdot K_f = \frac{x^2}{1^2}$

$\therefore$ $x = 4.9 \times 10^{-5}$ mol/litre

So mass of AgI required is,
$= 4.9 \times 10^{-5} \times 235 = 0.011$ g

25. (d) $TCl + NaOT \longrightarrow NaCl + T_2O$

Initial 2 3.75

milli-moles

milli-moles of remaining NaOT = 1.75

$\therefore [OT^-] = \frac{1.75}{25} = 7 \times 10^{-2}$ moles

$POT = 2 - \log 7$ $pT + pOT = 7.62 \times 2$

$\therefore pT = 15.24 - 2 + \log 7 = 13.24 + \log 7$

26. (c) $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$;

$[NH_4^+] = \sqrt{K_{SIC}}$ $K_{SIC} = [NH_4^+]\,[NH_2^-]$

$\therefore [NH_4^+] = 10^{-15}$ M $\because$ Number of NH_4^+ ions in $1000\ cm^3$

$= 10^{-15} \times 6.022 \times 10^{-23}$ $\therefore$ Number of NH_4^+ ions in $100\ cm^3$

$= 10^{-15} \times 6.022 \times 10^{23} \times \frac{100}{1000} = 6.022 \times 10^7$

27. (c) $HCOOH(aq.)\ H_2O(l) \rightleftharpoons$

$HCOO^-(aq.) + H_3O^+(aq.)$

C_{1-x} x x + y

$HF(aq.) + HO(l) \rightleftharpoons F^-(aq.) + H_3O^+(aq.)$

$C_2 - y$ y x + y

$\because$ α is very les for both acid so,

$K_a(HCOOH) = \frac{x(x+y)}{C_1}$; $K_a(HF) = \frac{y(x+y)}{C_2}$

$\therefore \frac{x}{y} = \frac{K_a(HCOOH)C_1}{K_a(HF)C_2}$

$\frac{[HCOO^-]}{[F^-]} = \frac{x}{y} = \frac{2\times10^{-4}\times0.2}{6.6\times10^{-4}\times0.1} = \frac{2}{3.3}$

28. (a) First dissociation $X(OH)_3 \longrightarrow X(OH)_2^+ + OH^-$

Second dissociation:

$X(OH)_2^+ \longrightarrow X(OH)_2^+ + OH^-$

Total $[OH^-] = 4 \times 10^{-3} + 2 \times 10^{-3} = 6 \times 10^{-3}$

$pOH = 3 - \log 6 \simeq 2.22$

$\therefore$ $pH = 11.78$

29. (a) $Ca(LaC)_2 \longrightarrow Ca^{2+} + 2LaC^-$

Initial concentration 0.6/2 = 0.3 M

After dissociation,

$[LaC^-] = 2 \times 0.3 \times 0.9 = 0.54$ M

$pH = \frac{1}{2}[pK_w + pK_a + \log(LaC^-)]$ 14–5.6

$= \frac{1}{2}[14 + pK_a + \log(0.54)]$

$pK_a = 2.8 - \log(0.54)$

30. (c) When half acid is neutralized $pH = pK_a$ and at the equivalent point

$pH = \frac{1}{2}[pK_w + pK_a + \log C]$

$= 9 = \frac{1}{2}[14 + 5 + \log C] = C = 0.1$

Let V mL of NaOH is used in titration milli eq. of NaOH = 0.25 × V = milli eq. of salt formed

$\therefore \frac{0.25 \times V}{V + 60} = 0.1 = V = 40$ mL

milli equivalent or milli-moles of acid = 10 wt. of acid = $10 \times 10^{-3} \times 82 = 0.82$ gm

wt. % of acid = $\frac{0.82}{1.025} \times 100 = 80\%$

31. (b) $AgCl \rightleftharpoons Ag^+ + Cl^-$

In $CaCl_2$

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$

0.01 0.01 2×0.01

In NaCl

$NaCl \rightleftharpoons Na^+ + Cl^-$

0.01 0.01 0.01

In $AgNO_3$

$AgNO_3$ Ag^+ + Cl^-

.05 0.05 0.05

common ion effect is maximum in $AgNO_3$

So, $S_1 > S_3 > S_2 > S_4$

$\therefore$ (b)

32. (b) $HA + NaOH \longrightarrow NaA + H_2O$

milli-moles of salt NaA or A^- = 40 × 0.1 = 4

Now	$A^- + H^+ \longrightarrow$	HA
Initial milli-moles	4	2
Final milli-moles	2 —	2

Acidic buffer solution is formed and $[A^-] = [HA]$

$pH = pK_a + \log\frac{[A^-]}{[HA]} \Rightarrow pK_a = 5$

Now, $HA + NaOH \longrightarrow NaA + H_2O$

hydrolysis of A^- will takes place

$$[NaA] = \frac{\text{milli moles of acid}}{\text{Total volume}} = \frac{20\times 0.2}{20+20} = 0.1$$

$$pH = \frac{1}{2}(pK_w + pK_a + \log C) = \frac{1}{2}[14 + 5 - 1] = 9$$

33. (b) Let s is initial milli-moles of HA and molarity of NaOh solution is x

$$HA + NaOH \longrightarrow NaA + H_2O$$

In both cases, solution is acidic, so acidic buffer solution is formed.

$$5 = pK_a + \log \frac{10x}{a-10x}$$

$$\Rightarrow \quad 5.60 = pK_a + \log \frac{20x}{a-20x}$$

$$\Rightarrow \quad 0.60 = \log \frac{20x}{(a-20x)} \times \frac{(1-10x)}{10x}$$

$$\Rightarrow \quad 4 = \frac{2(a-10x)}{(a-20x)}$$

$$\Rightarrow \quad a = 30x \qquad \therefore\ 5 = pK_a + \log \frac{10x}{20x}$$

or $pK_a = 5.3$

34. (c) At second equivalence point, the only species present at appreciable concentration is HA^{2-}

So, $pH = \frac{pK_2 + pK_3}{2} = \frac{8+12}{2} = 10 \quad [H^+] = 10^{-10}$

And $\frac{[H_3A]}{[A^{3-}]} = \frac{[H^+]^3}{K_{a_1}K_{a_2}K_{a_3}} = 10^{-7}$

35. (a) $[Ag^+]$ required for precipitation of AgCl

$$[Ag^+] = \frac{K_{sp}(AgCl)}{[Cl^-]} = 10^{-9}$$

$[Ag^+]$ required for precipitation of

$$Ag_2CrO_4 = \sqrt{\frac{K_{sp}(Ag_2CrO_4)}{[CrO_4^{2-}]}} = \sqrt{\frac{10^{-12}}{10^{-4}}} = 10^{-4}$$

At this point, the concentration of Cl^- ion in the solution can be calculated from K_{sp} (AgCl)

$$\therefore \quad [Cl^-] = \frac{K_{sp}(AgCl)}{[Ag^+]} = \frac{10^{-10}}{10^{-4}} = 10^{-6}\ M$$

36. (a) $AgCl(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + Cl^-(aq.)$

$$K_1 = 1.6\times 10^{-10}\times 10^7 = 1.6\times 10^{-3}$$

$$= \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

$AgCN(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + CN^-(aq.)$

$$K_2 = 2.5\times 10^{-16}\times 10^7 = 2.5\times 10^{-9}$$

$$= \frac{[Ag(NH_3)_2^+][CN^-]}{[NH_3]^2}$$

$$\frac{[Cl^-]}{[CN^-]} = \frac{1.6\times 10^{-3}}{2.5\times 10^{-9}} = 6.4\times 10^5$$

$$K_1 = \frac{x^2}{(1-2x)^2} \Rightarrow \frac{x}{1-2x} = 0.04$$

$$x = 0.037$$

$$\therefore \quad [CN^-] = \frac{0.037}{6.4\times 10^5} = 5.78\times 10^{-8}$$

37. (d) $Ag_2CrO_4(s) \rightleftharpoons \underset{2x+2y}{2Ag^+(aq.)} + \underset{x}{CrO_4^{2-}(aq.)}$

$Ag_2C_2O_4(s) \rightleftharpoons \underset{2y+2x}{2Ag^+(aq.)} + C_2O_4^{2-}(aq.)$

$$\frac{K_{sp_1}}{K_{sp_2}} = \frac{x}{y} = \frac{2\times 10^{-12}}{2\times 10^{-11}} \Rightarrow \frac{x}{y} = 0.1$$

$$2\times 10^{-11} = (2x+2y)^2 \cdot y$$

$$2\times 10^{-11} = 4.84\ y^3 \quad y = 1.6\times 10^{-4};$$

$$\therefore \quad x = 0.16\times 10^{-4}$$

Total $[Ag^+] = 2x + 2y = (2\times 0.16 + 2\times 1.6)\times 10^{-4}$
$= 3.52\times 10^{-4}$

38. (c)

Initially, C – –

$HA \rightleftharpoons H^+ + A^-$

At Equilibrium, $C(1-\alpha)$ $C\alpha$ $C\alpha$

$pH = 5 \Rightarrow [H^+] = C\alpha = 10^{-5}\ M$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$\Rightarrow 10^{-5} = \frac{(C\alpha)\alpha}{1-\alpha} = \frac{10^{-5}\alpha}{1-\alpha}$$

$$\alpha = 1 - \alpha$$

$$\Rightarrow \quad \alpha = 0.5$$

Possible mistake $\Rightarrow \alpha = \sqrt{\frac{Ka}{C}} = \sqrt{\frac{10^{-5}}{10^{-5}}} = 1$

39. (d)

$HA + NaOH \rightleftharpoons NaA + H_2O$

$HA + \overset{+}{N}a + \overset{-}{O}H \rightleftharpoons \overset{+}{N}a + A^- + H_2O$

The reverse reaction to neuralization is salt hydrolysis (andonic hydrolysis this time). If K_h is the

hydrolytic constant the equilibrium constant for neutralization would be

$$\frac{1}{K_h} = \frac{1}{\left(\frac{Kw}{Ka}\right)} = \frac{1}{\frac{10^{-14}}{10^{-6}}} = 10^8$$

From the value of equilibrium constant it seems that the neutralization almost proceeds to completion. We know weak acids are very little dissociated. How can any weak acid. Completely react with a strong base?

$$HA \rightleftharpoons H^+ + A^-$$
$$NaOH \longrightarrow Na^+ + \bar{O}H$$
$$H_2O$$

The H^+ produced due to the dissociation of weak acid is consumed by the $\bar{O}H$ furnished by the base. Therefore, the equilibrium for the weak acid is constantly shifted to the product side driving the neutralization almost to completion.

40. (c) $S^{2-} + H_2O \rightleftharpoons HS^- + \bar{O}H$ ..... K_{eq}

$HS^- \rightleftharpoons H^+ + S^{2-}$ ..... $K_2 = 10^{-14}$

$H_2O \rightleftharpoons H^+ + OH^-$ ..... $K_w = 10^{-14} = K_{eq} K_2$

$$K_{eq} = \frac{K_w}{K_2} = 1$$

41. (b) $Zn^{++} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$

$$\therefore \quad K_h = \frac{[Zn(OH)_2][H^+]^2}{[Zn^{++}]} \qquad \ldots (1)$$

$Zn(OH)_2 \rightleftharpoons Zn^{++} + 2OH^-$

$$\therefore \quad K_b = \frac{[Zn^{++}][OH^-]^2}{[Zn(OH)_2]}, \quad K_w = [H^+]\,[OH^-]$$

$$\therefore \quad \frac{K_w^2}{K_b} = K_h \qquad \therefore \text{ (b)}$$

42. (a) $K_{sp}\,(Ag_2CrO_4) = [Ag^+]^2\,[CrO_4^{2-}]$

$10^{-8} = [Ag^+]^2\ (0.1)$

$[Ag^+ = 10^{-7/2}\ M$

When $[Ag^+] > 10^{-3.5}$ M

Ag_2CrO_4 will be precipitated.

$K_{sp}\,(AgIO_3) = [Ag^+]\,[IO_3^-]$

$10^{-13} = [Ag^+]\ (0.005)$

$[Ag^+] = 2 \times 10^{-11}$ M

When $[Ag^+] > 2 \times 10^{-11}$ M $AgIO_3$ will precipitate out.

Hence, $AgIO_3$ will precipitate first.

43. (c) $pK_b\,(CN^-) = 4.7$

0.5 M

$$\underset{(0.5-x)}{CN^-} + H_2O(l) \rightleftharpoons \underset{x}{HCN} + \underset{x}{\bar{O}H}$$

$$K_b(CN^-) = \frac{[OH^-][HCN]}{[CN^-]} = \frac{x^2}{(0.5-x)} \approx \frac{x^2}{0.5} = 2x^2$$

$pK_b = 2\ pOH - \log_{10}{}^2$

$= 4.7 = 2\ [OH^-]^2$

pOH = 2.5 pH = 11.5

44. (b) $NH_4^+\ H_2O \rightleftharpoons NH_4OH + H^+$

$HCl \longrightarrow H^+ + Cl^-$

Salt hydrolysis can be ignored due to commonion effect.

Hence, pH will be governed by HCl only

Number of HCl = $2.0 \times 0.5 = 10$ mm

Total volume after mixing = 100 ml

$$[H^+] = \frac{10\,mm}{100\,ml} = 0.1 \qquad pH = 1$$

45. (b) $0.05 \times 2 = 0.1 = 10^{-1}$

$$K_h = \frac{K_w}{K_B} = \frac{10^{-14}}{10^{-5}} = 10^{-9} \qquad \alpha = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{10^{-9}}{10^{-1}}}$$

$= 10^{-4}$

$H^+ = \sqrt{10^{-9} \times 10^{-1}} = 10^{-5}$ pH = 5

$$pOH = 7 + \frac{1}{2}pK_B + \frac{1}{2}\log_{10}^{C}$$

46. (a) $pH = pK_a + \log_{10}\frac{[HCOO^-]}{[HCOOH]}$

$$= pK_a + \log_{10}\left[\frac{\text{no. of mm of } (HCO_2^-)}{\text{no. of mm of } (HCO_2H)}\right]$$

$= 5 + \log_{10}(8/2) = 5 + 2\log_{10}{}^2 = 5.6$

47. (a) $BaF_2(s) + 2Na^+(aq) + C_2O_4^{2-}(aq) \rightleftharpoons$

$BaC_2O_4 + 2Na^+(aq) + 2F^-(aq)$

This does not mean that Na is not present in solution. But it will not participate in chemical reaction.

$BaF_2(s) + C_2O_4^{2-}(aq) \rightleftharpoons BaC_2O_4^{2-} + 2F^-(aq)$

$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-$ ..... $K_{sp}\,(BaF_2)$ 1

or $Ba^{2+}(aq) + 2F^-(aq) \rightleftharpoons BaF_2$ ..... $K_{eq} = \frac{1}{K_{sp}}$

$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons BaC_2O_4(s)$ ... K_{eq}

$= \dfrac{1}{K_{sp}(BaC_2O_4)}$ 2

Adding 1 and 2,

$BaF_2 + C_2O_4^{2-} \rightleftharpoons Ba_2O_4 + 2F^-$

48. (a) $pH = pK_{in} + \log\dfrac{[In^-]}{[HIn]}$, where $pK_{in} = 6$

For acid colour to predominate $\dfrac{[In^-]}{[HIn]} \le \dfrac{1}{10}$

$\therefore$ $pH \le 6 - 1$ i.e, 5.0

For base colour to predominate $\dfrac{[In^-]}{[HIn]} \ge 5$

$\therefore$ $pH \ge 6 + \log 5 \Rightarrow pH \ge 6.7$

$\therefore$ (a) $K_{eq} = \dfrac{K_{sp}(BaF_2)}{K_{sp}(BaC_2O_4)}$

49. (c) $pH = pK_a + \log\dfrac{[Salt]}{[Acid]}$

$\therefore$ $4.5 = 4.2 + \log\dfrac{[Salt]}{[Acid]} = \log\dfrac{[Salt]}{[Acid]} = 0.3$

(since $\log 2 = 0.3$)

$\therefore$ $\dfrac{[Salt]}{[Acid]} = 2$

Let V ml 1M C_6H_5COOH solution and $(300 - V)$ 1M C_6H_5COONa solution be mixed together

$[Acid] = \dfrac{V \times 1}{1000} \times \dfrac{1000}{300}$; $[Salt] = \dfrac{(300 - V)}{1000} \times \dfrac{1000}{300}$

$[Acid] = \dfrac{V}{300}$; $[Salt] = \dfrac{300 - V}{300}$

$\therefore$ $\dfrac{300 - V/300}{V/300} = 2$

$= 300 - V = 2V$ $\therefore$ $V = 100$ ml

$\therefore$ (c)

50. (a) $K_{sp}(Ag_2CrO_4) = [Ag^+]^2\,[CrO_4^{2-}]$

$10^{-8} = [Ag^+]^2\ (0.1)$

$[Ag^+ = 10^{-7/2}$ M

When $[Ag^+] > 10^{-3.5}$ M

Ag_2CrO_4 will be precipitated.

$K_{sp}(AgIO_3) = [Ag^+]\,[IO_3^-]$

$10^{-13} = [Ag^+]\ (0.005)$

$[Ag^+] = 2 \times 10^{-11}$ M

When $[Ag^+] > 2 \times 10^{-11}$ M $AgIO_3$ will precipitate out.

Hence, $AgIO_3$ will precipitate first.

51. (c) $pK_b(CN^-) = 4.7$

0.5 M

$\underset{(0.5-x)}{CN^-} + H_2O(l) \rightleftharpoons \underset{x}{HCN} + \underset{x}{\bar{O}H}$

$K_b(CN^-) = \dfrac{[OH^-][HCN]}{[CN^-]} = \dfrac{x^2}{(0.5 - x)} \approx \dfrac{x^2}{0.5}$

$= 2x^2 = 2\,[OH^-]^2$

$pK_b = 2\ pOH - \log_{10}2 = 4.7$

$pOH = 2.5 \Rightarrow pH = 11.5$

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. Which of the following mixture will act as buffer?

(a) H_2CO_3 + NaOH (3 : 2 mole ratio)

(b) H_2CO_3 + NaOH (3 : 4 mole ratio)

(c) NH_4OH + HCl (5 : 4 mole ratio)

(d) NH_4OH + HCl (4 : 5 mole ratio)

2. Dalton's law of partial pressure is not applicable to, at normal conditions

(a) H_2 and N_2 mixture

(b) H_2 and Cl_2 mixture

(c) H_2 and CO_2 mixture

(d) H_2 and O_2 mixture

3. The solubility of CH_3COOAg (K_{sp} = X) in a buffer solution of pH = Y(Y < 7)

(a) increases as the value of Y decreases

(b) decreases as the value of Y decreases

(c) will be greater if the K_a value of the CH_3COOH is greater

(d) will be smaller if the K_a value of the CH_3COOH is greater

4. An acid-base indicator has a Ka of 3.0×10^{-5}. The acid form of the indicator is red and the basic form is blue, then:
   (a) pH is 4.05 when indicator is 75% red
   (b) pH is 5.00 when indicator is 75% blue
   (c) pH is 5.00 when indicator is 75% red
   (d) pH is 4.05 when indicator is 75% blue
5. In the following reaction:
   (a) A is an acid and B the base
   (b) A is a base and B the acid
   (c) C is the conjugate acid of A, and D is the conjugate base of B
   (d) C is the conjugate base of A, and D is the conjugate acid of B
6. When HCl(g) is passed through a saturated solution of common salt, pure NaCl is precipitated because
   (a) HCl is highly soluble in water.
   (b) the ionic product $[Na^+]\,[Cl^-]$ exceeds its solubility product (Ksp).
   (c) the k_{sp} of NaCl is lowered by the presence of Cl^- ions.
   (d) HCl causes precipitation.

ANSWER KEYS

1. (a, c, b) **2.** (b) **3.** (a, d) **4.** (a, b) **5.** (b, c) **6.** (b, d)

HINTS AND EXPLANATIONS

1. (a, c, b) number of meq of weak acid > no of meq of strong base mixed ⇒ Acidic buffer
   number of meq of weak abase > no of meq of strong acid mixed ⇒ Basic buffer
2. (b) H_2 and Cl_2 reacts to form HCl; Dalton's law of partial pressure is valid only for the gases which do not react at ordinary conditions
   ∴ (b)
3. (a, d) $CH_3COOAg \underset{a}{\rightleftharpoons} CH_3COO^- + Ag^+$ ..... K_{sp}

   $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$ ..... $\frac{1}{K_a}$

   (S–a) $\approx 10^{-pH}$ (buffer solution)

   $K_{sp} = (S–a)\,(s)$ 1

   $\frac{1}{K_a} = \frac{(a)(10^{-pH})}{(10^{-pH})(S-a)}$ 2

   solving 1 and 2 we get

   $S = \sqrt{K_{sp}(1+\frac{10^{-pH}}{K_a})}$
4. (a, b)
5. (b, c)
6. (b, d)

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I (ONE OPTION CORRECT)

A weak monoacidic base BOH is titrated against HCl. The pH **of the** solution after the addition of 20 ml and 40 ml HCl are 9 and 8 respectively.

Based on the above write up answer the following questions. Given ($\log_{10}2 = 0.3$)

1. What volume of HCl will be required to reach the equivalence point?
   (a) 40 ml
   (b) 45 ml
   (c) 35 ml
   (d) 50 ml

2. The pK_b value of the weak base BOH is
   (a) 5.4 (b) 4.4
   (c) 6.2 (d) 5.1

3. The pH of the titrant mixture when 5 ml HCl was added is
   (a) 9.8 (b) 11.2
   (c) 4.2 (d) 11.5

COMPREHENSION-II (ONE OPTION CORRECT)

A solution contains 0.01 M conc. each of Zn^{2+}, Mg^{2+}, Cu^{2+} and Mn^{2+} ions, they are to be precipitated as their sulphide by passing H_2S gas (0.1 M) into the solution.

$$K_{sp(ZnS)} = 10^{-18},\ K_{sp(MnS)} = 10^{-22},\ K_{sp(MgS)} = 10^{-12},$$

$$K_{sp(CuS)} = 10^{-13},\ K_{a(H_2S)} = 10^{-21}.$$

4. The pH range within which only MnS is precipitated is
   (a) 1 to 3 (b) 3 to 5.5
   (c) pH > 6 (d) 5.5 to 6

5. In pH range (1 to 5.5), which ions get precipitated
   (a) Mn^{2+}, Zn^{2+}
   (b) Zn^{2+}, Cu^{2+}
   (c) Mg^{2+}, Zn^{2+}
   (d) Mg^{2+}, Cu^{2+}

6. MgS gets precipitated with pH range
   (a) pH > 6
   (b) 3 to 5.5
   (c) 1 to 3
   (d) 5.5 to 6

ANSWER KEYS

1. (b) 2. (d) 3. (a) 4. (a) 5. (a) 6. (a)

HINTS AND EXPLANATIONS

COMPREHENSION-I

1. (b) Let us consider

V= Volume of HCl in ml required to reach equivalence point

N = normality of HCl

VN = number of meq. of base BOH taken

Note V > 80 because pH at equivalence point much be less than 7.

$$BOH + HCl \longrightarrow BCl + H_2O$$

VN	20 N	–	–
(V–20)N	–		20 N

$$pOH = 5 = pK_b + \log\left(\frac{20}{V-20}\right)$$

$$\text{Similarly, } pOH = 6 = pK_b + \log\left(\frac{40}{V-40}\right)$$

$$\log\left(\frac{40}{V-40}\right)\left(\frac{V-20}{20}\right) = 1 = \log 10$$

$$\frac{V-20}{V-40} = 5 \qquad V = 45 \text{ ml}$$

2. (d) $6 = pK_b + \log_{10}\frac{40}{5} = pK_b + 3\log\frac{2}{10}$

$$pK_b = 6 - 3\log\tfrac{2}{10} = 6 - 3\,(0.3) = 5.1$$

3. (a) $pOH = pK_b + \log_{10}\left(\frac{5}{40}\right) = 5.1 - 3\log 2$

$$= 5.1 - 3\,(0.3) = 4.2$$

Hence, pH = 14 – 4.2 = 9.2

COMPREHENSION-II

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

With increase in the concentration of H^+ the equilibrium moves to the reactant side due to common ion effect.

Hence, the greater the pH of the medium the greater is the concentration of S^{2-}.

$K_{sp}(ZnS) = 10^{-10} = [Zn^{2+}][S^{2-}]$

$= (0.01)[S^{2-}]$

$[S^{2-}] = 10^{-16}$

$$10^{-21} = K_a(H_2S) = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{[H^+]^2 10^{-16}}{(0.1)}$$

$[H^+]^2 = 10^{-6}$ M

$[H^+] = 10^{-3}$ M

Hence, pH > 3 ⇒ ZnS will precipitate

$K_{sp}(MnS) = 10^{-22} = [Mn^{2+}][S^{2-}] = (0.01)[S^{2-}]$

$[S^{2-}] = 10^{-20}$

$$10^{-21} = K_a H_2S) = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{[H^+]^2(10^{-20})}{(0.1)}$$

$[H^+] = 0.1$ is

⇒ pH > 1 ⇒ MnS will precipitate.

Similarly, pH > 6 MgS will precipitate.

pH > 5.5 CuS will precipitate.

MATCH THE COLUMN TYPE QUESTIONS

1. For $CH_3COOH(K_a = 10^{-5})$.
Match the following:

	Column I		Column II
(a)	0.1 M 200 ml CH_3COOH +0.1 M 100 ml NaOH	(p)	pH = 5 – log 3
(b)	0.1 M 200 ml CH_3COOH +0.1 M 100 ml NaOH + 0.11 M 100 ml HCl	(q)	pH = 5 + log 3
(c)	0.1 M 200 ml CH_3COOH +0.1 M 50 ml NaOH	(r)	pH = 2 + $2\log_{10} 2$
(d)	0.1 M 200 ml CH_3COOH + 0.1 M 150 ml NaOH	(s)	pH = 5

2. Given K_{sp} of AgCl = 10^{-10} and K_{sp} of $Ag_2SO_4 = 4 \times 10^{-15}$

Column I		Column II	
(a)	Solubility of AgCl in water (saturated solution)	(p)	10^{-5} M
(b)	Solubility of Ag_2SO_4 in water	(q)	1.435×10^{-6} g/ml
(c)	Solubility of Ag_2SO_4 in 0.1 M $AgNO_3$	(r)	4×10^{-13} M
(d)	Solubility of Ag_2SO_4 in 0.1 M Na_2SO_4	(s)	10^{-7} M

ANSWER KEYS

1. (a); s (b); s (c); p (d); q **2.** (a); q (b); r (c); r (d); s

HINTS AND EXPLANATIONS

1. a→ s b→s c→p d→ q

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

(a) 20 mm 10 mm – –
10 mm – 10 mm ″
$pH = pK_a + \log_{10}1 = pK_a = 5$ Hence A → S

(b) 20 mm CH_3COOH in 400 ml

$[CH_3COOH] = C = \frac{2}{400}M = \frac{1}{20}M$

$[H^+] = \sqrt{KaC} = \sqrt{10^{-5}\frac{1}{20}} = 2^{-1/2} \times 10^{-2}$

(c) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
20 mm 5 mm – –
15 mm – 5 mm″

$pH = pK_a + \log_{10}\left(\frac{5}{15}\right) = 5 - \log_{10}3$

Hence C → P

(d) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
20 mm 15 mm – –
15 mm – 5 mm –
5 mm – 15 mm″
$pH = pKa + \log_{10}(15/5) = 5 + \log 3$

(b) 11 mm HCl + 10 mm NaOH ⇒ 1 mm HCl increases in Total vol. 400 ml
Neglecting contribution of CH_3COOH

$[H^+] = \frac{1mm}{400ml} = \frac{1}{400}M$ $pH = 2 + 2\log 2$

2. a→q b→p c→r d→ s

(a) $K_{sp} = S^2$

$S = 10^{-5}$ moles of AgCl in moles/litre
$\equiv 10^{-8}$ moles of AgCl in moles/ml
$\equiv 143.5 \times 10^{-8}$ g/ml
$\equiv 1.435 \times 10^{-6}$ g/ml

(b) $K_{sp} = 4S^3$
$4 \times 10^{-15} = 4S^3$

$S^3 = \frac{10^{-15}}{4}$

$S^3 = \frac{10^{-12}}{400}$ $S = \frac{10^{-4}}{\sqrt{400}} = \frac{10^{-4}}{\sqrt{400}}$

(c) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$
$(2S_1 + 0.1)$ S_1
0.1

$AgNO_3(aq) \longrightarrow Ag^+(0.1) + NO_3^-$

Because of common ion present, the solubility will decrease because the equilibrium will shift towards reactant side.

$S_1 < 10^{-5}$ (Because solubility has now decreased)

$K_{sp} = 4 \times 10^{-5}(2S_1 + 0.1)^2S_1$
$= 4S_1^3$ ..... $(S < 10^{-15})$
$\approx (0.1)^2 S_1$
$S \approx 4 \times 10^{-13}$ M

S_2 $2S_2$ $0.1 + S_2$

(d) $Ag_2SO_4(s) \rightleftharpoons 2Ag^+ + SO_4^{2-}$
$Na_2SO_4(aq) \longrightarrow 2Na^+ + SO_4^{2-}$
0.1 2×0.1 0.1

ASSERTION/REASON TYPE QUESTIONS

In each of the following questions, two statements are given one labelled as the Assertion (A) and the other labelled as the Reason (R). Examine these statements carefully and mark the correct choice as per following instructions.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not a correct explanation of A
(c) A is true but R is false
(d) A is false but R is true

1. Statement-1
The aqueous solution of $CF_3COO^-Na^+$ is more basic than the aqueous solution of $CH_3COO^-Na^+$ for same concentration of salt.
Statement-2
The salt derived from weak acid and strong base hydrolyses to generate basic solution.

2. Statement-1
pH = 5 ⇒ low H^+ concentration in the solution because

Statement-2
The solution must be of weak acid.

3. **Statement-1**
The solubility of AgCl in water decreases if NaCl is added to it.
Statement-2
NaCl is highly soluble in water where as AgCl is sparingly soluble.

4. **Statement-1**
Pure water is neutral at any temperature.
Statement-2
When pH = 7 the solution is neutral at any temperature.

5. **Statement-1**
A sparingly soluble salt (like AgCl) is hardly dissolved in water.
Statement-2
The dissolved part of sparingly soluble salt does not ionize to an appreciable extent.

ANSWER KEYS

1. (d) 2. (c) 3. (b) 4. (c) 5. (c)

HINTS AND EXPLANATIONS

1. (d) CF_3COOH is stronger acid than CH_3CO_2H. Hence, $CF_3CO_2^-$ will hydrolyse to a lesser extent making the medium less basic.

SUBJECTIVE QUESTIONS

1. How much solid $Na_2S_2O_3$ should be added to 1.0 L of water so that 0.0005 mole Cd (OH_2) could just barely dissolve?
K_1 and K_2 for $S_2O_3^-$ complexation with Cd^{++} are 8.3×10^3 and 2.5×10^2, respectively. Ksp $(Cd(OH)_2 = 4.5\times10^{-15}$

2. What is solubility of PbS (a) ignoring the hydrolysis of ions (b) including the hydrolysis of ions (assume pH of solution = 7)?
Given that:
$K_{b_2} Pb(OH)^+ = 1.5\times10^{-8}$
$K_{a_1}(H_2S) = 1\times10^{-7}$
$K_{sp(pbs)} = 1\times10^{-7}$, $Ka_2(H_2S) = 10^{-14}$

3. Calculate the pH after the addition of 90 ml and 100ml respectively of 0.1N NaOH to 100 ml 0.1N CH_3COOH (Given pK_a for CH_3COOH = 4.74).

4. A solution contains a mixture of Ag^+ (0.1M) and Hg_2^{+2} (0.1M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated?
K_{sp} (AgI) = 8.5×10^{-17}
K_{sp} $(Hg_2I_2) = 2.5\times10^{-26}$

5. Calculate the molar solubility of $Mg(OH)_2$ in 1MNH_4Cl.
$K_{sp}Mg(OH)_2 = 1.8\times10^{-11}$
$K_b(NH_3) = 1.8\times10^{-5}$

6. Equal volumes of 0.02 M Ag NO_3 and 0.02 M HCN were mixed. Calculate $[Ag^+]$ at equilibrium given, Ksp (AgCN)= 2.2×10^{-16}
Ka (HCN)= 6.2×10^{-10}

[redacted]TS AND EXPLANATIONS

1. $Cd(OH)_2 \rightleftharpoons Cd^{++} + 2OH^-$

$Ksp = [Cd^{++}]\,[OH^-]^2 = 4.5\times10^{-15}$

$Cd^{++} + S_2O_3^- \rightleftharpoons Cd(S_2O_3)$

$$K_1 = \frac{[Cd(S_2O_3)]}{[Cd^{++}][S_2O_3^{--}]} = 8.3\times10^3$$

$Cd(S_2O_3) + S_2O_3^- \rightleftharpoons Cd(S_2O_3)_2^-$;

$$K_2 = \frac{[Cd(S_2O_3)_2^{--}]}{[Cd][S_2O_3)][S_2O_3^{--}]}$$

2.5×10^2

Assume that $S_2O_3^-$ dose not hydrolyze

$[Cd^{++}] + [Cd(S_2O_2)] + [Cd(S_2O_3)_2^-] = 0.00050$

$[Cd^{++}] + K_1\,[Cd^{++}]\,S_2O_3^-] + K_1K_2\,[Cd^{++}]\,[S_2O_3^-]^2 = 0.00050$

$$\therefore\ [Cd^{++}] = \frac{Ksp}{[OH^-]^2} = \frac{4.5\times10^{-15}}{(0.001)^2} = 4.5\times10^{-9}M$$

Let $[S_2O_3^-] = x$

Then,

$$1 + K_1x + K_1K_2x^2 = \frac{5\times10^{-4}}{4.5\times10^{-9}} = 1.1\times10^5$$

$x = 0.2009$

$$\frac{wt}{m.wt} = .2009 \Rightarrow wt = .2009\times158 = 31.74$$

2. (a) $Pbs(S) \rightleftharpoons Pb^{++} + S^{--}$

$K_{sp} = [Pb^{++}]\,[S^{--}] = S\times S = S^2 = 7\times10^{-29}$

$\therefore\ S = 8.4\times10^{-15}$

(b) Including hydrolysis: The equilibria of interest are,

The equilibria of interest are,

$Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)^+ + H_3O^+$;

$$Kh_1 = \frac{[Pb(OH)]^+[H_3O^+]}{[Pb^{2+}]} = \frac{K_w}{Kb_2(Pb(OH)^+}$$

$$= \frac{10^{-14}}{1.5\times10^{-8}} = 6.7\times10^{-7} \qquad \text{---- (i)}$$

$S^{--} + H_2O \rightleftharpoons HS^- + OH^-$,

$$\frac{K_{H_2} = [HS^-]\times[OH^-]}{[S^{--}]} = \frac{K_w}{K_{a_2}(H_2S)} = 1 \qquad \text{..... (ii)}$$

$HS^- + H_2O \rightleftharpoons HS^- + {}^-OH;\ K_{H_3}$

$$= \frac{K_w}{Ka_1(H_2S)} = 9.1\times10^{-8}$$

$$= \frac{[H_2S][{}^-OH]}{[HS^-]} \qquad \text{----- (iii)}$$

Mass balance expression are:

$[Pb^{2+}]_o = [Pb^{2+}] + [Pb(OH)]^+$ ---------- (a)

$[S^-]_o = [S^-] + [HS^-] + [H_2S]$ ------- (b)

Substituting the value of $[Pb(OH)^+]$ from equation (i) into equation (a)

$$[Pb^{++}]_o = [Pb^{++}] + \frac{Kh_1\times[Pb^{++}]}{[H_3O^+]}$$

$$= [Pb^{++}] = \left\{1 + \frac{Kh_1}{[H_3O^+]}\right\}$$

$$\therefore\ [Pb^{++}] = \frac{[Pb^{2+}]_o}{1 + \frac{Kh_1}{[H_3O^+]}} \qquad \text{-------- (c)}$$

Similarly, using equation (ii) and (iii) in equation (b) we have,

$$[S^{--}] = \frac{[S^{--}]_o}{1 + \frac{Kh_2}{[OH]} + \frac{Kh_2\times Kh_3}{[OH]^2}} \qquad \text{---------- (d)}$$

Now, $PbS(s) \rightleftharpoons Pb^{++} + S^-$

$K_{sp} = [Pb^{++}]\,[S^{--}]$

Substituting the values of $[Pb^{++}]$ and $[S^{--}]$ from equations (c) and (d), we get,

$$K_{sp}(Pbs) = \frac{[Pb^{2+}]_o[S^{--}]_o}{\left(1 + \frac{Kh_1}{[H_3O^+]}\right)\left(1 + \frac{Kh_2}{[\bar{O}H^-} + \frac{Kh_2\times Kh_3}{[\bar{O}H]^2}\right)}$$

If y be the amount of PbS dissolve then,

$[Pb^{2+}]_o = [S^{--}]_o =$ [pH = 7,

$\therefore\ [H_3O^+] = 10^{-7} = [{}^-OH]]$

$$\therefore\ K_{sp}(PbS) = \frac{y^2}{\left(1 + \frac{6.7\times10^{-7}}{10^{-7}}\right)\left(1 + \frac{1}{10^{-7}} + \frac{9.1\times10^{-3}}{10^{-7}}\right)}$$

$$= 7\times10^{-29}$$

On solving, $Y = 1.0146\times10^{-10}$

3. If 90 ml. Of .1N NaOH is added to 100 ml. Of .1N CH_3COOH, acidic buffer will form as,

H_3CCOOH + NaOH	$\longrightarrow$	$H_3CCOONa$ +	H_2
t = 0 .01 eq.		.009 eq.	0 0
.001 eq.		0	.009 eq.

$$pH = pKa + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= 4.74 + \log \frac{9}{1} = 4.74 + .9542 = 5.694$$

If 100 ml of 0.1N NaOH is added to 100 ml of 0.1N CH_3COOH, complete neutralization takes place and the concentration of $H_3CCOONa$

$$= \frac{0.1}{2} M = .05M$$

Now, $$pH = 7 - \frac{1}{2} pKa - \frac{1}{2} \log C$$

$$pH = 5.28$$

4. Let us first calculate $[I^-]$ to precipitate AgI and Hg_2I_2

$$K_{sp}[AgI] = [Ag^+]\,[I^-]$$

$$8.5 \times 10^{-17} = (0.1)\,[I^-]$$

$\therefore$ $[I^-]$ to precipitate as AgI $= \frac{8.5 \times 10^{-17}}{0.1}$

$$K_{sp}(Hg_2I_2) = [Hg_2^{+2}]\,[I^-] = 8.5 \times 10^{-16}\ M$$

$$2.5 \times 10^{-26} = 0.1\,[I^-]^2$$

$\therefore$ $[I^-]$ to precipitate $Hg_2I_2 = 5.0 \times 10^{-13}$ M

$[I^-]$ to precipitate AgI is smaller. Therefore, Ag I will start precipitating first. On further addition of I^- more AgI will precipitate and when $[I^-] \geq 5.0 \times 10^{-13}$ J, Mg_2I_2 will start precipitating. The maximum concentration of Ag^+ at this stage will thus be calculated as:

$$K_{sp}(AgI) = [Ag^+]\,[I^-]$$

$$8.5 \times 10^{-17} = [Ag^+]\,(5.0 \times 10^{-13})$$

or, $$[Ag^+] = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}}$$

$$= 1.7 \times 10^{-4}\ M$$

$\therefore$ Percentage of Ag^+ remained precipitated

$$= \frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17\%$$

Thus percentage of Ag^+ precipitated = 99.83%

5. $Mg(OH)_2(s) \rightleftharpoons Mg^{++} + 2OH^-$ $\quad K_1 = K_{sp}$

$2NH_4^+ + 2^-OH \rightleftharpoons 2NH_4OH$ $\quad K_2 = \frac{1}{K_b^2}$

Add $Mg(OH)_2(s) + 2NH_4^+ \rightleftharpoons$

$Mg^{++} + 2NH_4OH$ $\quad K = \frac{K_{sp}}{K_b^2}$

1M x 2x

Let molar solubility of $Mg(OH)_2$ in 1MNH_4Cl be x

$$\frac{1.8 \times 10^{-11}}{1.8 \times 1.8 \times 10^{-10}} = \frac{x \times (2x)^2}{1^2} = 4x^3 = \frac{.1}{1.8} = \frac{1}{18}$$

$\therefore$ x = .24 M

6. Initially, assume complete precipitation

$Ag^+ + HCN \rightarrow AgCN + H^+$, since the solution were diluted to double volume

$\therefore$ concentration of $[H^+] = \frac{0.02}{2} = 0.01$ M

Now consider the equilibrium,

$AgCN \rightleftharpoons Ag^+ + CN^-$

$Ksp = 2.2 \times 10^{-16} = [Ag^+]\,[CN^-]$

$HCN \rightleftharpoons H^+ + CN^-$

$$Ksp = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]}$$

Since every dissolved CN^- also hydrolyzes into HCN up to a certain extent,

so, $$[Ag^+] = [CN^-] + [HCN]$$

or, $$\frac{2.2 \times 10^{-16}}{[CN^-]} = [CN^-] + \frac{[CN^-](0.01)}{6.2 \times 10^{-10}}$$

$$\Rightarrow \quad [CN^-]^2 = \frac{(2.2 \times 10^{-16})(6.2 \times 10^{-10})}{0.01}$$

$$\Rightarrow \quad [CN^-] = 3.7 \times 10^{-12}$$

so, $$[Ag^+] = \frac{Ksp}{[CN^-]} = \frac{2.2 \times 10^{-16}}{3.7 \times 10^{-12}} = 5.9 \times 10^{-5}\ M$$

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

1. The degree of dissociation of water in a 0.1 M aqueous solution of HC1 at a certain temperature t°C is 3.6×10^{-15}. The temperature t must be:
(a) < 25°C
(b) = 25°C
(c) > 25°C
(d) insufficient data to predict

2. Which one is the correct expression below for the solution containing 'n' number of weak acids?
(a) $[H^+] = \sqrt{\sum_{i=1}^{n} \frac{K_i}{C_i}}$ (b) $[H^+] = \sqrt{\sum_{i=1}^{n} K_i C_i}$
(c) $[H^+] = \sqrt{\sum_{i=1}^{n} K_i C_i}$ (d) none of these

3. The pH of glycine at the first half equivalence point is 2.34 and that at second half equivalence point is 9.60. At the equivalence point (The first inflection point) The pH is:
(a) 3.63 (b) 2.34
(c) 5.97 (d) 11.94

4. The ionization constant *of benzoic acid is* 6.46×10^{-5} *and* lc for silver benzoate is 2.5×10^{-13}. How many times silver benzoate is more soluble in a buffer of pH = 3.19 as compared to its solubility in pure water?
(a) 3.317 (b) 9.5
(c) 1000 (d) 7.5

5. A certain acid-base indicator is red in acid solution and blue in basic solution 75% of the indicator is present in the solution in its blue form at pH = 5. Calculate the pH at which the indicator shows 90% red form?
(a) 3.56 (b) 5.47
(c) 2.5 (d) 7.4

6. Which of the following concentrations of NH_4+ will be sufficient to prevent the precipitation of $Mg(OH)_2$ from a solution which is 0.01 M $MgCl_2$ and 0.1 M NH_3 (aq). Given that: K_5 of Mg $(OH)_2 = 2.5 \times 10^{-11}$ and K_b for NH_3(aq) $= 2 \times 10^{-6}$.
(a) 0.01 M (b) 0.02 M
(c) 0.001 M (d) 0.04 M

7. Calculate the molar solubility of zinc tetrathiocyanato-N-mercurate (II) if its $K_{sp} = 2.2 \times 10^{-7}$.
(a) 0.00380 (b) 0.000469
(c) 0.0095 (d) 0.0183

8. An acid-base indicator which is a weak acid has a pK_a value = 5.45. At what cocentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms? pK_a of acetic acid = 4.75. [log 2 = 0.3]
(a) 4 : 1 (b) 7 : 1
(c) 5 : 1 (d) 2 : 1

9. The indicator constant of phenolphthalein is approximately 10^{-10}. A solution is prepared by adding 100.01 c.c. of 0.01 N sodium hydroxide to 100.00 c.c. of 0.01N hydrochloric acid. If a few drops of phenolphthalein are now added, what fraction of the indicator is converted to its coloured form?
(a) $\frac{2}{3}$ (b) $\frac{3}{4}$
(c) $\frac{1}{2}$ (d) $\frac{9}{11}$

10. A certain mixture of HCI and $CH_3 - COOH$ is 0.1 M in each of the acids. 20 ml of this solution is titrated against 0.1M NaOH. By how many units does the pH change from the start to the stage when the HCI is almost completely neutralized? K_a for acetic acid = 1.8×10^{-6}.
(a) 2.03 (b) 0.775
(c) 2.325 (d) 3.172

11. A buffer solution is made by mixing a weak acid HA ($K_a = 10^{-6}$) with its salt NaA in equal amounts.

What should be the amount of acid or salt that should be added to make 90 ml of buffer solution of buffer capacity. 0.1?

(a) 10 mmoles
(b) 22 mmoles
(c) 9 mmoles
(d) 11 mmoles

12. A sample of water has a hardness expressed as 80 ppm of Ca^{2}+. This sample is passed through an ion exchange column and the Ca^{2}+ is replaced by H+. What is the pH of the water after it has been so treated? [Atomic mass of Ca = 40]

(a) 3 (b) 2.7
(c) 5.4 (d) 2.4

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

13. A 1 litre solution of pH = 1 diluted upto 10 times. What volume of a solution with pH = 2 is to be added in diluted solution, so that pH does not change:

(a) 1 litre (b) 10 litre
(c) 100 litre (d) 25 litre

14. The solubility of a sparingly soluble salt A. B_y in water at 25°C 1.4×10^{-4} M. The solubility product is 1.1×10^{-11}. The possibilities are:

(a) x = 1, y = 2 (b) x = 2, y = 1
(c) x = 1, y = 3 (d) x = 3, y = 1

15. The variation of pH during the titration of 0.5 N Na_2CO3 with 0.5 N HCI is shown in the given graph. The following table indicates the colour and pH ranges of different indicators:

Indicator	*Range of colour change*	*Colour in acid*	*Colour in base*
Thymol blue	1.2 to 2.8	Red	Yellow
Bromocresol red	4.2 to 6.3	Red	Yellow
Bromothymol blue	6.0 to 7.6	Yellow	Blue
Cresolpheth-alein	8.2 to 9.8	Colourless	Red

Based on the graph and the table, which of the following statements are true?

(a) The first equivalence point can be detected by cresolphthalein.
(b) The complete neutralization can be detected by bromothymol blue
(c) The second equivalence point can be detected by bromocresol red.
(d) The volume of HCI required for the first equivalence point is half the volume of HCI required for the second equivalence point.

16. Which of the following solutions when added to 1L of a 0.1 M CH_3COOH solution will cause no change in either the degree of dissociation of CH_3COOH or the pH of the solution. $K_a = 1.8 \times 10^{-5}$ for CH_3COOH?

(a) 3 mM HCOOH ($K_a = 6 \times 10^{-4}$)
(b) 0.1 M CH_3COONa
(c) 1.34 mM HCI
(d) 0.1 M CH_3COOH

17. Buffer solution A of a weak monoprotic acid and its sodium salt in the concentration ratio x : y has pH = (pH),. Buffer solution B of the same acid and its sodium salt in the concentration ratio y : x has pH = $(pH)_2$. If $(pH)_2$—(pH), = 1 unit and (pH), + $(pH)_2$ = 9.5 units, then

(a) $pK_a = 4.75$ (b) $\frac{x}{y} = 2.36$
(c) $\frac{x}{y} = 3.162$ (d) $pK_a = 5.25$

ASSERTION/REASON TYPE QUESTIONS

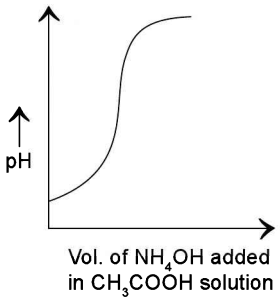
18. **Statement-1:** Solubility of $BaSO_4$ in 0.1 M Na_2SO_4 is 10^{-9} M hence its K_8 is 10^{-18}.

Statement-2: Because for $BaSO_4$ K_8p = (s)2 [symbols have their usual meanings].

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

19. **Statement-1:** It is difficult to distinguish the strengths of the strong acids such as HCI, H2SO4, HNO3,HBr, HI or $HClO_4$ in dilute aqueous solutions.
Statement-2: In dilute aqueous solution all strong acids donate a proton to water and are essentially 100% ionized to produce a solution containing H_30+ ions plus the anions of strong acid .
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation forStatement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

20. **Statement-1:** The titration curve for weak acid and weak base is as follows:

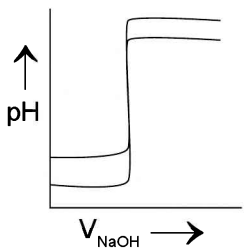


For this titration no suitable indicator is present.
Statement-2: Indicator should change its colour sharply for indication of reaction to be complete, so its pH-range should lie perfectly with in sharp change to avoid experimental error.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

21. **Statement-1:** 0.20 M solution of NaCN is more basic than 0.20 M solution of NaF.
Statement-2: 0.20 M solution of NaCN is more basic than 0.20 M solution of
CH_3COONa.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

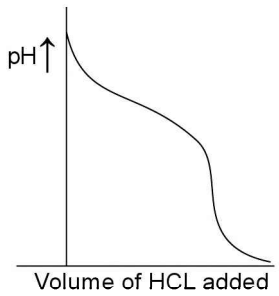
TRUE AND FALSE TYPE QUESTIONS

22. (a) In any strong acid's solution, the concentration of $[OH^-]$ will be zero.
(b) If $\Delta G°$ of a reaction is positive, then the reaction will not proceed at all, in the forward direction for any concentrations of reactants and products.
(c) When titration curves are drawn for
(i) 1M HCI (50 mL) with 1 M NaOH and
(ii) 0.01 M HCI (50 mL) with 0.01 M NaOH on the same graph paper they look like:

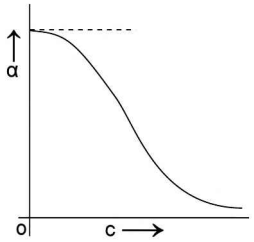


(a) T, T, F
(b) F, F, T
(c) F, T, F
(d) T, F, T

23. (a) When 100 ml of 0.1 M NaCN solution is titrated with 0.1 M HCI solution the variation of pH of solution with volume of HCI added will be



(b) Variation of degree of dissociation a with concentration for a weak electrolyte at a particular temperature is best represented by:



(c) 0.1 M acetic acid solution is titrated against 0.1 M NaOH solution. The difference in pH between 1/ 4 and 3/4 stages of neutralization of acid will be 2 log 3.

(a) T, F, T
(b) F, F, F
(c) T, T, T
(d) F, T, F

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

Read the paragraph and answer the questions (24 – 26) given below:

When 100 ml of $CaCl_2$ solution (1.780 g/L) is mixed with 100 ml Na_2CO_3 solution (1.700 g/L) the pH is adjusted 10 and A precipitate is formed.

Given $pK_{a_1} H_2CO_3 = 6.00$, $pK_{a_2} HCO_3^- = 10.00$
$K_{sp}\ Ca(OH)_2 = 6.46 \times 10^{-6}\ mol^3L^{-3}$,
$K_{sp}\ CaCO_3 = 3.5 - 10^{-9}\ mol^2L^{-2}$

than answer the following question using reasonable assumptions.

24. The pH of Na_2CO_3 solution is
(a) between 8–9 (b) between 11–12
(c) between 9–10 (d) can not be predicted

25. Initial concentration of CO_3^{2-} in solution of mixture is
(a) 7.41×10^{-3} M (b) 8.0×10^{-3} M
(c) 3.31×10^{-3} M (d) 6.94×10^{-3} M

3. About the above passage correct option is
(a) $Ca(OH)_2$ will be found in the form of ppt.
(b) $CaCO_3$ will be found in the form of ppt.
(c) $CaCO_3$ will not be found in the form of ppt.
(d) $CaCO_3$ and $Ca(OH)_2$ both will be found in form of ppt.

COMPREHENSION-2

Consider a solution of CH_3COONH_4 which is a salt of weak acid &weak base. The equilibrium involved in the solutions are:

$CH_3C00^- + H_20$ $CH_3COOH + OH^-$ ……..(1)
$NH_4^- + H_2O$ $NH_4OH + H^+$ ……..(2)
$H^+ + OH^-$ H_2O ……..(3)

If we add these three reactions, then the net reaction is

$CH_3C00^- + NH_4+ + H_20$ ----' $CH_3COOH + NH_4OH$ ……..(4)

Both CH_3C00^- and NH_4' get hydrolyzed independently and their hydrolysis depends on

- their initial concentration
- the value of $\mathbf{K_h}$ which is $\frac{K_W}{K_a}$ for CH_3COO^- and $\frac{K_W}{K_b}$ for NH_4^+.

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore, unless and until the value of $\frac{K_W}{K_a}$ and K_b is same, the degree of hydrolysis of ion cannot be same.

To explain why we assume that degree of hydrolysis of cation and anion is same, we need to now look at the third reaction i.e., combination of H+ and OH– ions. It is obvious that this reaction happens only because one reaction produced H+ ion and the other produced OH– ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason if for any reason a reaction is made to occur to a greater extent by the consumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore, we conclude that firstly, the hydrolysis of both the ions occurs more in the presence of each other (due to consumption of the product ions) than in each other is absence. Secondly, the hydrolysis of the ion which

occurs to a lesser extent (due to smaller value of Kh) is affected more than the one whose Kh is greater. Hence, we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolyzed in the presence of each other.

27. In the hydrolysis of salt of weak acid & weak base:
(a) degree of hydrolysis of cation and anion is different
(b) degree of hydrolysis of cation and anion is same
(c) degree of hydrolysis of cation and anion is different and they can never be assumed same.
(d) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolyzed in the presence of each other.

28. For 0.1 M CH_3COONH_4 salt solution given, $K_{a_{CH_3COOH}} = K_{b_{NH_4OH}} = 2\times10^{-5}$.

In this case: degree of hydrolysis of cation and anion is
(a) exactly same
(b) slightly different
(c) cannot say
(d) different but can be take approximatly same

29. In a solution of $NaHCO_3$, the amphiprotic anion can under ionization to form H^+ ion and hydrolysis to from OH^- ion.

ionization

$$HCO_3^- + H_2O \quad CO_3^{2-} + H_2O$$

hydrolysis

$$HCO_3^- + H_2O \quad HCO_{32} + OH$$

To calculate PH, suitable approximation is:
(a) $[CO_3^{2-}] = [HCO_3]$
(b) degree of ionization = degree of Hydrolysis
(c) both (A) and (b)
(d) neither 'A' nore 'B'

COMPREHENSION-3

When aluminium salts are added to water, $Ae^{3}+$ ions are immediately attracted to the negative end of polar water molecules. They form hexaaquaaluminum(III) ions, $[Al(H_20)_6]^{3}+$. This is often written simply as $Al+^{3}(aq)$. However, the electric field associated with small, highly charged $Al+^{3}$ ion is so intense that it draws electrons in the 0 – H bonds of water towards itself. This enables the water molecules to become donors. In aqueous solution, free water molecules act as bases and the following equilibrium is established;

$$[Al(H_2O)_6]^{3+} + H_2O \quad [Al(OH)(H_2O)_5]^{2+} + H_3O^+$$

Thus, solutions of $Al+^{3}$ salts are acidic, in fact as acidic as vinegar. When a base stronger than H_2O, e.g. $S^{2-}$is added to aqueous aluminium salts further H+ ions are removed from $[Al(H_20)_6]^{3}+$ and insoluble aluminium hydroxide precipitates.

$$2[Al(H_20)_6]^{3}+ (aq) + 3S^{2-} (aq)\ 2[Al(OH)_3(H_20)_3](s) + 3H_2S(g)$$

More stronger base can remove 4H+ ions as follows:

$$[Al(H_20)_6]^{3}+ + 40H^- \quad [Al(OH)_4(H_20)]^- (aq) + 4H_20(\ell)$$

30. Which of $[Al(H_2O)_6]^{3}+$, H_2S or H_20 is the strongest acid?
(a) $[Al(H_2O)_6]^{3+}$ (b) H_2S
(c) H_2O (d) all same.

31. A base which will behave just like S^{2-}:
(a) CO_3^{2-} (b) CH_3OH
(c) NH_4^+ (d) NH_2^-

32. Another ion that would behave similar to $AI+^{3}$ (aq) in forming an acidic salvation:
(a) $Be^{4+2}(aq)$ (b) Ba2(aq)
(c) Na^{+1} (d) $T\ell^+$

MATCH THE COLUMN TYPE QUESTIONS

33. Match the following:

If k_a of HCN = 5×10^{-10}, k_a of HOCN = 3.2×10^{-4}, k_b of NH_3 = 1.8×10^{-5}, k_a of CH_3COOH = 1.8×10^{5}

Column-I	Column-II
(a) 10^{-2} M NaA	(p) pH > 7
(b) 100 ml of 10^{-1} M NaCI + 100 ml of 10^{-1} M HCI + 300 ml of 10^{-1} M NaOH	(q) pH # 7
(c) 10^{-1} M HCI + 10^{-1} M HCN	(r) pH < 7
(d) 10^{-1} M NH_4OCN	(s) pH = 7

34. Match the effect of addition of 0.1 M KOH to 0.1 M, 50 ml H_3PO_4 Ka_1, Ka_2 Ka_3 are the I, II, III ionization constant of H_3PO_4:

Column-I	Column-II
(a) 75 ml of KOH	(p) pH = pKa_1
(b) 25 ml of KOH	(q) pH = pKa_2

(c) 150 ml of KOH (r) $pH = \frac{p^k a_2 + P^k a_3}{2}$

(d) 100 ml of KOH (s) $pH = 7 + \frac{1}{2}[p^k a_3 + \text{locC}]$

35. K_1 and K_2 are first and second ionization constant of H_2CrO_4, K_3 is dissociation constant for NH_3.
Match the following:

Column I	**Column II**
(a) 0.1 M H_2Cr0_4	(p) $pH = 7 + 1/2pK_2 - 1/2pK_3$
(b) 0.1 M $KHCrO_4$	(q) $pH = 7 + 1/2pK_2 + 1/2\log C$
(c) 0.1 M $(NH_4)_2$ $Cr0_4$	(r) $pH = 1/2pK_1 - 1/2\log C$
(d) 0.1 M K_2Cr0_4	(s) $pH = 1/2(pK_1 + pK2)$

36. (Use log 1.8 = 0.26, k_a of formic acid = 1.8×10^{-4}, k_a of acetic acid = 1.8×10^{-5}, k_b of ammonia = 1.8×10^{-5}, k_{a1} of $H_2S = 10^{-7}$ and k_{a2} of $H_2S = 10^{-14}$, for the following matchings)

Match the entries of column II for which the equality or inequality given in the column I are satisfied

Column-I	**Column-II**
(a) 10^{-5}M HCI solution > 0.1 M H_2S solution	(p) α_{water}(degree of dissociation of water)
(b) CH_3COOH solution at pH equal to 4.74 = NH_4OH solution at pH equal to 9.26	(q) $[OH^-]$
(c) 0.1 M CH_3COOH solution = 1.0 M HCOOH solution	(r) a (degree of dissociation of weak electrolytes)
(d) 0.1 M of a weak acid HA ($k_b = 10^{-5}$) solution < 0.01 M of a weak acid HA_2($k_a = 10^{-8}$) solution	(s) pH

SUBJECTIVE TYPE QUESTIONS

SHORT SUBJECTIVE:

37. The equilibrium constants for amino acids are given in terms of succesive ionization constants of the protonated form for example, equilibrium constants for Glycine (NH_2CH_2COOH) are $K_{a1} = 5 \times 10^{-3}$ M and $K_{a2} = 2 \times 10^{-10}$ M. What will be the pH at the Isoelectric point for this amino acid and pH of 0.02 M protonated Glycine in pure water respectively [Take log 2 = 0.30]

38. Given: $Zn(OH)_2$ (s) $Zn(OH)_2$ (aq); $K_1 = 10^{-6}$

$Zn(OH)_2$ (aq) $[Zn(OH)]+ + OH^-$; $K_2 = 10^{-7}$

$[Zn(OH)]+$ (aq) $Zn^{+2} + OH^-$; $K_3 = 10^{-4}$

$Zn(OH)_2$ (aq) + OH^- $[Zn(OH)_3]^-$; $K_4 = 10^3$

$[Zn(OH)_3]^-$ (aq) + OH^- $Zn(OH)_4]^{2-}$; $K_5 = 10$

Find out the negative of logarithm of the solubility of solid $Zn(OH)_2$ at 25°C at pH = 6. Consider $Zn(OH)_2$ makes saturated solution at 25°C. (Write down in OMR sheet if your answer is 1.23 then etc.)

39. 200 mL of 0.2 M H_2SO_4 is diluted to 900 ml by adding water. Solution is then reacted with 100 mL, 0.6 M NaOH solution. The resulting sample is further reacted with 100 mL of 0.2 M $Ca(OH)_2$ solution and then 100 mL H_20 was vaporized. Calculate final pH and write your answer in the from of pH × 10^1.

40. When NaOH solution is gradually added to the solution of a weak acid (HA), the pH of the solution is found to be 5.0 at the addition of 10.0 mL of NaOH and 6.0 at the further addition of 10.0 mL of same NaOH. (Total volume of NaOH = 20 mL) calculate pK_a for HA [log 2 = 0.3]
[Fill your answer in the form of multiple of 10^{-1} for example if your answer is 2.1 then fill 21 as your answer]

41. The K_s of Barium oxalate is 1×10^{-8}. K_1, K_2 of oxalic acid are 1×10^{-3} and 1×10^{-5} respectively. Find the solubility of BaOx in water and the pH of the saturated solution formed.

42. What is ratio of moles of $Mg(OH)_2$ and $Al(OH)_3$ in 1 litre. Their saturated solution (lc of $Mg(OH)_2 = 4 \times 10^{-12}$ and K_{SP} of $Al(OH)_3 = 1 \times 10^{-33}$) give answer by multiplying it with by 10^{-16}.

ANSWER KEYS

1. (c)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (b)	**9.** (a)	**10.** (a)
11. (d)	**12.** (d)	**13.** (a, b, c, d)	**14.** (a, b)	**15.** (a, c, d)	**16.** (c, d)	**17.** (a, c)	**18.** (d)	**19.** (a)	**20.** (a)
21. (b)	**22.** (b)	**23.** (c)	**24.** (b)	**25.** (a)	**26.** (b)	**27.** (d)	**28.** (c)	**29.** (c)	**30.** (a)
31. (a)	**32.** (a)	**33.** (a – p, q), (b – p, q), (c – q, r), (d – q, r)				**34.** (a – q), (b – p), (c – s), (d – r)			
35. (a – r), (b – s), (c – p), (d – q)		**36.** (a – p, q, r, s), (b – p, r), (c – r), (d – p, q, s)				**40.** (51)			

HINTS AND EXPLANATIONS

1. (c) $K_w = 55.5 \times 3.6 \times 10^{-15} \times 0.1 = 2 \times 10^{-14}$
Hence temperature must be > 25°C

2. (b) $HA \rightleftharpoons H^+ + A^-$; $K_1 = \dfrac{[H^+][A^-]}{[HA]}$

$HB \rightleftharpoons H^+ + B^-$; $K_2 = \dfrac{[H^+][B^-]}{[HB]}$

By mass balance,

$[HA]_{initial} = [HA]_{eq} + [A^-] = C_1$

$[HB]_{initial} = [HB]_{eq} + [B^-] = C_2$

By charge balance,

$$[H^+] = \frac{K_1[HA]}{[H^+]} + \frac{K_2[HB]}{[H^+]}$$

$[H^+]^2 = K_1[HA] + K_2[HB] = K_1\{C_1 - [A^-]\} + K_2\{C_2 - [B^-[\}$

If K_1, K_2 are very less then

$$[H^+] = \sqrt{K_1C_1 + K_2C_2 + \ldots K_nC_n} = \sqrt{\sum_{i=1}^{n} K_iC_i}$$

for 'n' number of weak acids

3. (c) $pH = pKa_1 = 2.34$.

$pH = pKa_2 = 9.6$.

$$pH = \frac{pKa_1 + pKa_2}{2} = 5.97.$$

4. (a) In pure water: $C_6H_5COOAg \rightleftharpoons C_6H_5COO^- + Ag^+$

$(s - x)$ s

$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$

$(s - x)$ x x

$s(s - x) = 2.5 \times 10 - 13$ ..... (1)

$$\frac{x^2}{(s-x)} = \frac{10^{-14}}{(6.46 \times 10^{-5})}$$ ..... (2)

Calculate s.

In buffer: $C_6H_5COOAg \rightleftharpoons C_6H_5COO^- + Ag^+$

$(s' - x')$ s'

$C_6H_5COO^- + H^+ \rightleftharpoons C_6H_5COOH$

$S'(s' - x') = 2.5 \times 10^{-13}$ ..... (3)

$$\frac{(s' - x') \times 10^{-3.19}}{x'} = 6.46 \times 10^{-5}$$ ..... (4)

solve for s'.

Calculate $\dfrac{s'}{s}$.

5. (a) $$pH = pK_1 + \log \frac{[In^-]}{[HIn]}$$

$$5 = pK1 + \log \frac{75}{25}$$

$\Rightarrow pK_1 = 4.523$

$\Rightarrow K_1 = 3 \times 10^{-5}$

$$pH = 4.523 + \log \frac{10}{90} = 4.523 - 0.954 = 3.56$$

7. (b) $Zn[Hg(NCS)_4] \rightleftharpoons Zn^{+2} + [Hg(NCS)_4]^{2-}$

$\Rightarrow K_{SP} = S_2$

$\Rightarrow S = \sqrt{22 \times 10^{-8}} = 4.69 \times 10^{-4}$ mol/L

8. (b) Indicator is weak acid $HIN \rightleftharpoons H^+ + In^-$
given it shows colour at half way of ionization

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$ so $pK_a = pK_a = pH = 5.45$

but for CH_3COOh and CH_3 COONa buffer

$$pH = pKa + \log \frac{[Salt]}{[Acid]}$$

$$5.45 = 4.75 + \log \frac{[Salt]}{[Acid]} \Rightarrow \frac{[Salt]}{[Acid]} = \frac{5}{1}$$

9. (a) $NaOH + HCl \rightarrow NaCl + H_2O$

mm 100.01×0.01 100×0.01

conc. $\dfrac{0.001}{200}$ 0 1 1

$HPh \rightleftharpoons H^+ + Ph^-$

$$K_a = \frac{[H^+][Ph^-]}{[HPh]}$$

$$\Rightarrow 10^{-10} = \frac{k_w[Ph]}{[OH^-]+[HPh]} = \frac{10^{-14}\times[Ph]}{\frac{0.01}{200}[HPh]}$$

$$\frac{[Ph}{[HPh]} = \frac{2}{1}$$

so $$\frac{[Ph^-]}{[Ph^-]+[HPh]} = \frac{2}{3}.$$

10. (a) Initial $[H^+] = 0.1$ (H^+ from weak acid can neglect) after neutralization of HCl concentration of $CH_3COOH = \frac{0.1\times 20}{40} = 0.05$

volume would double $[H^+] = \sqrt{K_aC}$

$[H^+] = \sqrt{1.8\times10^{-5}\times0.05} = 9.48 \times\sigma\ 10^{-4}$

pH = 3.03

change in pH unit = 3.03 – 1 = 2.03

11. (d) For buffer capacity of 0.1, we should have $\left(\frac{c+0.1}{c-0.1}\right) = 10$

where c is concentration of weak acid or salt in the buffer solution

So, $(c + 0.1) = 10\ (c - 0.1)$ so $9c = 1.1$

or $c = \frac{1.1}{9}$

So, moles required for 90 solution $= \frac{1.1}{9} \times 90 \times 10^{-3}$ moles = 11 m moles.

12. (d) 10^6 ml water contains 80 gm of $Ca^{2+} = \frac{80}{40}$ moles

= 2 moles of Ca^{2+} = 2 × 2 moles of H^+ ions so 10^3 ml of H_2O will have = 4×10^{-3} moles of H^+ ions so pH = 3 – log 4 = 3 – 0.6 = 2.4.

13. (a, b, c, d)

After dilution $[H^+] = 10^{-2} \Rightarrow$ pH = 2

Let V litre solution of pH = 2 is added in original solution so that pH remains fixed

$$\therefore\ [H^+] = \frac{10^{-2}x + Vx10^{-2}}{10+V} = 10^{-2}$$

This result is independent of volume taken.

14. (a, b)

$K_{SP} = 1.1 \times 10^{-11} = (1.4 \times 10^{-4})^{x+y}\ x^x \cdot y^y$

so we have x + y = 3 (by comparing values)

so, $x^x \cdot y^y = \frac{1.1\times10^{-11}}{1.4\times1.4\times1.4\times10^{-12}} = \frac{110}{1.96\times1.4} = 4$

Hence x = 1, y = 2 or y = 1, x = 2

16. (c, d)

$[H^+] = \sqrt{1.8\times10^{-5}\times0.1} = 1.34\times10^{-3}$M

to which the solution in (C & D) are ISOHYDRIC.

17. (a, c)

$(pH)_1 = pK_a + \log (y/x)$

$(pH)_2 = pK_a + \log (x/y)$

$$(pH)_2 - (pH)_1 = \log\left(\frac{x}{y}\right) - \log\left(\frac{y}{x}\right) = 1$$

$$\Rightarrow \quad \log\left(\frac{x^2}{y^2}\right) = 1$$

so $\frac{x^2}{y^2} = 10 \quad \Rightarrow \quad \frac{x}{y} = 3.162$

$$(pH)_2 + (pH)_1 = 2pK_a + \log\left(\frac{x}{y}\right) + \log\left(\frac{y}{x}\right) = 2$$

$pK_a = 9.5$

so, $pK_a = \frac{9.5}{2} = 4.75$

18. (d) $BaSO_4\ (s) \rightleftharpoons Ba^{2+} + SO_4^{\ 2-}$

s s + 0.1 $K_{SP} = (s)\ (s + 0.1)$

$s < 10^{-9}$

19. (a) All are strong ($\alpha = 1$) (leavelling effect).

21. (b) CN^- is more basic than F^- K_a (HCN) < K_a (HF)

CN^- is more basic than CH_3COO^- K_a (HCN) < K_a (CH_3 COOH)

22. (b) (a) False, $[OH^-] = \frac{10^{-14}}{[H^+]}$ at 25°C

$= \frac{K_w}{[H^+]}$ at any other temperature

(b) False, $\Delta G° > 0$ then only in standard state reaction will not proceed in forward direction.

23. (c) (a) Initially pH will decrease fast, then slowly due to buffer formation and then will decrease fast as buffer action diminishes.

(b) For a weak electrolyte

$$Ka = \frac{C\alpha^2}{(1-\alpha)}$$

When $\alpha << 1$ the $\alpha = \sqrt{\frac{k_a}{C}}$

as C increases $\Rightarrow$ α decreases

as C is tending to zero $\Rightarrow$ α will be unity

(c) At 1/4th neutralisation

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$\left(0.1\times\frac{3}{4}\right)$ $\left(0.1\times\frac{1}{4}\right)$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log\left(\frac{1}{3}\right)$$

at 3/4th neutralization

$pH = pK_a + \log 3$

so difference in pH = $\Delta(pH) = \log 3 - \log \frac{1}{3} =$ 2 log 3.

24. (b) $K_{b_2} = \frac{10^{-14}}{K_{a_2}} = \frac{10^{-14}}{10^{-10}} = 10^{-4}$

$$K_{b_1} = \frac{10^{-14}}{K_{a_1}} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

$K_{b_2} >>> K_{b_1}$ only one protonation step of the CO_3^{2-} has to be considered.

Concentration of Na_2CO_3

$$= \frac{1.700}{105.99} = [CO_3^{2-}] = 0.016 \text{ molL}^{-1}$$

$$K_{b_2} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{[H^+][OH^-]}{\frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}} = \frac{K_w}{K_{a_2}}$$

$$10^{-4} = \frac{[OH^-]^2}{0.016}$$

$[OH^-]^2 = 16 \times 10^{-7}$

$$[OH^-] = \sqrt{160 \times 10^{-8}} = 1.2 \times 10^{-3}$$

$pH = 14 - \log(1.2 \times 10^{-3}) = 14 - 3 + \log 1.2$
$= 14 - 3 + (\log 12 - \log 10)$
$= 14 - 3 + (2\log 2 + \log 3 - 1)$
$= 14 - 3 + (2 \times 0.3010 + 0.4778 - 1)$
$= 11 + (0.6020 + 0.4778 - 1)$
$= 11 + (1.0798 - 1) = 11.0798$

$pH \cong (11 - 12)$

Hence (**B**) is correct.

25. (a) In mixture $[Na_2CO_3]$

$$= \frac{1.700 \text{ g/L}}{105.99 \times 2 \text{ gmol}^{-1}} = 8.0 \times 10^{-3} \text{ mol/L}$$

$$[HCO_3^-] = \frac{K_{b_2}}{[OH^-]} \times [CO_3^{2-}]$$

$$[HCO_3^-] = \frac{10^{-4}}{1.2 \times 10^{-3}} [CO_3^{2-}] = 0.08\,[CO_3^{2-}]$$

also $[CO_3^{2-}] + [HCO_3^-]$ = concentration (Na_2CO_3) in mixture = 8×10^{-3} mol/L

$$[CO_3^{2-}] + 0.08 \times [CO_3^{2-}] = 8 \times 10^{-3}$$

$$[CO_3^{2-}] = \frac{8 \times 10^{-3}}{1.08} = 7.41 \times 10^{-3}$$

Hence **(A)** is correct.

26. (c) $[Ca^{2+}] = \frac{1.780}{110.98 \times 2} = 8.0 \times 10^{-3}$ mol/L

$[OH^-] = 10^{-4}$ $\because$ pH = 10

$K_{IP}\, Ca(OH)_2 = 8 \times 10^{-11} < 6.46 \times 10^{-6}$
(K_{sp} of $Ca(OH)_2$)

$K_{IP} < K_{sp}$ Hence no precipitate of $Ca(OH)^2$ will form.

For $CaCO_3$

$K_{sp} = 8.0 \times 10^{-3} \times 7.41 \times 10^{-3}$
$= 8.0 \times 10^{-5} > 3.31 \times 10^{-4}$

$K_{IP} > K_{sp}$ Hence precipitate will form.

Hence (**B**) is correct.

28. (c) $\because K_a = K_b$

29. (c) $\because PH = \frac{PK_{a_1} + PK_{a_2}}{2}$

33. (a – p, q); (b – p, q); (c – q, r); (d – q, r)

33. (a – q), (b – p), (c – s), (d – r)

33. (a – r), (b – s), (c – p), (d – q)

(a) diprotic weak acid, H^+ only comes from first ionization (K_1)

(b) $HCrO_4^-$ is amphiprotic anion.

(c) $(NH_4)_2\, CrO_4$ it is salt of weak base and weak acid.

(d) Hydolysis of CrO_4^{2-} (polyvalent anion), but only first hydrolysis is apprecitable

36. (a – p, q, r, s); (b – p, r); (c – r); (d – p, q, s)

37. At isoelectric point $pH = \frac{1}{2}[pKa_1 + pKa_2] = \frac{1}{2}[2.3 + 9.7] = 6$

$[H^+] = \sqrt{5 \times 10^{-3} M \times 0.2} = \sqrt{10 \times 10^{-5}} = 10^{-2}$

$pH = -\log [H^+] = 2$

38. Dissolved $[Zn(OH)_2] = [Zn^{+2}]_{aq} + [Zn(OH^+)_2]_{aq} + [Zn(OH_2)_{aq} + [Zn(OH)_3^-] + [Zn)OH)_4]^{2-}$

Now, $[Zn(OH)_2]_{aq} = 10^{-6}$ M in saturated solution.

so, $[Zn(OH]^+ = \frac{10^{-6} \times 10^{-7}}{[OH^-]} = \frac{10^{-13}}{[OH^-]}$

Similarly, $[Zn^{+2}] = \frac{10^{-17}}{[OH^-]^2}$, $[Zn(OH)_3] = 10^{-3}\,[OH^-]$,

$[Zn(OH)_4^{2-}] = K_5\,[Zn(OH)_3^-]\,[OH^-] = (10^{-2}\,M^{-1})\,[OH^-]^2$

Dissolved $Zn(OH)_2 = \frac{10^{-17}}{[OH^-]^2} + \frac{10^{-13}}{[OH^-]} + 10^{-6} + 10^{-3} \times [OH^-] + 10^{-2}\,[OH^-]^2$

$= \frac{10^{-17}}{10^{-16}} + \frac{10^{-13}}{10^{-8}} + 10^{-6} + 10^{-3} \times 10^{-8} + 10^{-18} = 10^{-1} + 10^{-5} + 10^{-6} + 10^{-11} = 10^{-1} - \log Zn(OH)_2\,(aq) = 1$

39. $[H^-] = \left|\frac{(N_1V_1) - (N_2V_2 - N_3V_3)}{V_1+V_2+V_3+700-100)}\right|$

$= \left|\frac{200\times0.2\times2 - 0.6\times100 - 0.2\times2\times100}{200+100+100+700-100}\right|$

$= \left|\frac{80-60-40}{1000}\right| = \frac{20}{1000} = 2\times10^{-2}$

pOH = 1.7

pH = 12.3 so $pH \times 10^1 = 123$

40. Let initial concentration Of HA and NaOH be C_1 & C_2 mol/L and initial volume of HA = V_1mL

$\therefore\ 5.0 = pK_a + \log \frac{10C_2}{(C_1V_1 - 10C_2)}$ ..... (1)

$6.0 = pK_a + \log \frac{10C_2}{(C_1V_1 - 20C_2)}$ ..... (2)

from these we get

$C_1V_1 = 22.5\,C_2$

$\therefore\ 5.0 = pK_a + \log \frac{10C_2}{(C_1V_1 - 10C_2)} = pK_a + \log(0.8)$

$\therefore\ pK_a = 5.1$

$\therefore$ 51

41. $K_{SP} = S^2$

$\Rightarrow$ S 10^{-4} mol/L

Hence in mmol/10L it is 1.

Now $C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$

$[OH^-] = \sqrt{10^{-9}\times10^{-4}} = \sqrt{10^{-13}\ M}$

$\therefore\ [H^+] = \frac{1}{\sqrt{10}}\times10^{-7}\ M = \sqrt{10}\times10^{-7}\ M$

$\therefore\ Ph = 7 + \frac{1}{2}\log 10 = 7 + \frac{1}{2} = 7.5$

$\therefore\ 10^{PH} = 75$

42. $Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2OH^-$

x 2x + 3y K_{SP} of $Mg(OH)_2 > K_{SP}$ of $Al(OH)_3$

$Al(OH)^3 \rightleftharpoons Al^{3+} + 3OH^-$

y 3y + 2x so x >> y

$2x + 3y \simeq 2x$

$\because\ 4\times10^{-12} = [Mg^{2+}]\,[OH^-]^2$

$= x \times (2x)^2$

$x = 10^{-4}$

$1\times10^{-33} = [Al^{3+}]\,[OH^-]^3$

$1\times10^{-33} = (y)\,(2x)^3$

$1\times10^{-33} = y \times (10^{-4}\times2)^3$

$y = \frac{10^{-21}}{8}$

so $\frac{x}{y} = 8\times10^{17}$

$8\times10^{17}\times10^{-16} = 80$

SUBJECTIVE ANSWER TYPE QUESTIONS

25. 0.16 g of N_2H_4 are dissolved in water and the total volume made upto 500 mL. Calculate the percentage of N_2H_4 that has reacted with water in this solution. The K_b for N_2H_4 is 4.0×10^{-6} M.

Sol.

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

Before dissociation	1	0	0
After dissociation	1 − α	α	α

Also $K_b \frac{C\alpha^2}{(1-\alpha)}$

Assuming $1 - a \simeq 1$

$k_b = C\alpha^2$

$[N_2H_4] = C = \frac{0.16\times1000}{32\times500} = 0.01$

Given $k_b = 4\times10^{-6}$ M

$\therefore \quad \alpha^2 = \dfrac{4\times10^{-6}}{0.01} = 4 \times 10^{-4}$

$\therefore \quad \alpha = 2 \times 10^{-2}$

i.e., $\alpha = 0.02$ or 2%

26. Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.

Sol. $\because \quad NH_4OH \rightleftharpoons NH_4^+ + OH^-$

1	0	0
$1-\alpha$	α	α

Given, pH = 11

$\therefore \quad [H^+] = 10^{-11}$

$\therefore \quad [OH^-] = 10^{-3} = C\alpha$

Since, C = 0.05

$\therefore \quad \alpha = \dfrac{10^{-3}}{C} = \dfrac{10^{-3}}{0.05} = 2 \times 10^{-2}$ or 2%

27. A certain buffer solution contains equals concentration of X^- and HX.K_b for X^- is 10^{-10}. Calculate pH of buffer.

Sol. $\because \quad K_{b(x^{-1})} = 10^{-10}$

Also for conjugate acid – base pair

$K_{a(HX)} \times K_{b(x^{-1})} = 10^{-14}$

$\therefore \quad K_{a(HX)} = 10^{-4}$

Now $[HX] = [X^-]$
(acid) (salt)

$$pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

$$= -\log 10^{-4}$$

$$pH = 4$$

28. $M(OH)_X$ has $K_{sp} = 27 \times 10^{-12}$ and solubility in water is 10^{-3} M. Calculate the value of x.

Sol. $M(OH)_x \rightleftharpoons \underset{s}{M^{x+}} + \underset{xs}{XOH^-}$

$\therefore \quad K_{sp} = s(Xs)^x = X^x \,.\, S^{(1+x)}$

$27 \times 10^{-12} = X^x \,.\, 10^{-3(1+x)}$

$\therefore \quad X = 3$

Thus, hydroxide is M $(OH)_3$

29. Calculate pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{2+} ions. K_{sp} of $Mg(OH)_2 = 1 \times 10^{-11}$.

Sol. When $Mg(OH)_2$ starts precipitation, then,

$[Mg^{2+}]\,[OH^{-2}] = K_{sp}$ of $Mg(OH)_2$

$[0.1]\,[OH^-]^2 = 1 \times 10^{-11}$

$\therefore \quad [OH^{-1}] = 10^{-5}$ M

$\therefore \quad pOH = 5$

$\therefore \quad pH = 14 - pOH$

$\therefore \quad pH = 14 - 5 = 9$

30. 0.1 millimole of $CdSO_4$ are present in 10 mL acid solution of 0.08 N HCI. Now H_2S is passed to precipitate all the Cd^{2+} ions. What would be the pH of solution after filtering off precipitate, boiling of H_2S and making the solution 100 mL by adding H_2O?

Sol. $CdSO_4 + HCI + H_2S \rightarrow CdS + H_2SO_4$

Millimole added 0.1 $10 \times 0.08 = 0.8$

Millmole after reaction 0 0.8 0.1 0.1

$\therefore$ Millimole of H^+ left = $0.8 + 0.1 \times 2 = 1.0$
(from HCI) (from H_2SO_4)

Total volume = 100 mL

$\therefore \quad [H^+] = \dfrac{1}{100} = 10^{-2}$ M

$\therefore \quad pH = 2$

31. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0 \times 10^{-5}$)?

Sol. The two conditions when colour of indicator will be visible are derived by

$$PH = pK_a + \log \frac{[In^-]}{[HIn]}$$

(i) $pH = 5 + \log 10 = 6$

(ii) $pH = 5 + \log 0.1 = 4$

Thus, minimum change in pH = 2

32. K_a for butyric acid is 2.0×10^{-5}. Calculate pH and hydroxyl ion concentration in 0.2 M aqueous solution of sodium butyrate.

Sol. Concentration before hydrolysis

Concentration after hydrolysis

$NaBu + H_2O \rightleftharpoons NaOH + BuH$

1	0	0
$1-h$	h	h

$$\therefore \quad [OH^-] = C.h = C.\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{K_H.C} = \sqrt{\left(\frac{K_w}{K_a}.C\right)}$$

$$[OH^-] = \frac{10^{-14}\times 0.2}{2\times10^{-5}} = \sqrt{10^{-10}} = 10^{-5}$$

$\therefore \quad pOH = 5$

Also $pH + pOH = 14$

$\therefore$ $pH = 14 - 5 = 9$

33. The acid ionization constant for

$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$

is 1.0×10^{-9}. Calculate the pH of 0.0010 M solution of $ZnCl_2$. Also calculate basic dissociation constant of $Zn(OH)^+$.

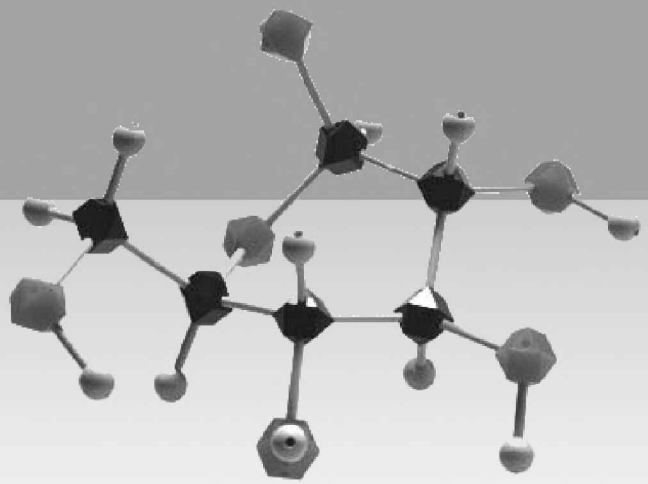
Sol. $Zn^{2+} + H_2O \rightleftharpoons [Zn(OH)]^+ + H^+ \quad K_H = 1.0 \times 10^{-9}$

$\therefore \quad [H^+] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)}$

$= \sqrt{10^{-9} \times 0.001} = 10^{-6}$ Now, $[H^+] = 10^{-6}$

$\therefore$ $pH = 6$

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CHAPTER 8

Liquid Solution and Colligative Properties

In chemistry, a **mixture** is said to be formed when two or more different substances are mixed together but not combined chemically. While there are no chemical changes to its constituents, the physical properties of a mixture, such as its melting point, may differ from those of the components. Mixtures are either homogeneous or heterogeneous.

Homogeneous mixtures are a type of mixture that are perfectly uniform in their composition, as opposed to heterogeneous mixtures.

A homogeneous mixture does not scatter light and its particles can not be separated by filtration. Its particle size is about10^{-9}cm. Its particles are very difficult to differentiate even under a microscope. They are normally known as solution.

SOLUTION



A **solution** is a homogeneous mixture (beyond the dimension of molecules, ions and atoms) composed of two or more substances.

In such a mixture, a **solute** is dissolved in another substance, known as a **solvent**.

Being homogeneous, a solution is a one phase system.

Usually, the substance present in a greater amount is considered as the solvent. Solvents can be gases, liquids, or solids. The solution formed has the same physical state as the solvent.

Solution can have only one solvent but one or more than one solute. If one solute is present, it is called binary solution, if two solutes are present, it is called ternary solution and so on.

Gas as Solvent

If the solvent is a gas, only gases can be dissolved. An example for a gaseous solution is air (oxygen and other gases dissolved in nitrogen).

Liquid as Solvent

If the solvent is a liquid, gases, liquids, and solids can be dissolved. Examples are:

- Liquid in liquid:
  - Alcoholic beverages are basically solutions of ethanol in water.
  - Petroleum is a solution of various hydrocarbons.

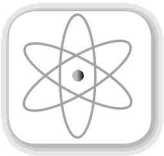
- Solid in liquid:
  - Sucrose (table sugar) in water
  - Sodium chloride or any other salt in water forms an electrolyte: When dissolving, salt dissociates into ions.

Solid as Solvent

If the solvent is a solid, gases, liquids, and solids can be dissolved.

- Gas in solid:
  - Hydrogen dissolves rather well in metals, especially in palladium; this is studied as a means of hydrogen storage.
- Liquid in solid:
  - mercury in gold, forming an amalgam
  - Hexane in paraffin wa
- Solid in solid:
  - Steel, basically a solution of carbon atoms in a crystalline matrix of iron atoms.
  - Alloys like bronze and many others.

LIQUID SOLUTIONS



In principle, all types of liquids can behave as solvents: liquid noble gases, molten metals, molten salts, molten covalent networks, molecular liquids. In the practice of chemistry and biochemistry, most solvents are molecular liquids. They can be classified into polar and non-polar, according to whether or not molecules possess a permanent electric dipole moment. Another distinction is whether or not, molecules are able to form hydrogen bonds (protic and aprotic solvents). Water, the most commonly used solvent, is both polar and sustaining hydrogen bonds.

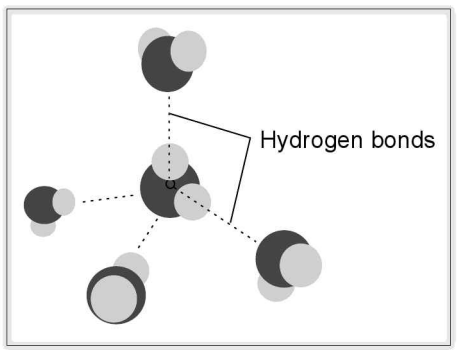


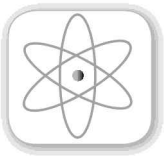
Fig. 8.1

Water is a good solvent because the molecules are polar and capable of forming hydrogen bonds. Salts dissolve in polar solvents, forming positive and negative ions that are attracted to the positive and negative ends of the solvent molecule, respectively.

For non-ionic solutes, the general rule is: like dissolves like.

Polar solutes dissolve in polar solvents, forming polar bonds or hydrogen bonds. As an example, all alcoholic beverages are aqueous solutions of ethanol. On the other hand, non-polar solutes dissolve better in non-polar solutes. Examples are various hydrocarbons like oil and grease that easily mix with each other, while being incompatible with water.

CONCENTRATION



It represents the amount of solute in the solution.
The concentration can be expressed in different units.
We are going to discuss some commonly used units.

Mass Versus Volume

Units of concentration—particularly the most popular one, molarity—require knowledge of a substance's volume, which unlike mass is variable depending on ambient temperature and pressure.

In fact, volumes are not necessarily completely additive when two liquids are added and mixed. Volume-based measures for concentration are therefore not to be recommended for non-dilute solutions or problems where relatively **large** differences in temperature are encountered

Molarity

Molarity (in units of mol/L, molar, or M) or molar concentration denotes the number of moles of a given substance per litre of solution. A capital letter M is used to abbreviate units of mol/L. For instance:

$$\frac{2.0 \text{ moles of dissolved particles}}{4.0 \text{ litres of liquid}} = \text{solution of } 0.5 \text{ mol/L}$$

The actual formula for **molarity** is: $\frac{\text{Moles of solute}}{\text{Liters of solution}}$ = Molarity of solution.

Such a solution may be described as "0.50 molar." It must be emphasized a 0.5 molar solution contains 0.5 moles of solute in 1.0 litre of solution. This is not equivalent to 1.0 litre of **solvent**. A 0.5 mol/L solution will contain either slightly more or slightly less than one litre of solvent because the process of dissolution causes volume of liquid to increase or decrease.



Worked-out Example

1. The density (in g mL^{-1}) of a 3.60 M sulphuric Acid solution that is 29% H_2SO_4 [Molar mass = 98 g mol^{-1}) by mass will be **[AIEEE-2007]**

(a) 1.45 (b) 1.64 (c) 1.88 (d) 1.22

Solution (d) According to the question, one litre of the solution contains 3.6 mole H_2SO_4. Let 'd' be the density of the solution in gmL^{-1}.

Hence, the mass of 1L solution will be 10^3 d g and the mass of H_2SO_4 in it will be $(3 \times 6{\cdot}98)$ g

Hence it follows that $\frac{\text{mass of } H_2SO_4}{\text{mass of solution}} = \frac{(3.6 \times 98)\cancel{g}}{(10^3 d)\cancel{g}} = \frac{29}{100}$ So, $d = \left(\frac{98 \times 3.6}{10 \times 29}\right) = 1.22$

Molality

Molality (mol/kg, molal, or m) denotes the number of moles of solute per kilogram of solvent (not solution). For instance: adding 1.0 mole of solute to 2.0 kilograms of solvent constitutes a solution with a molality of 0.50 mol/kg. Such a solution may be described as "0.50 molal". The term molal solution is used as a shorthand for a "one molal solution", i.e., a solution which contains one mole of the solute per 1000 grams of the solvent.

In a dilute aqueous solution near room temperature and standard atmospheric pressure, molarity and molality will be very similar in value. This is because 1 kg of water roughly corresponds to a volume of

1 L at these conditions, and because the solution is dilute, the addition of the solute makes a negligible impact on the volume of the solution.

However, in all other conditions, this is usually not the case.

Mole fraction

The mole fraction X, (also called molar fraction) denotes the number of moles of solute as a proportion of the total number of moles in a solution. For instance: 1 mole of solute dissolved in 9 moles of solvent has a mole fraction of 1/10 or 0.1. Mole fractions are dimensionless quantities. (The mole percentage or molar percentage, denoted "mol %" and equal to 100% times the mole fraction, is sometimes quoted instead of the mole fraction.)

$$X_B = \frac{n_B}{n_A + n_B} \qquad X_A = \frac{n_A}{n_A + n_B}$$

Hence, $X_A + X_B = 1$ for binary solution.

Mass Percentage (Fraction)

Mass percentage denotes the mass of a substance in a mixture as a percentage of the mass of the entire mixture. (Mass fraction x_m can be used instead of mass percentage by dividing mass percentage to 100.)

For instance: if a bottle contains 40 grams of ethanol and 60 grams of water, then it contains 40% ethanol by mass or 0.4 mass fraction ethanol. Note that the total weight of the solution will be 100 grams, but the total volume of the solution will be more than 100 milliliters because ethanol is less dense than water.

Mass-Volume Percentage

Mass-volume percentage, (sometimes referred to as weight-volume percentage or percent weight per volume and often abbreviated as % m/v or % w/v) describes the mass of the solute in g per 100 ml of the resulting solution. Mass-volume percentage is often used for solutions made from a solid solute dissolved in a liquid. For example, a 40% w/v sugar solution contains 40 g of sugar per 100 ml of resulting solution.

Volume-Volume Percentage

Volume-volume percentage (sometimes referred to as percent volume per volume and abbreviated as % v/v) describes the volume of the solute in ml per 100 ml of the resulting solution. This is most useful when a liquid-liquid solution is being prepared, although it is used for mixtures of gases as well. For example, a 40% v/v ethanol solution contains 40 ml ethanol per 100 ml total volume. The percentages are only additive in the case of mixtures of ideal gases.

Normality

Normality highlights the chemical nature of salts: in solution, salts dissociate into distinct reactive species (ions such as H^+, Fe^{3+}, or Cl^-). Normality accounts for any discrepancy between the concentrations of the various ionic species in a solution. For example, in a salt such as $MgCl_2$, there are two moles of Cl^- for every mole of Mg^{2+}, so the concentration of Cl^- is said to be 2 N (read: "two normal"). Further examples are given below. It may also refer to the concentration of a solute in any solution. The normality of a solution is the number of gram equivalent weight of a solute per litre of its solution. For example, hydrochloric acid (HCl). One litre of aqueous solution of HCl acid contains 36.5 grams HCl. It is called 1N (one normal) solution of HCl. It is given by the following formula:

$$\text{Normality, N} = \left(\frac{\text{gram equivalents}}{\text{Liters solution}} \right)$$

Definition

A **normal** is one gram equivalent of a solute per liter of solution. The definition of a gram equivalent varies, depending on the type of chemical reaction that is discussed-it can refer to acids, bases, redox species, and ions that will precipitate.

Usage

It is critical to note that normality measures a single ion which takes part in an overall solute. For example, one could determine the normality of hydroxide or sodium in an aqueous solution of sodium hydroxide, but the normality of sodium hydroxide itself has no meaning. Nevertheless, it is often used to describe solutions of acids or bases, in those cases it is implied that the normality refers to the H^+ or OH^- ion. For example, 2 Normal sulfuric acid (H_2SO_4), means that the normality of H^+ ions is 2, or that the molarity of the sulfuric acid is 1. Similarly, for 1 molar H_3PO_4 the normality is 3 as it contains three moles of H^+ ions for every mole of PO_4^{3-}.

Equivalents

Expression of concentration in equivalents per liter (or more commonly, milliequivalents per liter) is based on the same principle as normality. A normal solution is one equivalent per liter of solution (Eq/L). The use of equivalents and milliequivalents as a means of expressing concentration is losing favour, but medical reporting of serum concentrations in mEq/L still occurs.

Formal

The formal (F) is yet another measure of concentration similar to molarity. Formal concentrations are sometimes used when solving chemical equilibrium problems. It is calculated based on the formula weights of chemicals per liter of solution. The difference between formal and molar concentrations is that the formal concentration indicates moles of the original chemical formula in solution, without regard for the species that actually exist in solution. Molar concentration, on the other hand, is the concentration of species in solution.

For example: if one dissolves sodium carbonate (Na_2CO_3) in a liter of water, the compound dissociates into the Na^+ and CO_3^{2-} ions. Some of the CO_3^{2-} reacts with the water to form HCO_3^- and H_2CO_3. If the pH of the solution is low, there is practically no Na_2CO_3 left in the solution. So, although we have added 1 mol of Na_2CO_3 to the solution, it does not contain 1 M of that substance. (Rather, it contains a molarity based on the other constituents of the solution.) However, it was once said that such solutions contain 1 F of Na_2CO_3.

"Parts-Per" Notation

It describes the amount of one substance in another, and is thus related to the mass fraction. It is the ratio of the amount of the substance of interest to the amount of that substance plus the amount of the substance it is in.

- Parts per hundred (denoted by '%' [the per cent symbol], and very rarely 'pph')-denotes the amount of a given substance in a total amount of 100 regardless of the units of measure as long as they are the same. Example, 1 gram per 100 gram. 1 part in 10^2.
- Parts per thousand (denoted by '‰' [the per mille symbol], and occasionally 'ppt', but this usage can be confusing because it more often denotes parts per trillion) denotes the amount of a given substance in a total amount of 1000 regardless of the units of measure as long as they are the same. Example, 1 milligram per gram, or 1 gram per kilogram. 1 part in 10^3.
- Parts per million ('ppm') denotes the amount of a given substance in a total amount of 1,000,000 regardless of the units of measure used as long as they are the same. Example, 1 milligram per kilogram. 1 part in 10^6.
- Parts per billion ('ppb') denotes the amount of a given substance in a total amount of 1,000,000,000 regardless of the units of measure as long as they are the same. Example, 1 milligram per tonne. 1 part in 10^9.
- Parts per trillion ('ppt') denotes the amount of a given substance in a total amount of 1,000,000,000,000 regardless of the units of measure as long as they are the same. Example, 1 milligram per kilotonne. 1 part in 10^{12}.
- Parts per quadrillion ('ppq') denotes the amount of a given substance in a total amount of 1,000,000,000,000,000 regardless of the units of measure as long as they are the same. Example, 1 milligram per megatonne. 1 part in 10^{15}.

Table of concentration measures



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Frequently Used Standards of Concentration

Measurement	*Notation*	*Generic formula*	*Typical units*
Atomic percentage (A)	at.%	$\left(\frac{\text{number of atoms of dopant} \times 100}{\text{number of atoms of solution}}\right)$	%
Atomic percentage (B)	at.%	$\left(\frac{\text{number of stoms of dopant} \times 100}{\text{number of substitutable atoms of solution}}\right)$	%
Mass percentage	wt%	$\left(\frac{\text{grams solute} \times 100}{\text{grams solution}}\right)$	%
Mass-volume percentage	-	$\left(\frac{\text{grams solute} \times 100}{\text{milliliters solution}}\right)$	% though strictly %g/mL
Volume-volume percentage	vol%	$\left(\frac{\text{milliters solute} \times 100}{\text{milliliters solution}}\right)$	%
Molarity	M	$\left(\frac{\text{moles solute}}{\text{liters solution}}\right)$	mol/L (or M or mol/dm^3)
Molinity	-	$\left(\frac{\text{moles solute}}{\text{kilograms solution}}\right)$	mol/kg
Molality	m	$\left(\frac{\text{moles solute}}{\text{kilograms solvent}}\right)$	mol/kg (or m**)
Molar fraction	X (chi)	$\left(\frac{\text{moles solute}}{\text{moles solution}}\right)$	(decimal)
Formal	F	$\left(\frac{\text{moles undissolved solute}}{\text{liters solution}}\right)$	mol/L (or F)
Normality	N	$\left(\frac{\text{gram equivalents}}{\text{liters solution}}\right)$	N
Parts per hundred	% (or pph)	$\left(\frac{\text{dekagrams solute}}{\text{kilograms solution}}\right)$	dg/kg
Parts per thousand	‰ (or ppt*)	$\left(\frac{\text{grams solute}}{\text{kilograms solution}}\right)$	g/kg
Parts per million	ppm	$\left(\frac{\text{milligrams solute}}{\text{kilograms solution}}\right)$	mg/kg
Parts per billion	ppb	$\left(\frac{\text{micrograms solute}}{\text{kilograms solution}}\right)$	µg/kg
Parts per trillion	ppt*	$\left(\frac{\text{nanograms solute}}{\text{kilograms solution}}\right)$	ng/kg
Parts per quadrillion	ppq	$\left(\frac{\text{picograms solute}}{\text{kilograms solution}}\right)$	pg/kg

* Although 'ppt' is usually used to denote 'parts per trillion', it is on occasion used for 'parts per thousand'. Sometimes 'ppt' is also used as an abbreviation for precipitate.

** Obsolete unit symbols.



Worked-out Examples

2. Calculate the molality, molarity and mole fraction of ethanol in a solution of total volume 95 ml prepared by adding 50 ml ethanol (density = 0.789 g/ml) to 50 ml water (density = 1.00 g/ml). Also calculate the molality of water in alcohol.

Solution The number of moles of ethanol and of water present in 50 ml of each are calculated as follows:

$(0.789\ g\ ml^{-1})\ (50\ ml)/46.0\ g\ mol^{-1} = 0.86\ mol\ C_2H_5OH$

$(1.0\ g\ ml^{-1})\ (50\ ml)/18.0\ g\ mol^{-1} = 2.8\ mol\ H_2O$

$$\therefore \quad \text{Molality of } C_2H_5OH,\ m = \frac{0.86\ mol\ C_2H_5OH}{0.050\ kg\ H_2O} = 17\ mol\ kg^{-1}$$

$$\text{Mole fraction of } C_2H_5OH,\ x_1 = \frac{0.86mol}{0.86mol + 2.8mol} = 0.23$$

$$\text{Molarity of } C_2H_5OH,\ M = \frac{0.86\ mol}{0.095dm^3} = 9.1\ mol\ dm^{-3}$$

$$\text{Molality of } H_2O,\ m = \frac{2.8\ mol\ H_2O}{(0.050dm^3)(0.780\ kg/dm^{-3})} = 71.8\ mol\ kg^{-1}$$

3. Derive the following formula:

$$\frac{D}{M} = \left[\frac{1}{m} + \frac{M^0}{1000}\right]$$

D = density of solution in g/ml
M = molarity of solution
m = molaltiy of a solution
M^0 = Molecular weight of solute in g

Solution $$\text{Density} = \frac{\text{Total weight of solution}}{\text{Total volume of solution}}$$

$$= \frac{\text{Wt of solute} + \text{Wt of solvent}}{\text{Volume of solution}}$$

$$= \frac{\text{Wt of solute}}{\text{Volume of solution}} + \frac{\text{Wt of solvent}}{\text{Volume of solution}}$$

$$= \frac{\dfrac{\text{Wt of solute}}{\text{Molecular weight solute}}}{\dfrac{\text{Volume of solution}}{\text{Molecular weight of solute}}} + \frac{\text{Wt of solvent}}{\text{Volume of solution}}$$

$$= \frac{\text{Number of moles of solute} \times M^{\circ}}{\text{Volume of solution}} + \frac{\text{Wt of solvent}}{\text{Volume of solution}}$$

If volume of solution = 1 lit, then

$$\frac{\text{number of moles solute}}{\text{volume of solution}} = \text{molarity of solution} = M$$

$$\therefore \quad \text{Denstiy} = M \times M^0 + \text{Wt of solvent}$$

$$\text{now } m = \frac{\text{moles of solute}}{\text{Wt of solvent}} \times 1000$$

$$\therefore \quad \text{Wt of solvent} = \frac{\text{moles of solute}}{m} \times 1000$$

$\because$ volume of solution is 1 lit

$\therefore$ moles of solute = M

$$\therefore \quad \text{Density} = M \times M^0 + \frac{M}{m} \times 1000$$

$$\frac{\text{Density}}{M} = \frac{1000}{m} + M^0$$

this density of in g/lit

$$\therefore \quad \text{density in g/ml } D = \frac{\text{Density in g/lit}}{1000}$$

i.e., $$\frac{D \times 1000}{M} = \frac{1000}{m} + M^0$$

or $$\frac{D}{M} = \frac{1}{m} + \frac{M^0}{1000}$$

HENRY'S LAW

The ability of one compound to dissolve in another compound is called solubility

The solubility of a gas in a liquid depends on temperature, the partial pressure of the gas over the liquid, the nature of the solvent and the nature of the gas. The most common solvent is water.

The solubility of a gas is always limited by the equilibrium between the gas and a saturated solution of the gas. The dissolved gas will always follow Henry's law.

The concentration of dissolved gas depends on the partial pressure of the gas. The partial pressure, in effect, controls the number of gas molecule collisions with the surface of the solution. In fact, the partial pressure is proportional to the number of collisions with the surface will double. The increased number of collisions produce more dissolved gas.

The illustration shows that if the pressure is doubled then the concentration of dissolved gas will double.

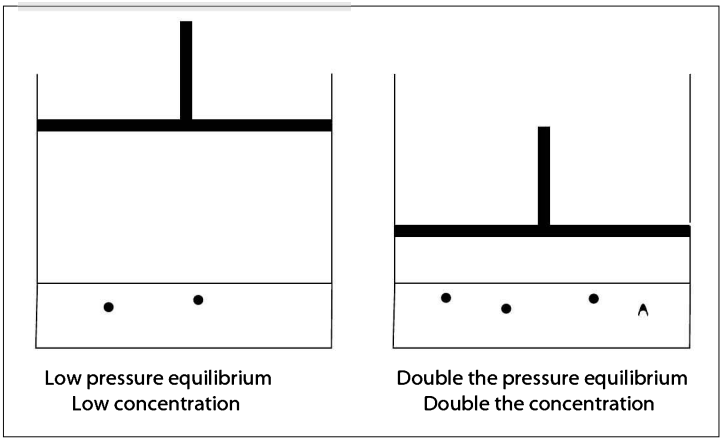


Fig. 8.2

The dissolving process for gases is an equilibrium..

$$O_2(g) \rightleftharpoons O_2(aq)$$

If the temperature stays constant increasing the pressure will shift the above equilibrium to the right side. Hence, more amount of gas will be dissolved. **The above relation was** formulated by William Henry in 1803. It states that:

At a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

An equivalent way of stating the law is that the solubility of a gas in a liquid at a particular temperature is proportional to the pressure of that gas above the liquid. Henry's law Iis applicable to wide range of dilute solutions.

Henry's law can be put into mathematical terms (at constant temperature) as

$$p = k_H c \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where p is the partial pressure of the solute in the gas above the solution, c is the concentration of the solute and k_H is a constant with the dimensions of pressure divided by concentration.

The constant, known as the Henry's law constant, depends on the solute, the solvent and the temperature(not on the partial pressure as it is a proportionality constant).

Some values for k_H for gases dissolved in water at 298 kelvin include:

hydrogen (H_2) : 1282.1 L·atm/mol

oxygen (O_2) : 769.2 L·atm/mol

carbon dioxide (CO_2) : 29.4 L·atm/mol

According to equation (1), the greater the value of k_H under constant pressure, the lesser is the solubility of the gas. Normally, a gas with greater intermolecular attraction (greater critical temperature) is found to be more soluble in water.

There are other forms of Henry's Law, each of which defines the constant k_H differently and requires different dimensional units. In particular, the "concentration" of the solute in solution may also be expressed as a mole fraction or as a molality

Other Forms of Henry's Law

There are various other forms Henry's Law which are discussed in the technical literature.

Some forms of Henry's law and constants (gases in water at 298 K), derived from

equation:	$k_{H,pc} = \frac{p}{c}$	$k_{H,cp} = \frac{c}{p}$	$k_{H,px} = \frac{p}{x}$	$k_{H,cc} = \frac{c_{ap}}{c_{gas}}$
units:	$\frac{L \cdot atm}{mol}$	$\frac{mol}{L \cdot atm}$	***atm***	***dimensionless***
O_2	769.23	1.3×10^{-3}	4.259×10^{4}	3.180×10^{-2}
H_2	1282.05	7.8×10^{-4}	7.099×10^{4}	1.907×10^{-2}
CO_2	29.41	3.4×10^{-2}	0.163×10^{4}	0.8317
N_2	1639.34	6.1×10^{-4}	9.077×10^{4}	1.492×10^{-2}
He	2702.7	3.7×10^{-4}	14.97×10^{4}	9.051×10^{-3}
Ne	2222.22	4.5×10^{-4}	12.30×10^{4}	1.101×10^{-2}
Ar	714.28	1.4×10^{-3}	3.955×10^{4}	3.425×10^{-2}
CO	1052.63	9.5×10^{-4}	5.828×10^{4}	2.324×10^{-2}

where:

c = amount concentration of gas in solution (in mol/L)
p = partial pressure of gas above the solution (in atm)
x = mole fraction of gas in solution

As can be seen by comparing the equations in the above table, the Henry's law constant $k_{H,pc}$ is simply the inverse of the constant $k_{H,cp}$. Since all k_H may be referred to as Henry's law constants, readers of the technical literature must be quite careful to note which version of the Henry's Law equation is being used.

It should also be noted the Henry's Law is a limiting law that only applies for sufficiently dilute solutions. The range of concentrations in which it applies becomes narrower the more the system diverges from ideal behaviour.

It also only applies simply for solutions where the solvent does not react chemically with the gas being dissolved. A common example of a gas that does react with the solvent is carbon dioxide, which forms carbonic acid (H_2CO_3) to a certain degree with water.

Temperature Dependence of the Henry Constant

When the temperature of a system changes, the Henry constant will also change. This is why some people prefer to name it Henry coefficient. There are multiple equations assessing the effect of temperature on the constant. This form of the van't Hoff equation is one example:

$$k_H(T) = k_H(T^{\ominus}) \exp\left[-C\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right]$$

where

k_H for a given temperature is the Henry's Law constant (as defined in the first section of this article), identical with $k_{H,pc}$ defined in Table 1,

T is the thermodynamic temperature,

$T^{\ominus}$ refers to the standard temperature (298 K).

This equation is only an approximation, and should be used only when no better, experimentally-derived formula is known for a given gas.
The following table lists some values for constant C (in kelvins) in the equation above:

Values of C

Gas	O_2	H_2	CO_2	N_2	He	Ne	Ar	CO
C(K)	1700	500	2400	1300	230	490	1300	1300

Because solubility of permanent gases usually decreases with increasing temperature at around the room temperature, the partial pressure a given gas concentration has in liquid must increase. While heating water (saturated with nitrogen) from 25 °C to 95 °C the solubility will decrease to about 43% of its initial value. This can be verified when heating water in a pot: small bubbles evolve and rise, long before the water reaches boiling temperature. Similarly, carbon dioxide from a carbonated drink escapes much faster when the drink is not cooled because of the increased partial pressure of CO_2 in higher temperatures. The constant C may be regarded as:

$$C = -\frac{\Delta_{solv}H}{R} = -\frac{d[\ln k_H(T)]}{d(1/T)}$$

where

ΔH_{solv} is the enthalpy of solution
R is the gas constant.

The solubility of gases does not always decrease with increasing temperature. For aqueous solutions, the Henry-law constant usually goes through a maximum (i.e., the solubility goes through a minimum). For most permanent gases, the minimum is below 120°C. It is often observed that the smaller the gas molecule (and the lower the gas solubility in water), then the lower the temperature of the maximum of the Henry-law constant. Thus, the maximum is about 30°C for helium, 92 to 93°C for argon, nitrogen and oxygen, and 114°C for xenon.

The value for k is the same for the same temperature, gas and solvent. This means the concentration to pressure ratio is the same when pressures change. The following equation can be used to relate pressure and concentration changes.

$$\frac{C_1}{P_1} = \frac{C_2}{P_2}$$

Example

The concentration of dissolved oxygen is 0.44g/100 ml solution. The partial pressure of oxygen is 150 mm Hg. What is the predicted concentration if the partial pressure for oxygen is 56 mm Hg?

Solution

$$\frac{C_1}{P_1} = \frac{C_2}{P_2}$$

$P_1 = 150$ mm Hg $\quad C_1 = 0.44$ g O_2/100 ml solution

$P_2 = 56$ mm Hg $\quad C_2 = ?$

$$\frac{0.44 \text{ g } O_2}{150 \text{ mm Hg}} = \frac{C_2}{56 \text{ mm Hg}}$$

$$C_2 = (56 \text{ ~~mm Hg~~}) \left(\frac{0.44 \text{ g } O_2/100 \text{ mL solution}}{150 \text{ ~~mm Hg~~}} \right)$$

$C_2 = 0.15$ g O_2/100 ml solution



Worked-out Example

4. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1.0×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from air dissolved in 10 moles of water at 298 K and 5 atm pressure is **[IIT-2009]**

(a) 4.0×10^{-4} (b) 4.0×10^{-5}

(c) 5.0×10^{-4} (d) 4.0×10^{-6}

Solution (a) $p_{N_2} = 0.8 \times 5 = 4$ atm

From Henry's Law:

$p_{N_2} = K_H . X_{N_2}$

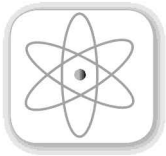
This means 1 mole of solution will contain 4×10^{-5} mole of N_2 and $1 - 4 \times 10^{-5} \approx 1$ mole water.

Thus, 1 mole of water is association with 4×10^{-5} mole N_2

$\therefore$ 10 moles of water is associated with 4×10^{-5} mole N_2

Hence (a)

AN INTRODUCTION TO SATURATED VAPOUR PRESSURE



We will see how the equilibrium between a liquid (or a solid) and its vapour leads to the idea of a saturated vapour pressure. We will also discuss how saturated vapour pressure varies with temperature, and the relationship between saturated vapour pressure and boiling point.

The Origin of Saturated Vapour Pressure

The evaporation of a liquid

The average energy of the particles in a liquid is governed by the temperature. The higher the temperature, the higher the average energy. But within that average, some particles have energies higher than the average, and others have energies lower than the average.

Some of the more energetic particles on the surface of the liquid can be moving fast enough to escape from the attractive forces holding the liquid together. They evaporate.

The diagram shows a small region of a liquid near its surface.

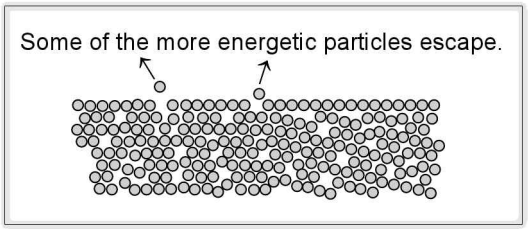


Fig. 8.3

Notice that evaporation only takes place on the surface of the liquid. That's quite different from boiling which happens when there is enough energy to disrupt the attractive forces throughout the liquid. That's why, if you look at boiling water, you see bubbles of gas being formed all the way through the liquid.

If you look at water which is just evaporating in the sun, you do not see any bubbles. Water molecules are simply breaking away from the surface layer.

Eventually, the water will all evaporate in this way. The energy which is lost as the particles evaporate is replaced from the surroundings. As the molecules in the water jostle with each other, new molecules will gain enough energy to escape from the surface.

The Evaporation of a Liquid in a Closed Container

Now imagine what happens if the liquid is in a closed container. Common sense tells you that water in a sealed bottle doesn't seem to evaporate—or at least, it doesn't disappear over time.

But there is constant evaporation from the surface. Particles continue to break away from the surface of the liquid—but this time they are trapped in the space above the liquid.

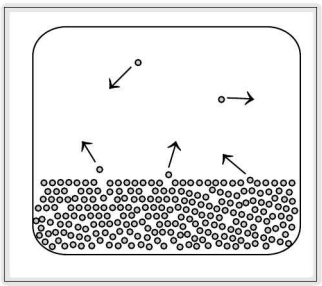


Fig. 8.4

As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and will be trapped there. This is called condensation. **The rate of condensation increases with time, but rate of evaporation remain constant (the surface area of liquid is constant).** There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it.

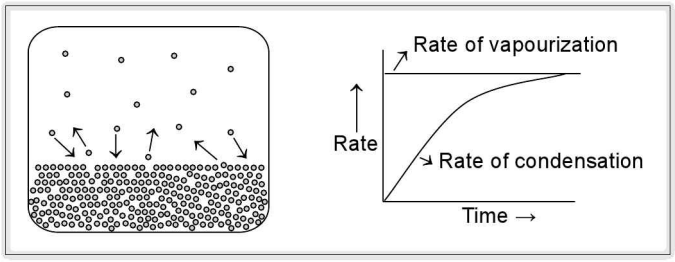


Fig. 8.5

In this equilibrium, there will be a fixed number of the gaseous particles in the space above the liquid.

When these particles hit the walls of the container, they exert a pressure. This pressure is called the **saturated vapour pressure** (also known as **saturation vapour pressure**) of the liquid.

Measuring the Saturated Vapour Pressure

If you have a mercury barometer tube in a trough of mercury, at 1 atmosphere pressure the column will be 760 mm tall. 1 atmosphere is sometimes quoted as 760 mmHg ("millimetres of mercury").

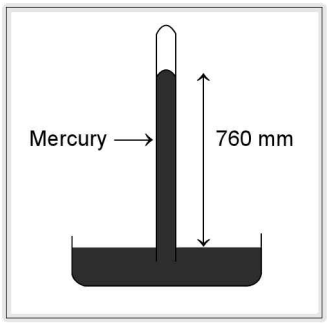


Fig. 8.6

If you squirt a few drops of liquid into the tube, it will rise to form a thin layer floating on top of the mercury. Some of the liquid will evaporate and you will get the equilibrium we've just been talking about-provided there is still some liquid on top of the mercury. It is only an equilibrium if both liquid and vapour are present.

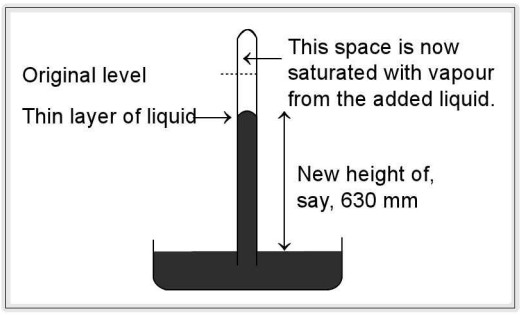


Fig. 8.7

The saturated vapour pressure of the liquid will force the mercury level down a bit. You can measure the drop-and this gives a value for the saturated vapour pressure of the liquid at this temperature. In this case, the mercury has been forced down by a distance of 760–630 mm. The saturated vapour pressure of this liquid at the temperature of the experiment is 130 mmHg.

Molecular Interpretation of Vapour Pressure

We know pretty well that the molecules in liquid are 'bound' by attractive forces to their neighbours. Then, why some are able to leave the liquid? The answer of this lies in the fact that not all the molecules in the liquid possess the same energy. Even if the average potential energy which binds the molecules in the liquid is substantial, there would be some molecules which have enough kinetic energy to overcome the binding forces and enter the vapour phase. If the latent heat of vaporization per mole of a liquid is ΔH_v, the energy for a molecule to escape, ε is

$$\varepsilon = \frac{\Delta H_v}{N_A} \tag{4.1}$$

where N_A is the *Avogadro's number.*

It follows that the average potential energy of the molecules in the vapour phase is greater than the mean value in the liquid phase by an amount ε. Consequently, if N_v' and N_l' represent the number of molecules per unit volume in the vapour, and liquid phases respectively, then in accordance with the Boltzmann distribution law,

$$\frac{N_v'}{N_i'} = \exp(-\varepsilon/kT) = \exp(-\Delta H_v/kN_AT)$$

or

$$\frac{N_v'}{N_i'} = \exp(-\Delta H_v/RT) \tag{4.2}$$

N_v' depends upon' the temperature, but N_l' remains virtually constant and since, the vapour pressure, P is directly proportional to the number of molecules per unit volume (N_v') in the gaseous phase, Eq.4.2 can be rewritten as,

$$P = A \exp(-\Delta H_v/RT) \tag{4.3}$$

where A is a constant.

The process of quantitative determination of amount of a substance by measuring the amount of a suitable reagent required to bring about a definite reaction to just completion is called a titration. The determination of the end point of a titration by means of conductance measurements is known as *conductometric titration.* If sufficient care is taken regarding the temperature control, and a correction is applied for the volume changes during the course of titration, the results with a high degree of precision can be achieved. The titrant is taken nearly ten times as strong as the solution to be titrated, to minimize the dilution effect. One of the most outstanding feature of these titrations is that even the titration of a highly coloured solution can be carried out conductometrically.

The Variation of Saturated Vapour Pressure with Temperature

The Effect of Temperature on the Equilibrium Between Liquid and Vapour

When the space above the liquid is saturated with vapour particles, you have this equilibrium occurring on the surface of the liquid:

$$\text{liquid} \rightleftharpoons \text{vapour } \Delta H \text{ is +ve}$$

The forward change (liquid to vapour) is endothermic. It needs heat to convert the liquid into the vapour.

According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means that increasing the temperature increases the amount of vapour present, and so increases the saturated vapour pressure.

The Effect of Temperature on the Saturated Vapour Pressure of Water

If you look at the equilibrium

$$\text{liquid} \rightleftharpoons \text{vapour} \ldots\ldots K_P = P^{\circ}_{vap}$$

The vapour pressure of pure liquid is found to be equal to the K_p value. Since reaction is endothermic K_P or P°_{vap} increases with increasing temperature.

The graph shows how the saturated vapour pressure (svp) of water varies from 0°C to 100 °C. The pressure scale (the vertical one) is measured in kilopascals (kPa). 1 atmosphere pressure is 101.325 kPa.

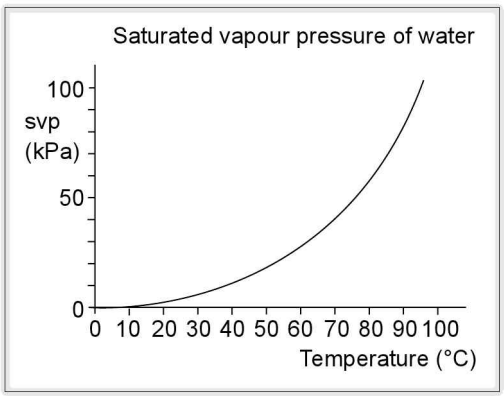


Fig. 8.8

Saturated Vapour Pressure and Boiling Point

A liquid boils when its saturated vapour pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapour to form throughout the liquid—these are the bubbles you see when a liquid boils.

If the external pressure is higher than the saturated vapour pressure, these bubbles are prevented from forming, and you just get evaporation at the surface of the liquid.

If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapour pressure becomes equal to 1 atmosphere (or 101325 Pa or 101.325 kPa or 760 mmHg). This happens with water when the temperature reaches 100°C.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Roult's Law of Vapour Pressure

The vapour pressure and composition in equilibrium with a solution can yield valuable information regarding the thermodynamic properties of the liquids involved. Raoult's law relates the vapor pressure of components to the composition of the solution. The law assumes ideal behavior. It gives a simple picture of the situation just as the ideal gas law does. The ideal gas law is very useful as a limiting law. As the interactive forces between molecules and the volume of the molecules approach zero, the behavior of gases approach the behavior of the ideal gas. Raoult's law is similar in that it assumes that the physical properties of the components are identical. The more similar the components the more their behaviour approaches that described by Raoult's law. This law is applied for a solution of liquid in liquids and can be stated as follows.

"The partial vapour pressure of any component in the solution is directly proportional to its mole fraction".

$P_A \propto X_A$ Where, P_A = Partial vapour pressure of A

$P_A = KX_A$ X_A = Mole fraction of A in solution

For pure liquids $X_A = 1$

Then $K = P^0_A$ Where P^0_A is the vapour pressure of component A in pure state

Hence, $\mathbf{P_A = X_A P^0_A}$

Similarly, for component B , $\mathbf{P_B = X_B P^{\circ}_B}$

Raoult's Law in Combination with Dalton's Law of Partial Pressure

Using the example of a solution of two liquids, A and B, if no other gases are present the total vapor pressure P_{tot} above the solution is equal to the sum of the vapor pressures of the two components, P_A and P_B.

$$P_{tot} = P_A + P_B$$

Of the two components are very similar, or in the limiting case, differ only in isotopic content, then the vapor pressure of each component will be equal to the vapor pressure of the pure substance P^o times the mole fraction in the solution. This is Raoult's law.

$$P_i = P_i^o x_i$$

Thus the total pressure above solution of A and B would be $P_{tot} = P_A^o x_A + P_B^o x_B$

Graphically, this can be represented by a diagram in which the horizontal axis gives the composition from one pure component to the other as shown below:

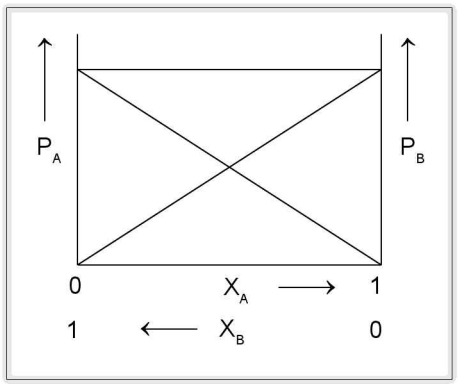


Fig. 8.9

Composition of the Vapour

The composition of the liquid and vapour that are in mutual equilibrium are not necessarily the same, the common sense suggest that the vapour pressure should be richer in the more volatile component. This expectation can be confirmed as follows

Let the mole fractions of A and B in vapour phase be Y_A and Y_B, then from Dalton's law,

$$Y_A = \frac{P_A}{P_T} \quad \ldots(1)$$

$$\text{and } Y_B = \frac{P_B}{P_T} \quad \ldots(2)$$

Provided the mixture of vapours behaves as an ideal gas

Rewriting equation (1) $Y_A = \dfrac{X_A P_A^o}{P_B^o + (P_A^o - P_B^o)X_A}$, and, $Y_B = 1 - Y_A$



Worked-out Example

5. Liquids A and B form an ideal solution. The vapour pressure of A and B at 100°C are 300 and 100 mm Hg respectively. Suppose that vapour above solution is composed of 1 mole of A and 1 mole of B is collected and condensed. This condensate is then heated at 100°C and vapour are again condensed to form a liquid L. What is the mole fraction of A in the vapours of L?

Solution Vapour pressure due to vapours above solution

$$P_T = X_A P_A^o + X_B P_B^o ; P_T = 300X_A + 100\, X_B$$

It is given that in vapour phase, each of A and B are one mole each hence each of them has mole fraction 0.5 in vapour phase.

$$0.5 = \frac{300X_A}{P_T} \quad \ldots(1)$$

$$0.5 = \frac{100X_B}{P_T} \quad \ldots(2)$$

and $X_A + X_B = 1$ $\ldots(3)$

Solving equation (1), (2) and (3), we get

$X_A = 0.25$ and $X_B = 0.75$

$P_T = 300 \times 0.25 + 100 \times 0.75 = 75 + 75 = 150$ mm

After condensation of vapours

In condensate (1) $X'_A = 0.5 \times X'_B = 0.5$

$P'_T = 0.5 \times 300 + 0.5 \times 100 = 150 + 50 = 200$ mm

Mole fraction of A and B in vapour phase of condensate

$$Y'_A = \frac{P_A}{P} = P^\circ_A = 0.75;\ Y'_B = 1 - 0.75 = 0.25$$

When the vapours of the condensate (1) will again be vapourized in condensate (2) liquid L

$X_A'' = 0.75$ $X_B'' = 0.25$, where X_A'' and X_B'' are mole fractions of A and B in liquid L

$P_T'' = 300 \times 0.75 + 100 \times 0.25 = 225 + 25 = 250$ mm

and mole fraction of A in vapour phase of the condensate (2) is given by

$$Y_A'' = \frac{225}{250} = 0.9$$

Vapour Pressure/Composition Diagrams

Suppose you have an ideal mixture of two liquids A and B. Each of A and B is making its own contribution to the overall vapour pressure of the mixture-as we've seen above.

Let's focus on one of the liquid-A, for example

Suppose you double the mole fraction of A in the mixture (keeping the temperature constant). According to Raoult's Law, you will double its partial vapour pressure. If you triple the mole fraction, its partial vapour pressure will triple-and so on.

In other words, the partial vapour pressure of A at a particular temperature is proportional to its mole fraction. If you plot a graph of the partial vapour pressure of A against its mole fraction, you will get a straight line.

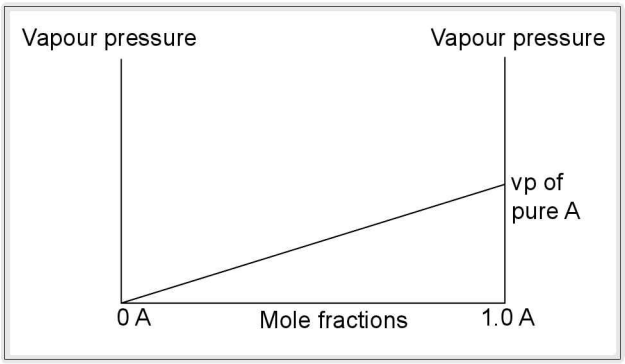


Fig. 8.10

Now we will do the same thing for B-except that we will plot it on the same set of axes. The mole fraction of B falls as A increases so the line will slope down rather than up. As the mole fraction of B falls, its vapour pressure will fall at the same rate.

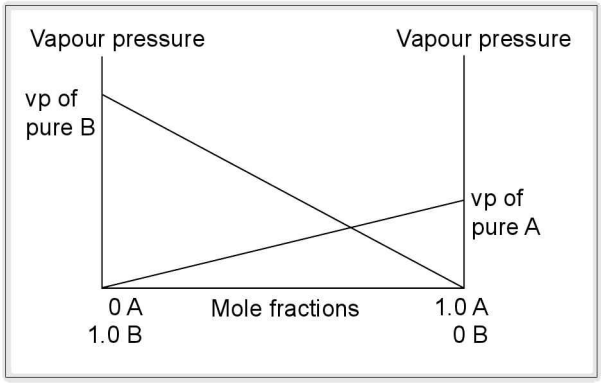


Fig. 8.11

Notice that the vapour pressure of pure B is higher than that of pure A. That means that molecules must break away more easily from the surface of B than of A. B is the more volatile liquid.

To get the total vapour pressure of the mixture, you need to add the values for A and B together at each composition. The net effect of that is to give you a straight line as shown in the next diagram.

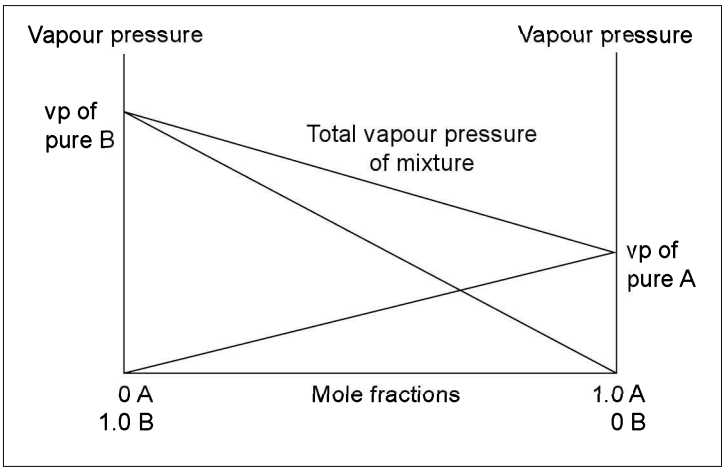


Fig. 8.12

Ideal Solution

An ideal solution may be defined as the one which obeys Raoult's law over all concentration ranges at a given temperature. The total vapour pressure of an ideal solution containing liquids A and B is given by the following equation.

$$P_T = (P_A^\circ X_A + P_B^\circ X_B)$$

Ideality of solutions is analogous to ideality for gases, with the important difference that intermolecular interactions in liquids are strong and can not simply be neglected as they can for ideal gases. Instead, we assume that the mean strength of the interactions are the same between all the molecules of the solution.

More formally, for a mix of molecules of A and B, the interactions between unlike neighbors (U_{AB}) and like neighbours U_{AA} and U_{BB} must be of the same average strength i.e., $2U_{AB}=U_{AA}+U_{BB}$ and the longer-range interactions must be nil (or at least indistinguishable). If the molecular forces are the same between AA, AB and BB, i.e., $U_{AB}=U_{AA}=U_{BB}$, then the solution is automatically ideal.

If the molecules are almost identical chemically, example 1-butanol and 2-butanol, then the solution will be ideal. Since the interaction energies between A and B are the same, it follows that there is no overall energy (enthalpy) change when the substances are mixed. The more dissimilar the nature of A and B, the more strongly the solution is expected to deviate from ideality.

Characteristics of Ideal Solution: Mixing of two substances results in an ideal solution only when:

1. They obey Raoult's Law
2. $\Delta H_{mixing} = 0 \Rightarrow$ that is no heat is absorbed or released during dissolution
3. $\Delta V_{mixing} = 0 \Rightarrow$ that is the total volume of the solution is equal to the sum of the volume of the pure liquids mixed to form the solution.

Since the enthalpy of mixing (solution) is zero, the change in Gibbs free energy on mixing is determined solely by the entropy of mixing. Hence the molar Gibbs free energy of mixing is

$$\Delta G_{m,mix} = RT \sum_{i} x_i \ln x_i$$

or for a two component solution

$$\Delta G_{m,mix} = RT(x_A \ln x_A + x_B \ln x_B)$$

where m denotes molar i.e., change in Gibbs free energy per mole of solution, and x_i is the mole fraction of component i.

Note that this free energy of mixing is always negative (since each x_i is positive and each $\ln x_i$ must be negative) i.e., ideal solutions are always completely miscible.
then

$$\Delta s_{i,mix} = -R \sum_{i} \ln x_i$$

$$\Delta S_{mix} = -R \sum_{i} x_i \ln x_i$$



Worked-out Examples

6. In mixture *A* and *B*, components show –ve deviations as: **[AIEEE-2002]**

(a) ΔV_{mix} is + ve
(b) *A-B* interaction is weaker than *A-A* and *B-B* interaction.
(c) ΔH_{mix} is + ve
(d) *A-B* interaction is stronger than *A-A* and *B-B* interaction.

Solution (d) It is a required condition along with ΔV = –ve and ΔH = –ve

7. If liquid *A* and *B* form ideal solution, than: **[AIEEE-2003]**

(a) $\Delta G_{mix} = 0$ (b) $\Delta H_{mixing} = 0$
(c) $\Delta G_{mix} = 0, \Delta S_{mix} = 0$ (d) $\Delta S_{mix} = 0$

Solution (b) For ideal solution $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$

8. Which liquid pair shows a positive deviation from Raoult's law? **[AIEEE-2004]**

(a) Acetone—chloroform (b) Benzene—methanol
(c) Water—nitric acid (d) Water—hydrochloric acid

Solution (b)

Completely Immiscible Liquid Pairs

Examples of completely immiscible liquid pairs are water-benzene, water-cyclohexame, water-cyclohexane, water-ether etc. The vapour existing above the liquid mixture contains molecules of both the liquids, say A dn B. The total vapour pressure p of the system will be the sum of he individual vapour pressures p_A and p_B. If n_A and n_B represent the number of moles of A and B respectively in the vapour phase, then

$$p = p_A + p_B$$

with, $$p_A = \frac{n_A}{n_A + n_B} p$$

$$p_B = \frac{n_B}{n_A + n_B} P$$

So, $$\frac{p_A}{p_B} = \frac{n_A}{n_B}$$

The ratio p_A/p_B is constant at a constant temperature, and hence the composition of the vapour phase is also fixed. If $_A$ and w_B are the amounts of A and B, respectively, in the vapour phase then

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} = \left(\frac{w_A/M_A}{w_B/M_B}\right)$$

or $$\frac{w_A}{w_B} = \frac{p_A M_A}{p_B M_B}$$

where M_A, and M_B are the molar masses of A and B respectively. Since a liquid boils only when the vapour pressure of the liquid equals the external pressure, and because the total vapour pressure of the system is greater than any one of the individual vapour pressures p_A and P_B, the liquid mixture will boil at a temperature which is less than the boiling point of either A or B. For example, let the external pressure be 1 atmosphere. Then, pure A will boil when p_A = 1 atmosphere, and pure B will boil when p_B = 1 atmosphere. The mixture boils, however, when p = 1 atmosphere, and since p_A or $p_B < p$, then-the individual liquids are still below their normal boiling points. Thus the mixture will boil below the boiling point of either A or B. During boiling as long as both the components are present in the mixture, the total pressure remains constant, and hence the composition of the vapour will remain constant. So if the two liquids are taken together and boiled, boiling will occur at a definite temperature and the composition of the distillate will be constant being given by 12.27. This principle forms the basis of steam distillation.

Steam Distillation

The principle described above is utilized in *steam distillation.* If steam is passed into a liquid which is immiscible with water, then the liquid vaporizes with steam, even if the boiling point of the liquid is higher than that of water. The vapour thus obtained may be condensed to give two liquid layers. This is known as *steam distillation.* Steam distillation is widely used in separating high boiling liquids that decompose near their boiling points from dissolved impurities. Such a liquid vaporizes below 100°C, the boiling point of water, under normal pressure. The liquid layer can be separated from the aqueous layer in the distillate with the help of a separating funnel. For example, let us consider the purification of iodobenzene having a boiling point of 188°C. Steam distillation of iodobenzene occurs at 98°C. At the boiling temperature of the mixture, the partial pressures of water and iodobenzene are 712 torr and 48 torr respectively. The molecular weight of iodobenzene is 204. So, the relative amounts of iodobenzene (A) and water (B) in the distillate are,

$$\frac{w_A}{w_B} = \frac{p_A M_A}{p_B M_B} = \frac{48 \times 204}{712 \times 18} = 0.764$$

Thus, 0.764 g iodobenzene vaporizes along with 1 g water. If the composition of the distillate is determined, the molecular weight of an unknown liquid can also be calculated using 12-27.

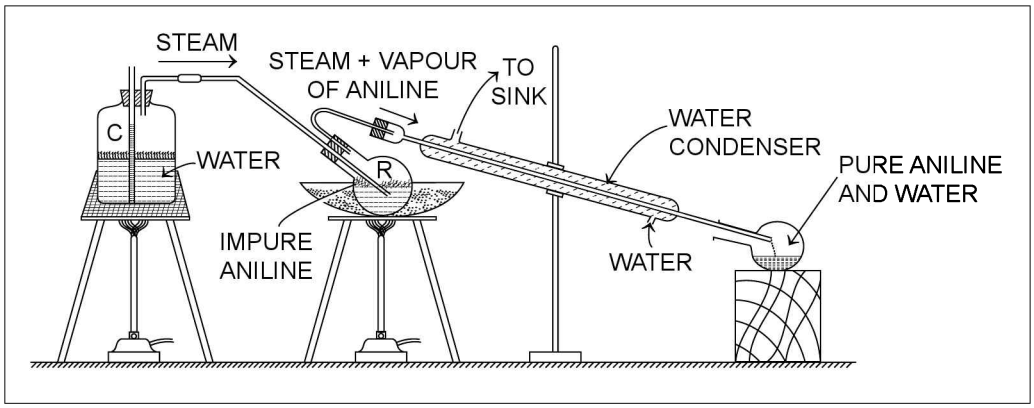


Fig. 8.13 An experimental set up for steam distillation

Non-Ideal Solution

Raoult's law only works for ideal mixtures. In these, the forces between the particles in the mixture are exactly the same as those in the pure liquids. The tendency for the particles to escape is the same in the mixture and in the pure liquids. It not true in non-ideal mixtures.

There are two types of Non-Ideal Solutions:

1. Non-ideal solutions showing +ve deviation
2. Non-ideal solutions showing –ve deviation

Positive Deviations from Raoult's Law

In mixtures showing a positive deviation from Raoult's Law, the vapour pressure of the mixture is always higher than you would expect from an ideal mixture.

The deviation can be small-in which, the straight line in the last graph turns into a slight curve.

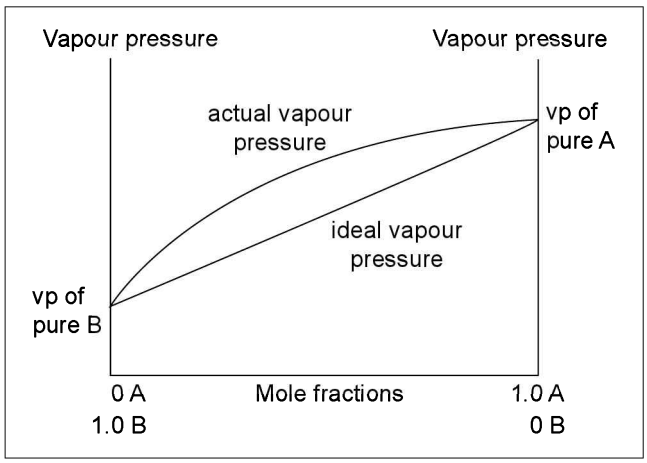


Fig. 8.14

Notice that the highest vapour pressure anywhere is still the vapour pressure of pure A. Cases like this, where the deviation is small, behave just like ideal mixtures as far as distillation is concerned, and we do not need to say anything more about them.

But some liquid mixtures have very large positive deviations from Raoult's Law, and in these cases, the curve becomes very distorted.

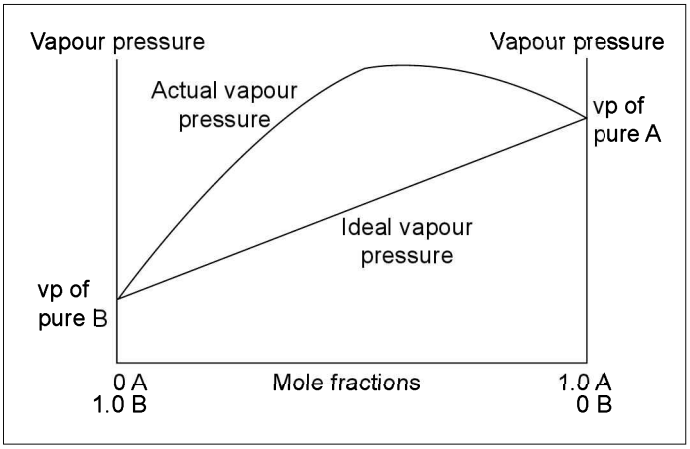


Fig. 8.15

Notice that mixtures over a range of compositions have higher vapour pressures than either pure liquid. The maximum vapour pressure is no longer that of one of the pure liquids. This has important consequences when we look at boiling points and distillation further down the page.

Explaining the Deviations

The fact that the vapour pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids.

That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

You can see this when you mix the liquids. Less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic.

The classic example of a mixture of this kind is ethanol and water. This produces a highly distorted curve with a maximum vapour pressure for a mixture containing 95.6% of ethanol by mass. For a solution with +ve deviation.

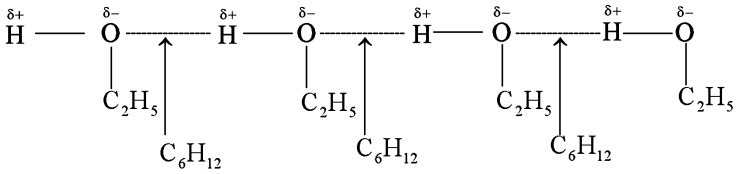
1. The liquids do not obey Raoult's law in solution i.e.,

   $P_A > P_A^\circ X_A$ and $P_B^\circ > P_B^\circ X_B$

2. ΔH_{mixing} is +ve (Heat is absorbed)
3. ΔV_{mixing} is +ve i.e., volume of the solution formed is more than the sum of the volumes of A and B mixed.

Solution of ethanol and cyclohexane show the deviation from ideality. In pure ethanol, ethanol molecules are hydrogen bonded i.e., there are strong attractive forces between ethanol molecule in liquid ethanol. When liquid cyclohexane is added to ethanol the cyclohexane molecules get in between the ethanol molecules and thus break up the H-bonds. This reduces the ethanol–ethanol intermolecular attractions and thus escaping tendency of the ethanol molecules increases. This makes the partial vapour pressure of

ethanol higher than that expected if the solution was ideal. Therefore solution of ethanol and cyclohexanes show non-ideal behaviour with +ve deviation from Raoult's law.



Examples:

Ethanol-water, ether-acetone, CS_2-acetone, CCl_4-methanol, acetone – benzene, CCl_4-$CHCl_3$.

Negative Deviations from Raoult's Law

In exactly the same way, you can have mixtures with vapour pressures which are less than would be expected by Raoult's Law. In some cases, the deviations are small, but in others they are much greater giving a minimum value for vapour pressure lower than that of either pure component.
For a solution with negative deviation.

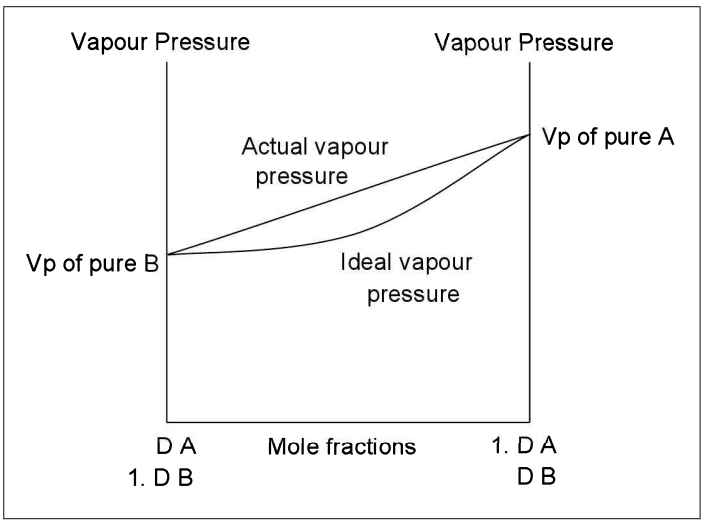


Fig. 8.16

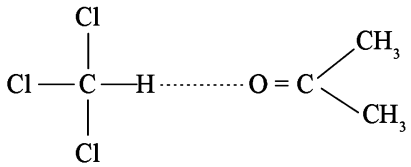
1. The liquid do not obey Raoult's law in solution

   $P_A < P_A^\circ X_A$, $P_B < P_B^\circ X_B$

2. ΔH_{mixing} is –ve $\Rightarrow$ heat is liberated.
3. ΔV_{mixing} is –ve $\Rightarrow$ volume decreases.

Solution of chloroform and acetone show –ve deviation from ideal behaviour. When $CHCl_3$ and CH_3COCH_3 are mixed together to form a solution, hydrogen bonding occurs between the molecules of $CHCl_3$ and CH_3COCH_3. There are new stronger attractive forces between chloroform and acetone molecules compared with the attractive forces between $CHCl_3$ — $CHCl_3$ molecules and CH_3COCH_3 – CH_3COCH_3 molecules.

The stronger attractive forces decreases the escaping tendencies of both the chloroform and acetone molecules and make the partial vapour pressure of each liquid less than that based on Raoult's law. Therefore, the total vapour pressure of the solution would be less than that predicted by Raoult's law and the solution thus shows –ve deviation from ideality.



Examples
Methanol–Acetic acid and water–HNO_3 Graphical representation of vapour pressure of non-ideal solution showing –ve deviation:

Explaining the Deviations

These are cases where the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

You can recognize this happening because heat is evolved when you mix the liquids-more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones.

Many (although not all) examples of this involve actual reaction between the two liquids. The example of a major negative deviation that we are going to look at is a mixture of nitric acid and water. These two covalent molecules react to give hydroxonium ions and nitrate ions.

$$H_2O_{(l)} + HNO_{3(l)} \rightleftharpoons H_3O^+(aq) + NO_3^-(aq)$$

You now have strong ionic attractions involved.

Boliling point/composition diagrams

The relationship between boiling point and vapour pressure

For two liquids at the same temperature:

The one with the higher vapour pressure is the one with the lower boiling point.

Constructing a boiling point/composition diagram for ideal solution

We have just ended up with this vapour pressure/composition diagram:

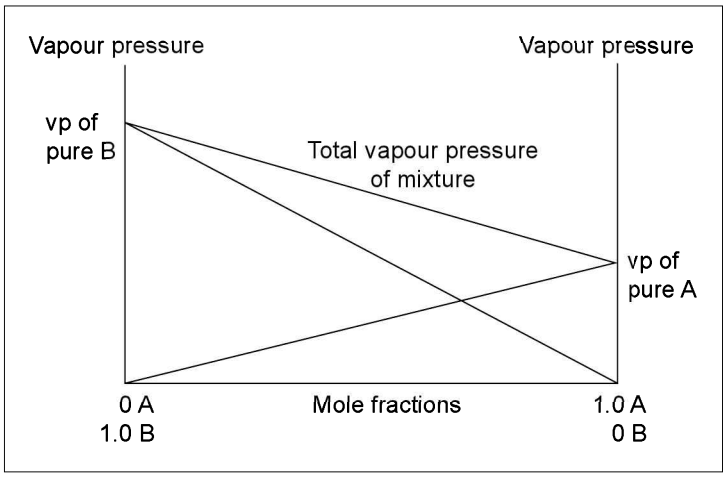


Fig. 8.17

We are going to convert this into a boiling point/composition diagram.

We will start with the boiling points of pure A and B.

B has the higher vapour pressure. That means that it will have the lower boiling point.

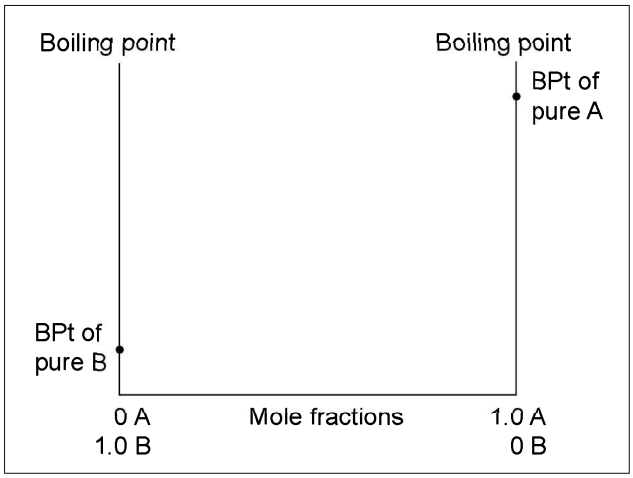


Fig. 8.18

For mixtures of A and B, you might perhaps have expected that their boiling points would form a straight line joining the two points we have already got. Not so!

In fact, it turns out to be a curve.

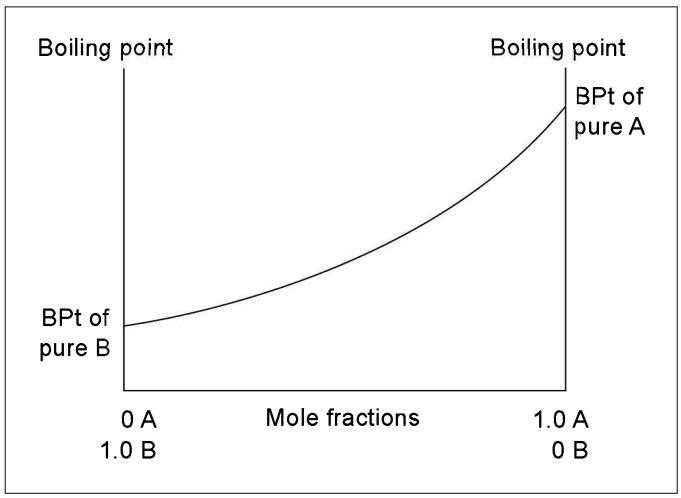


Fig. 8.19

To make this diagram really useful, we are going to add another line. This second line will show the composition of the vapour over the top of any particular boiling liquid.

If you boil a liquid mixture, you would expect to find that the more volatile substance escapes to form a vapour more easily than the less volatile one.

That means that in the case we've been talking about, you would expect to find a higher proportion of B (the more volatile component) in the vapour than in the liquid. You can discover this composition by condensing the vapour and analysing it. That would give you a point on the diagram.

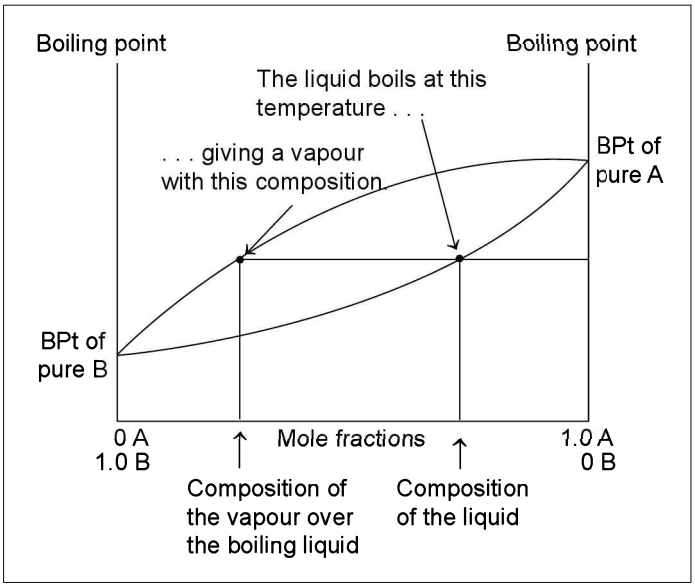


Fig. 8.20

The diagram just shows what happens if you boil a particular mixture of A and B. Notice that the vapour over the top of the boiling liquid has a composition which is much richer in B-the more volatile component.

If you repeat this exercise with liquid mixtures of lots of different compositions, you can plot a second curve—a vapour composition line.

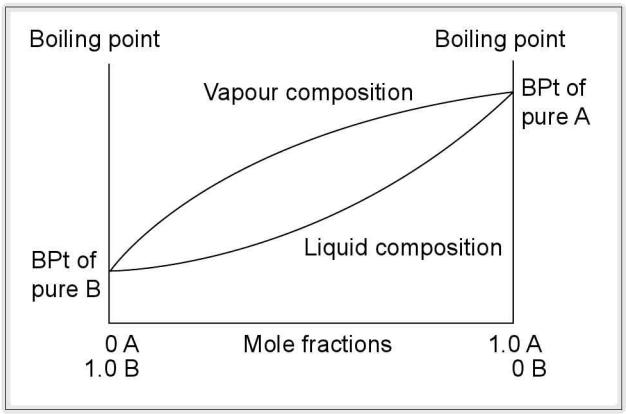


Fig. 8.21

This is now our final phase diagram

Using the phase diagram

The diagram is used in exactly the same way as it was built up. If you boil a liquid mixture, you can find out the temperature it boils at, and the composition of the vapour over the boiling liquid.

For example, in the next diagram, if you boil a liquid mixture C_1, it will boil at a temperature T_1 and the vapour over the top of the boiling liquid will have the composition C_2.

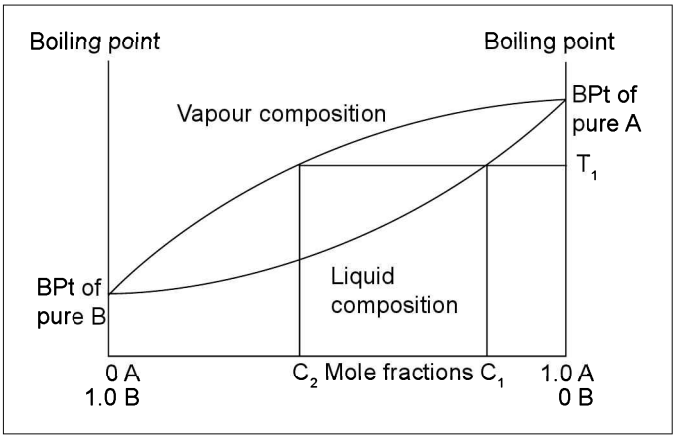


Fig. 8.22

All you have to do is to use the liquid composition curve to find the boiling point of the liquid, and then look at what the vapour composition would be at that temperature.

Notice again that the vapour is much richer in the more volatile component B than the original liquid mixture was.

The beginning of fractional distillation

Suppose that you collected and condensed the vapour over the top of the boiling liquid and reboiled it.

You would now be boiling a new liquid which had a composition C_2.

That would boil at a new temperature T_2, and the vapour over the top of it would have a composition C_3.

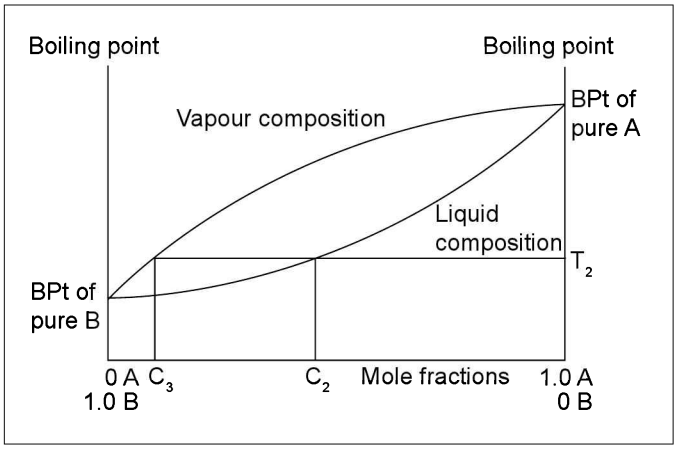


Fig. 8.23

You can see that we now have a vapour which is getting quite close to being pure B. If you keep on doing this, (condensing the vapour, and then reboiling the liquid produced) you will eventually get pure B.

This is obvious the basis for fractional distillation. However, doing it like this would be incredibly tedious, and unless you could arrange to produce and condense huge amounts of vapour over the top of the boiling liquid, the amount of B which you would get at the end would be very small.

Azeotropic Mixture or Azeotrope

Boiling point/composition diagrams for non-ideal mixtures

A Large Positive Deviation from Raoult's Law: Ethanol and Water Mixtures

If you look up the back page, you will remember that a large positive deviation from Raoult's Law produces a vapour pressure curve with a maximum value at some composition other than pure A or B.

If a mixture has a high vapour pressure it means that it will have a low boiling point. The molecules are escaping easily and you won't have to heat the mixture much to overcome the intermolecular attractions completely.

The implication of this is that the boiling point/composition curve will have a minimum value lower than the boiling points of either A or B.

In the case of mixtures of ethanol and water, this minimum occurs with 95.6% by mass of ethanol in the mixture. The boiling point of this mixture is 78.2°C, compared with the boiling point of pure ethanol at 78.5°C, and water at 100°C.

You might think that this 0.3°C doesn't matter much, but it has huge implications for the separation of ethanol/water mixtures.

The next diagram shows the boiling point/composition curve for ethanol/water mixtures. I have also included on the same diagram a vapour composition curve in exactly the same way as we looked at on the previous pages about phase diagrams for ideal mixtures.

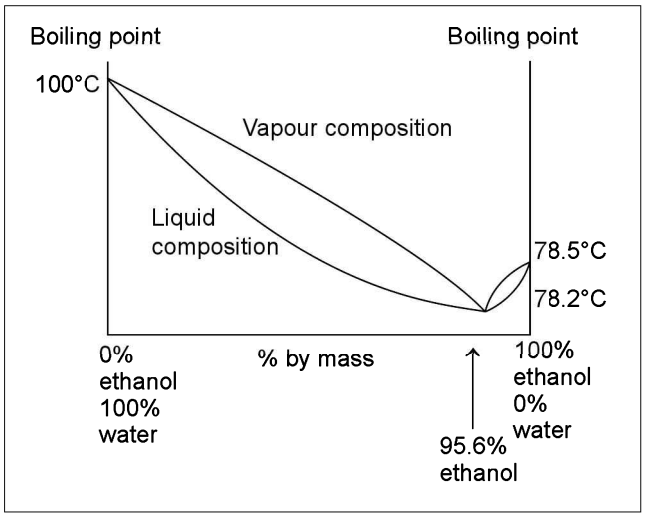


Fig. 8.24

Note: This diagram is drawn grossly distorted. Look, for example, at the temperature scale and the position of the 95.6% value on the composition scale. The shapes of the two separate areas between the curves are also exaggerated.

Using the Diagram

Suppose you are going to distil a mixture of ethanol and water with composition C_1 as shown on the next diagram. It will boil at a temperature given by the liquid curve and produce a vapour with composition C_2.

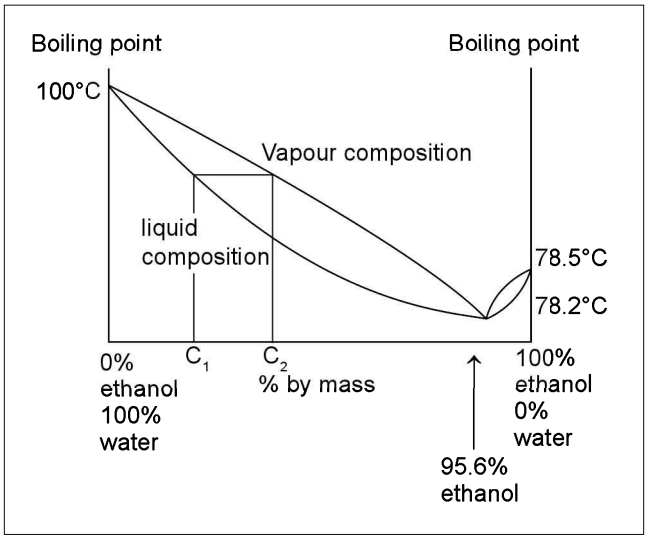


Fig. 8.25

When that vapour condenses it will, of course, still have the composition C_2. If you reboil that, it will produce a new vapour with composition C_3.

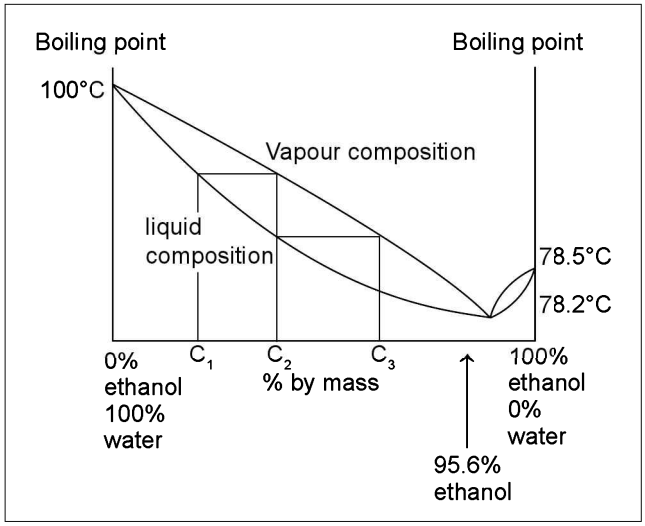


Fig. 8.26

You can see that if you carried on with this boiling-condensing-reboiling sequence, you would eventually end up with a vapour with a composition of 95.6% ethanol. If you condense that, you obviously get a liquid with 95.6% ethanol.

What happens if you reboil that liquid?

The liquid curve and the vapour curve meet at that point. The vapour produced will have that same composition of 95.6% ethanol. If you condense it again, it will still have that same composition.

You have hit a barrier. It is impossible to get pure ethanol by distiling any mixture of ethanol and water containing less than 95.6% of ethanoll.

This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapour composition is exactly the same as the liquid.

It is known as a **constant boiling mixture** or an **azeotropic mixture** or an **azeotrope**.

The implications of this for fractional distillation of dilute solutions of ethanol are obvious. The liquid collected by condensing the vapour from the top of the fractionating column cannot be pure ethanol. The best you can produce by simple fractional distillation is 95.6% ethanol.

What you can get from the mixture is pure water. As ethanol rich vapour is given off from the liquid boiling in the distillation flask, it will eventually lose all the ethanol to leave just wate .

To summarize:
Distilling a mixture of ethanol containing less than 95.6% of ethanol by mass, lets you collect:

- a distillate containing 95.6% of ethanol in the collecting flask (provided you are careful with the temperature control, and the fractionating column is long enough);
- pure water in the boiling flask

What if you distil a mixture containing more than 95.6% ethanol?
Work it out for yourself using the phase diagram, and starting with a composition to the right of the azeotropic mixture. You should find that you get

- a distillate containing 95.6% of ethanol in the collecting flask (provided you are careful with the temperature control, and the fractionating column is long enough);
- pure ethanol in the boiling flask

A Large Negative Deviation from Raoult's Law: Nitric Acid and Water Mixtures

Nitric acid and water form mixtures in which particles break away to form the vapour with much more difficulty than in either of the pure liquids. You can see this from the vapour pressure/composition curve discussed further up the page.

That means that mixtures of nitric acid and water can have boiling points higher than either of the pure liquids because it needs extra heat to break the stronger attractions in the mixture.

In the case of mixtures of nitric acid and water, there is a maximum boiling point of 120.5°C when the mixture contains 68% by mass of nitric acid. That compares with the boiling point of pure nitric acid at 86°C, and water at 100°C.

The phase diagram looks like this:

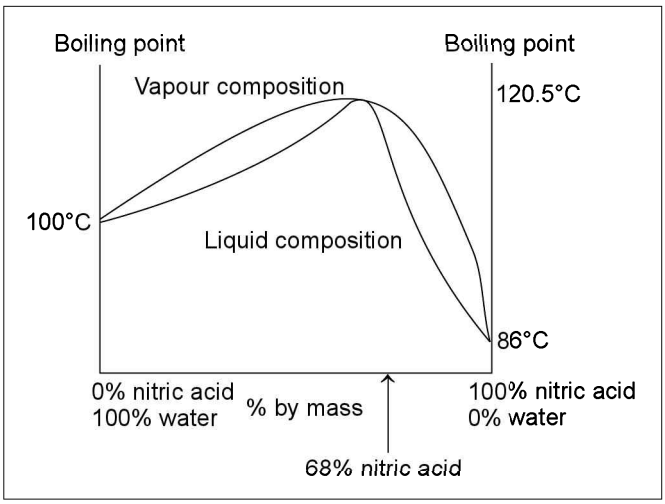


Fig. 8.27

Using the Diagram

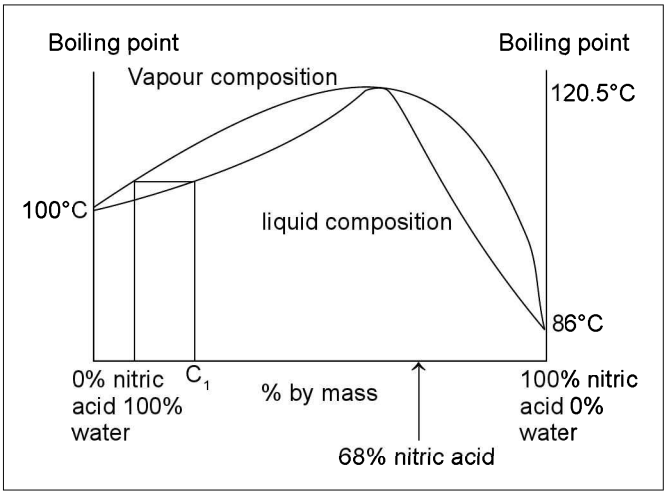


Fig. 8.28

The vapour produced is richer in water than the original acid. If you condense the vapour and reboil it, the new vapour is even richer in water. Fractional distillation of dilute nitric acid will enable you to collect pure water from the top of the fractionating column.

As the acid loses water, it becomes more concentrated. Its concentration gradually increases until it gets to 68% by mass of nitric acid. At that point, the vapour produced has exactly the same concentration as the liquid, because the two curves meet.

You produce a constant boiling mixture (or azeotropic mixture or azeotrope). If you distil dilute nitric acid, that's what you will eventually be left with in the distillation flask. You cannot produce pure nitric acid from the dilute acid by distilling it.

Distilling Nitric Acid More Concentrated Than 68% by Mass

This time you are starting with a concentration C_2 to the right of the azeotropic mixture.

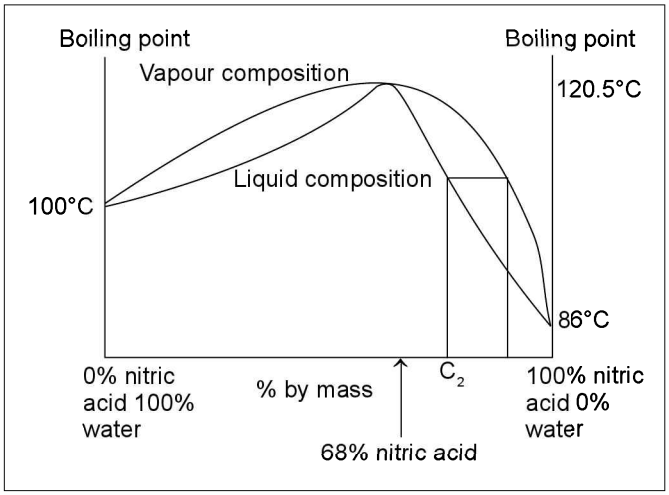


Fig. 8.29

The vapour formed is richer in nitric acid. If you condense and reboil this, you will get a still richer vapour. If you continue to do this all the way up the fractionating column, you can get pure nitric acid out of the top.

As far as the liquid in the distillation flask is concerned, it is gradually losing nitric acid. Its concentration drifts down towards the azeotropic composition. Once it reaches that, there cannot be any further change, because it then boils to give a vapour with the same composition as the liquid.

Distilling a nitric acid/water mixture containing more than 68% by mass of nitric acid gives you pure nitric acid from the top of the fractionating column and the azeotropic mixture left in the distillation flask.

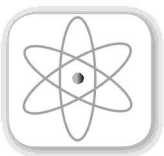
Example of Minimum Boiling Azeotrope

Components			*Boiling point (K)*		
A	***B***	***Mass% of B***	***A***	***B***	***Azeoterope***
H_2O	C_2H_5OH	95.57	373	351.3	351.10
H_2O	C_3H_7OH	71.69	373	370.0	350.72
$CHCl_3$	C_2H_5OH	67.00	334	351.3	332.30

Examples of Maximum Boiling Azeotrope

Components			*Boiling point (K)*		
A	***B***	***Mass% of B***	***A***	***B***	***Azeoterope***
H_2O	HCl	20.3	373	188	383
H_2O	HNO_3	58.0	373	359	393.5
H_2O	$HClO_4$	71.6	373	383	476

VAN'T HOFF FACTOR



In 1886, Van't Hoff, Jacobus Henricus (Dutch chemist, 1859–1911) introduced a factor 'i' known as Van't Hoff factor to express the extent to association or dissociation of a solute in solution. Van't Hoff factor may be defined as the ratio of normal molecular mass of the solute to the observed molecular mass using a colligative property.

$$i = \frac{\text{Normal molecular Mass (M)}}{\text{Observed Molecualr Mass } (M_C)} = \frac{\text{Moles of solute actually present in solution}}{\text{Moles of solute dissolved}}$$

$$= \frac{\text{Effective Molality}}{\text{Molality}} = \frac{\text{Colligative Molality}}{\text{Molality}}$$

(i) **For association of a solute, i is less than unity:** The value of 'i' to be 0.5 indicates that two molecules of solute associate to form a dimer. If the value of 'i' is slightly less than unity, say 0.91, this indicates that there are strong intermolecular forces between molecules of a solute in solution. For example, benzoic acid in benzene is found to have molecular mass which is just twice its normal molecular mass. It is found that compounds which are capable of forming hydrogen bonds, example, phenols, carboxylic aids, alcohols: because of association show decreased effect of colligative property.

(ii) **For dissociation of a solute, i is greater than unity:** If 'i' for a solute is 2, this indicates that a solute molecule ionizes in solution to give 2 particles. If 'i' for a solute is 3, a solute molecule ionizes in solution to give 3 particles (example $CaCl_2$, K_2SO_4). The value of 'i' for concentrated KCl solution is slightly less than two which indicates that KCl does not ionize fully in concentrated solution and its degree of dissociation is therefore less than 1. There are strong attractive forces between positively

charged K^+ ions and negatively charged Cl^- ions and a fraction of ions act together as ion-pairs. For dilute KCl solution, 'i' has a value of 2 indicating that the strength of attractive forces decreases with dilute and the electrolyte dissociates completely.

Calculation of Van't Hoff Factor

(i) **Degree of Dissociation and Colligative Property:**

	A_n	$\rightleftharpoons$	nA
Number of moles dissolved	1 mol		0
Number of moles after dissociation	$1-\alpha$		$n\alpha$
Total number of moles present in solution	$=(1-\alpha)+n\alpha$		

$$\text{Van't Hoff factor, } i = \frac{\text{Moles of solute actually present in solution}}{\text{Moles of solute dissolved}}$$

$$= \frac{(1-\alpha)+n\alpha}{1} = 1+(n-1)\alpha \quad \text{or} \quad \alpha = \frac{i-1}{n-1}$$

(ii) **Degree of Association and Colligative Property:** Let n moles of the solute, A, associate to form $(A)_n$. If α is the degree of association.

	nA	$\rightleftharpoons$	A_n
Number of moles dissolved	1 mol		0
Number of moles after dissociation	$1-\alpha$		α/n
Total number of moles present in solution	$=(1-\alpha)+\alpha/n$		

$$i = \left[1-\alpha\left(1-\frac{1}{n}\right)\right]$$

$$\text{Hence } \alpha = \frac{i-1}{\frac{1}{n}-1} = (i-1)\times\frac{n}{1-n}$$



Worked-out Example

9. If α is the degree of dissociation of Na_2SO_4, the van't Hoff factor (i) used for calculating molecular mass is: **[AIEEE-2005]**

(a) $1+\alpha$ (b) $1-\alpha$

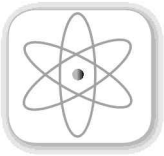
(c) $1+2\alpha$ (d) $1-2\alpha$

Solution (c) $Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

1	0	0
$1-\alpha$	2α	α

$$\therefore i = \frac{1-\alpha+2\alpha+\alpha}{1} = \frac{1+2\alpha}{1} = 1+2\alpha$$

COLLIGATIVE PROPERTIES



Non-colligative properties depend on the identity of the dissolved species and the solvent.

We can compare the properties of a 1.0 M aqueous sugar solution to a 0.5 M solution of table salt (NaCl) in water. Despite the concentration of sodium chloride being half of the sucrose concentration, both solutions have precisely the same number of dissolved particles because each sodium chloride unit creates two particles upon dissolution–a sodium ion, Na^+, and a chloride ion, Cl^-. Both solutions have the same freezing point, boiling point, vapour pressure, and osmotic pressure because those colligative properties of a solution only depend on the number of dissolved particles. The colligative properties are

1. Lowering of vapour pressure
2. Elevation of boiling point
3. Depression of freezing point
4. Osmotic pressure

Greater the number of particles of solute in solution, greater is the extent to which colligative property is affected.

Factors that Affect the Colligative Property: The number of solute particles in solution. To be more accurate, the colligative property depends upon the fraction of solute and solvent particles in solution.

(i) Nature of the solvent
(ii) Independent of the nature of the solute
(iii) Extent of association and dissociation of solute particles in solution.

Vapor Pressure Depression

Physical properties can be divided into two categories. Extensive properties (such as mass and volume) depend on the size of the sample. Intensive properties (such as density and concentration) are characteristic properties of the substance; they do not depend on the size of the sample being studied. This section introduces a third category that is a subset of the intensive properties of a system. This third category, known as **colligative properties**, can only be applied to solutions. By definition, one of the properties of a solution is a colligative property if it depends only on the ratio of the number of particles of solute and solvent in the solution, not the identity of the solute.

Very few of the physical properties of a solution are colligative properties. As an example of this limited set of physical properties, let's consider what happens to the vapor pressure of the solvent when we add a solute to form a solution. We will define P^o as the vapor pressure of the pure liquid i.e., the solvent and P as the vapour pressure of the solvent after a solute has been added.

P^o = vapour pressure of the pure liquid, or solvent

P = vapour pressure of the solvent in a solution

When the temperature of a liquid is below its boiling point, we can assume that the only molecules that can escape from the liquid to form a gas are those that lie near the surface of the liquid.

When a solute is added to the solvent, some of the solute molecules occupy the space near the surface of the liquid, as shown in the figure below. When a solute is dissolved in a solvent, the number of solvent molecules near the surface decreases, and the vapour pressure of the solvent decreases.

This has no effect on the rate at which solvent molecules in the gas phase condense to form a liquid. But it decreases the rate at which the solvent molecules in the liquid can escape into the gas phase. As a result, the vapour pressure of the solvent escaping from a solution should be smaller than the vapour pressure of the pure solvent.

$$P < P^{o}$$

vapour pressure of the solvent above a solution — vapour pressure of the pure solvent

According to Rault's Law

$$P = X_{solvent}\, P^{o}$$

vapour pressure of the solvent above a solution — vapour pressure of the pure solvent

This equation, which is known as **Raoult's law**, is easy to understand. When the solvent is pure, and the mole fraction of the solvent is equal to 1, P is equal to P^{o}. As the mole fraction of the solvent becomes smaller, the vapour pressure of the solvent escaping from the solution also becomes smaller.

Let's assume, for the moment, that the solvent is the only component of the solution that is volatile enough to have a measurable vapour pressure. If this is true, the vapor pressure of the solution will be equal to the vapour pressure of the solvent escaping from the solution. Raoult's law suggests that the difference between the vapour pressure of the pure solvent and the solution increases as the mole fraction of the solvent decreases.

The change in the vapour pressure that occurs when a solute is added to a solvent is therefore a colligative property. If it depends on the mole fraction of the solute, then it must depend on the ratio of the number of particles of solute to solvent in the solution but not the identity of the solute.

Lowering of vapour pressure is a colligative property. The vapour pressure of a solvent in solution is less than the vapour pressure of the pure solvent at the same temperature. If P°_{A} is the vapour pressure of the pure solvent and P_A that of the solvent in solution, the decrease in vapour pressure $P^{\circ}_{A} - P_A$ is called the lowering of vapour pressure which is directly proportional to the mole fraction of the solute in solution.

$$P_A = X_A P^{o}_{A} \Rightarrow P^{\circ}_{A} - P_A = P^{\circ}_{A}(1 - X_A) = P^{\circ}_{A} X_B$$

Higher the mole fraction of solvent in solution, higher is the partial vapour pressure of the solvent.

Vapour pressure lowering of a solution has already been explained under Raoult' Law. It was derived that the relative lowering of vapour pressure is given by the equation

$$\frac{P^{o}_{A} - P_A}{P^{o}_{A}} = X_B = \frac{n_B}{n_A + n_B}$$



Worked-out Examples

10. Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torn The partial vapour pressure of benzene at 20°C for a solution containing 78 g benzene and 46 g toluene in torr is: **[AIEEE-2005]**

(a) 50 (b) 25

(c) 375 (d) 53.5

Solution (a) $P'_A = P^{o}_{B}.X_B = 75 \times \dfrac{\frac{78}{78}}{\frac{78}{78}+\frac{46}{92}} = 75 \times \dfrac{1}{1+\frac{1}{2}} = 75 \times \dfrac{2}{3} = 50$

11. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure for this aqueous solution at 100°C is: **[AIEEE-2006]**

(a) 759 torr (b) 7.60 torr

(c) 76.0 torr (d) 752.40 torr

Solution (d) $\frac{P^\circ - P_S}{P_S} = \frac{n}{N} = \frac{18 \times 18}{180 \times 178.2} = 0.01$ $\therefore \frac{760 - P_S}{P_S} = 0.01$

($\because$ P° = 760 torr at b.pt. of H_2O) P_s = 752.47 torr

12. At 80°C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) **[AIEEE-2008]**

(a) 52 mol per cent (b) 34 mol per cent

(c) 48 mol per cent (d) 50 mol per cent

Solution (d) At 1 atmospheric pressure the boiling point of mixture is 80°C.
At boiling point the vapour pressure of mixture, P_T = 1 atmosphere = 760 mm Hg.
Using the relation,

$P_T = P_A^\circ X_A + P_B^\circ X_B$, we get

$P_T = 520\ X_A + 1000(1 - X_A)$

$\because$ P_A° = 520 mm Hg,

P_B° = 1000 mm Hg, $X_A + X_B$

or $760 = 520\ X_A + 1000 - 1000X_A$ or $480X_A = 240$

or $X_A = \frac{240}{480} = \frac{1}{2}$ or 50 mol. per cent

13. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be **[AIEEE-2008]**

(a) 17.325 mm Hg (b) 15.750 mm Hg

(c) 16.500 mm Hg (d) 7.500 mm Hg

Solution (a) On addition of glucose to water, vapour pressure of water will decrease. The vapour pressure of a solution of glucose in water can be calculated using the relation

$$\frac{P^\circ - P_S}{P_S} = \frac{\text{Moles of glucose in solution}}{\text{moles of water in solution}}$$

or $\frac{17.5 - P_S}{P_S} = \frac{18/180}{178.2/18}$ [$\because$ P° = 17.5]

or $17.5 - P_S = \frac{0.1 \times P_S}{9.9}$

or P_s = 17.325 mm Hg.

14. Two liquids X and Y form an ideal solution. At 300K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mmHg) of X and Y in their pure states will be, respectively: **[AIEEE-2009]**

(a) 200 and 300 (b) 300 and 400

(c) 400 and 600 (d) 500 and 600

Solution (c)

$P_T = P_x^o x_x + P_y^o x_y$

X_x = Mol fraction of X

X_y = mol fraction of Y

$$\therefore \quad 500 = P_x^o\left(\frac{1}{1+3}\right) + P_y^o\left(\frac{4}{1+4}\right)$$

$$= \frac{P_x^o}{4} + \frac{3P_y^o}{4}$$

$$\therefore \quad 550\,(4) = P_x^o + 3P_y^o \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Further 1 mol of Y is added and total pressure increases by 10 mm Hg.

$$\therefore \quad 550 + 10 = P_x^o\left(\frac{1}{1+4}\right) + p_y^o\left(\frac{4}{1+4}\right)$$

$$\therefore \quad 550\,(5) = P_x^o + 4P_y^o \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

By solving (1) and (2)

We get, $P_x^o = 400$ mm Hg

$P_y^o = 600$ mm Hg

15. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? **[AIEEE-2009]**

(a) The solution formed is an ideal solution

(b) The solution is not-ideal, showing +ve deviation from Raoult's law.

(c) The solution is non-ideal, showing –ve deviation from Raoult's law.

(d) n-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's law.

Solution (b) The interactions between n-heptane and ethanol are weaker than that in pure components.

Measurement of Relative Lowering of Vapour Pressure (Ostwald and Walker's Apparatus):

In this method, a stream of dry air is bubbled successively through (i) the solution (ii) the pure solvent and (iii) a reagent which can absorb the vapour of the solvent. As the solvent is usually water, the reagent is generally anhydrous calcium chloride. The complete assembly is shown in the figure

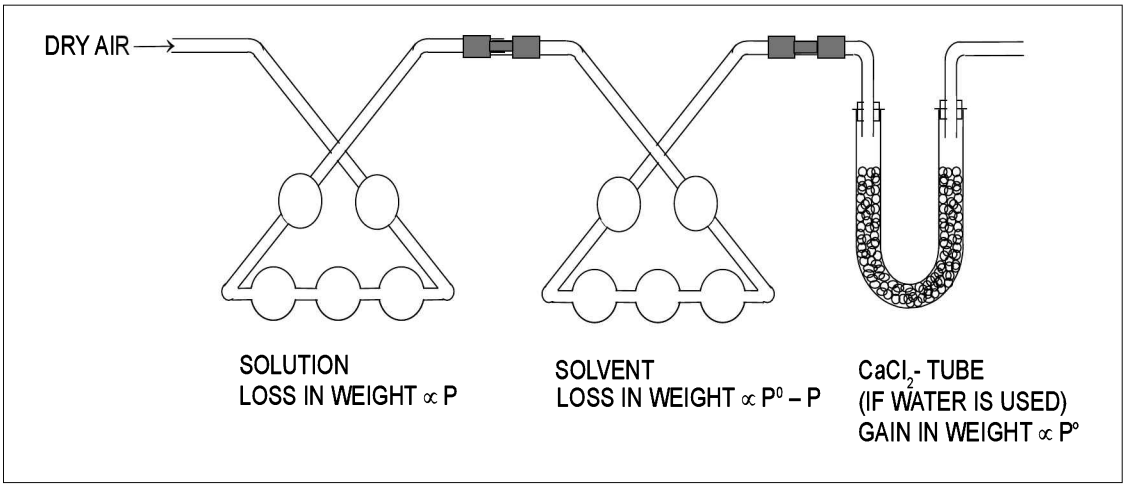


Fig. 8.30

The first three bulbs contain a weighed amount of the solution under examination and the next three bulbs contain a weighed amount of the pure solvent. A weighed amount of anhydrous calcium chloride is taken in the set of U-tubes at the end.

All the bulbs must be kept at the same temperature and air must be bubbled gradually to ensure that it gets saturated with the vapours in each bulb.

The dry air, as it passes through the solution, takes up an amount of vapour which is proportional to the vapour pressure of the solution at the prevailing temperature. This moist air passes through water (solvent), it takes up a further amount of vapour which is proportional to the difference in vapour pressure of the pure solvent and the solution.

It is evident that,

Loss in mass of solution $\propto P$

Loss in mass of solvent $\propto P^0$-P

Loss in mass of solution + loss in mass of solvent

$\propto P^0$–P + P $\propto P^0$

Where P° = Vapour pressure of pure solvent

P = Vapour pressure of solution

The calcium chloride tubes are weighed at the end of the experiment. The gain in mass should be equal to the total loss in mass of the solution and solvent which, in turn, is proportional to P^0, as shown above.

In other words, $$\frac{\text{loss in mass of solvent}}{\text{gain in mass of } CaCl_2 \text{ tubes}} = \frac{P^0 - P}{P^0}$$

Thus, knowing the loss in mass of the solvent and gain in the mass of the calcium chloride tubes, it is possible to calculate the lowering of vapour pressure.



Worked-out Examples

16. A current of dry air was bubbled 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 water bulb is 0.0870 g and gains in weight of $CaCl_2$ tube is 2.036 g. Calculate the molecular weight of the organic substance in the solution.

Solution As we know

$$\frac{\Delta P}{P^0} = X_{solute} = \frac{n_B}{n_A + n_B} = \frac{W_B/m_B}{(W_A/m_A) + (W_B/m_B)}$$

Here $A \rightarrow$ solvent, $B \rightarrow$ solute

$$\therefore \quad \frac{\Delta P}{P^0} = \frac{26.66 / m_B}{\left(\frac{200}{18}\right) + (26.66/m_B)}$$

$\Delta P \propto$ loss in wt. of water bulb

$\propto 0.087$

$P^0 \propto$ gain in weight of $CaCl_2$

$\propto 2.036$

From equation (1) and (2), we get

$$\frac{0.087}{2.036} = \frac{26.66 / m_B}{200/18}$$

then mol. wt , $m_B = 56.15$

17. Pure and dry nitrogen gas is slowly bubbled through a solution of 2.25 g of a non-volatile organic compound dissolved in 150 g of benzene and then bubbled through pure benzene. The solution is found to be 2.1540 g lighter, while pure benzene suffered a loss in weight of 0.0160 g. Calculate the molecular weight of non-volatile organic compound.

Solution We know,

$$\frac{\Delta P}{p^0} = X_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} \text{ (for dilute solution)}$$

$$\frac{\Delta p}{p^0} = \frac{W_B / m_B}{W_A / m_A} = \frac{W_B \times m_A}{W_A \times m_B} \qquad \text{(i)}$$

Given $W_B = 2.25$ g

$W_A = 150$ g

$M_A = 78$; $m_B = ?$

$\Delta p \; \alpha \; 0.016$

$p^0 \; \alpha \; 2.154$

Hence, from equation (i), we have

$$\frac{0.016}{2.154} = \frac{2.25 \times 78}{150 \times m_B}$$

$m_B = 157.5$

18. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be **[AIEEE-2007]**

(a) 360 (b) 350

(c) 300 (d) 700

Solution (b) p_A° =? Given p_B° = 200 mm, $x_A = 0.6$,

$x_B = 1 - 0.6 = 0.4$, $P = 290$

$P = P_A + P_B = P_A^\circ x_A + P_B^0 x_B$

$\Rightarrow \quad 290 = P_A^0 \times 0.6 + 200 \times 0.4 \qquad \therefore \; P_A^0 = 350$ mm

Boiling-point elevation

Boiling-point elevation describes the phenomenon that the boiling point of a liquid (a solvent) will be higher when another compound is added, meaning that a solution has a higher boiling point than a pure solvent. This happens whenever a non-volatile solute, such as a salt, is added to a pure solvent, such as water. The boiling point can be measured accurately using an ebullioscope.

Put in vapour pressure terms, a liquid boils at the temperature when its vapour pressure equals the surrounding pressure. For the solvent, the presence of the solute decreases its vapour pressure by dilution. A non-volatile solute has a vapour pressure of zero, so the vapour pressure of the solution is the same as the vapour pressure of the solvent. Thus, a higher temperature is needed for the vapour pressure to reach the surrounding pressure, and the boiling point is elevated.

For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Elevation of Boiling Point: The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. When the atmospheric pressure is 1 atm, boiling point is called the normal boiling point. The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it. The decreased vapour-pressure means that the solution would have to be heated to a higher temperature so that its vapour pressure becomes equal to the atmospheric pressure. In other words, the boiling point of the solution T_b is higher than the boiling point of the pure solvent T_b^0. The difference $T_b^s - T_b^0$ is called the boiling point elevation.

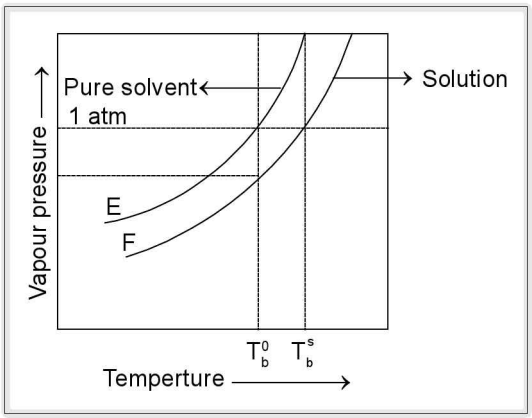


Fig. 8.31 Plot of variation of vapour pressure elevation of boiling point.

Boiling point elevation = $T_b - T_b^0$

- When non-volatile solute is added to pure solvent, the boiling point increases.

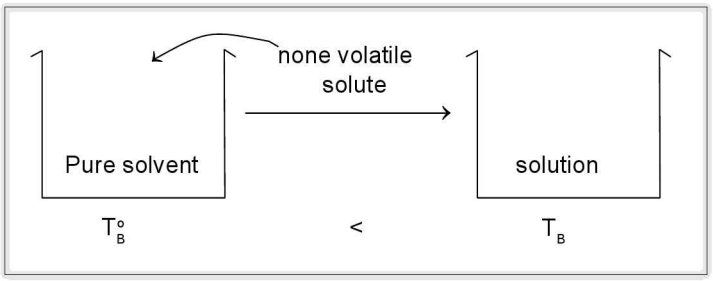


Fig. 8.32

Extent of elevation $\Delta T_B = (T_B - T_B^o)$

$$(T_B - T_B^o) = \Delta T_B = \frac{R(T_B^o)^2 X_B}{\Delta H_{vap}^o} \text{ mole fraction of solute}$$

R = Gas constant

T_B = boiling pt. of solution produced

ΔH_{vap}^o = molar ethalpy of vapourization for pure solvent

$$\Delta T_B = \left(\frac{RT_B^{o^2}}{\Delta H_{vap}^o}\right)\left(\frac{n_B}{n_A + n_B}\right)$$

$$\Delta T_B = \left(\frac{RT_B^{o^2}}{\Delta H_{vap}^o}\right)\left(\frac{n_B}{n_A}\right) \text{ (For dilute solution } n_A \gg n_B \text{ and } (n_A + n_B) \approx n_A)$$

$$\Delta T_B = \left(\frac{RT_B^{o2}}{M_A l_V}\right)\left(\frac{n_B}{n_A}\right) = \left(\frac{RT_B^{o^2}}{M_A l_V}\right).\left(\frac{n_B}{\frac{W_A}{M_A}}\right)$$

$$\Delta T_B = \frac{RT_B^{o2}}{l_V}\left(\frac{n_B}{W_A}\right) \text{ ..... approx = solution is very dilute}$$

If $W_A = 1000$ g, then by definition $n_B = m$ (molality of solution)

$$\Delta T_B = \frac{RT_B^{o2}}{h}\left(\frac{m}{10^3}\right) \text{ or, } \Delta T_B = \left(\frac{RT_B^{o2}}{10^3 lv}\right)m$$

$\left(\frac{RT_B^{o^2}}{10^3 lv}\right)$ will be constant for pure solvents.

$$\frac{RT_B^{o2}}{10^3 lv} = K_b \text{ =ebullioscopic constant}$$

The extent of boiling-point elevation can be calculated by applying Clausius-Clapeyron relation and Raoult's law together with the assumption of the non-volatility of the solute. The result is that in dilute ideal solutions, the extent of boiling-point elevation is directly proportional to the molal concentration of the solution according to the equation:

$$\Delta T_b = i K_b \cdot m_B$$

where

- ΔT_b, the boiling point elevation, is defined as $T_{b\,(solution)} - T_{b\,(pure\ solvent)}$.
- K_b, the ebullioscopic constant, which is dependent on the properties of the solvent. It can be calculated as $K_b = RT_b^2M/\Delta H_v$, where R is the gas constant, and T_b is the boiling temperature of the pure

solvent [in K], M is the molar mass of the solvent, and ΔH_v is the heat of vaporization per kg of the solvent.

$$\text{For water} \qquad K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$$

- m_B is the molality of the solution, calculated by taking dissociation into account since the boiling point elevation is a colligative property, dependent on the number of particles in solution. This is most easily done by using the van't Hoff factor i as $m_B = m_{solute} \cdot i$. The factor i accounts for the number of individual particles (typically ions) formed by a compound in solution. Examples:
  - i = 1 for sugar in water
  - i = 2 for sodium chloride in water, due to the full dissociation of NaCl into Na^+ and Cl^-
  - i = 3 for calcium chloride in water, due to dissociation of $CaCl_2$ into Ca^{2+} and $2Cl^-$

At high concentrations, the above formula is less precise due to nonideality of the solution. If the solute is also volatile, one of the key the assumptions used in deriving the formula is not true, since it derived for solutions of non-volatile solutes in a volatile solvent.



Worked-out Examples

19. A 10% solution of cane sugar has undergone partial inversion according to the reaction:
Sucrose + Water $\longrightarrow$ Glucose + Fructose.

If the boiling point of solution is 100.27°C.

(a) What is the average molecular mass of the dissolved materials?

(b) What fraction of the sugar has inverted?

Solution Let α-degree of inversion of sugar. The reaction is

$$C_{12}H_{22}0_{11} + H_2O \text{ (excess)} \longrightarrow \text{Glucose + fructose}$$

$$i = \frac{(1-\alpha)+\alpha+\alpha}{1} = 1+\alpha$$

From question, elevation in boiling point,

$$\Delta T_b = 100.27°C - 100°C = 0.27°C$$

As we know

$$\Delta T_b = K_b \times \frac{w}{m_0} \times \frac{1000}{W \text{ (in gm)}}, \qquad \text{where } m_o = \text{observed mol. wt.}$$

$$\Rightarrow \quad 0.27 = 0.52 \times \frac{10}{m_0} \times \frac{1000}{90} \qquad w = \text{wt. of solute} = 10 \text{ g}$$

$$\Rightarrow \quad m_0 = 213.99 \qquad \text{wt. of solvent} = W = (100 - 10) \text{ g} = 90 \text{ g}$$

as we know that

$$i = \frac{\text{normal mol. wt}}{m_0}$$

or, $1 + \alpha = \dfrac{342}{213.99}$

$\therefore \quad \alpha = 0.59 \approx 0.60$

1. Average molecular mass of the dissolved material = **213.99**
2. Fraction of sugar inverted = α = **0.60**

20. A pressure cooker reduces cooking time for food because: **[AIEEE-2003]**

(a) the higher pressure inside the cooker crushes the food material
(b) cooking involves chemical changes helped by rise in temperature
(c) heat is more evenly distributed in the cooking space
(d) boiling point of water involved in cooking increases

Solution (d) Liquid boils at the higher temperature if pressure is more.

21. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ (molecular weight = 134.4, K_b = 0.52 K molality^{-1}) in 1 kg water using the following information will be: **[AIEEE-2003]**

(a) 0.16 (b) 0.05 (c) 0.1 (d) 0.2

Solution (a) $\Delta T_b = \dfrac{1000 \times 0.52 \times 13.44}{134.4 \times 1000} \times (1 + 2\alpha)$ $\because a = 1$

$= 0.052 \times 3 = 0.156$

22. Which aqueous solution exhibits highest boiling point? **[AIEEE-2004]**

(a) 0.015M glucose (b) 0.01MKNO_3
(c) 0.0ISA/urea (d) 0.01MNa_2SO_4

Solution (d) Na_2SO_4 furnishes more particles i.e., C $(1-\alpha + 3\alpha) = 0.01 \times 3 = 0.03$

23. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (Molecular weight of $CuCl_2$ = 134.4 and K_b = 0.52 K molal^{-1}) **[IIT-2005]**

(a) 0.16 (b) 0.05 (c) 0.1 (d) 0.274

Solution (a) $CuCl_2 \longrightarrow Cu^{2+} + 2Cl^-$

1	0	0
$(1-\alpha)$	α	2α

$i = \dfrac{1+2\alpha}{1}$ $\quad i = 1+2\alpha$

Assuming 100% ionization So, i = 1 + 2 = 3

$\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156 \approx 0.16$



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Freezing-point depression

It describes the phenomenon in which the freezing point of a liquid (a solvent) is depressed when another compound is added, meaning that a solution has a lower freezing point than a pure solvent. This happens whenever a solute is added to a pure solvent, such as water. The phenomenon may be observed in sea water, which due to its salt content remains liquid at temperatures below 0°C, the freezing point of pure water.

Depression in Freezing Point: The freezing point of a liquid is the temperature at which it begins to freeze and the crystallized solid and liquid are in equilibrium. At freezing point, the vapour pressure of the solid is equal to the vapour pressure of the liquid. When a dilute solution is cooled to freezing point, it is assumed that crystals of pure solvent always separate out first. The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it. Therefore, a solid liquid equilibrium exists only at a temperature lower than the freezing point of the pure solvent. In other words, for a solid to have the same vapour pressure as that of the solution, the freezing point should lower down. If T_f^0 is the freezing point of the pure solvent and T_f that of the solution, the difference $T_f^0 - T^s_f$ is called the freezing point depression.

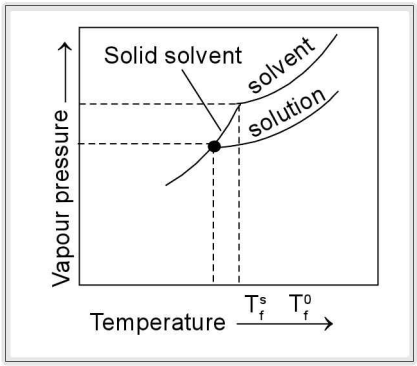


Fig. 8.33 Plot of variation of vapour pressure of a solution with temperature and depression in freezing point.

Freezing point depression = $T_f^0 - T^s_f$

Depression In Freezing Point

Solid liquid

$P_{vap}(s) = P_{vap}(l)$

solid → liquid latent heat is supplied latent heat of fusion = +ve

H_2O | $H_2O + NaCl$

↓ freezing at 0°C | ↓ freezing

this ice is freezing of pure solvent | ice | NaCl → freezing of solvent is solution

↓

pure solvent

When solute is added to pure solvent, the entropy increases. So freeze the solution, the entropy has to decrease to a greater extent as compared to that of solvent. Hence the melting (freezing) pt. of solution (T_f) will be lower than that of solvent (T_f°).

$$T_f^\circ - T_f = \Delta T_f = \left(\frac{RT_f^{\circ 2}}{\Delta H^\circ_{fusion}}\right) X_B$$

ΔH°_{fusion} = molar enthalpy of fusion the pure solvent.

$$\Delta T_f = \left(\frac{RT_f^{\circ 2}}{\Delta H^\circ_{fusion}}\right)\left(\frac{n_B}{n_A + n_B}\right) \quad (n_A >>> n_B \text{ for dilute sol}^n \text{ and } (n_A + n_B) \approx n_A)$$

$$\Downarrow$$

$$\Delta T_f = \left(\frac{RT_f^{\circ 2}}{\Delta H^\circ_{fusion}}\right)\left(\frac{n_B}{n_A}\right)$$

l_f = latent heat of fusion per gram of pure solvent $M_A l_f = \Delta H_{fus}$

$$\Downarrow$$

$M_A l_f = \Delta H^\circ_{fus}$ where M_A = Molar mass of solvent

$$\Delta T_f = \left(\frac{RT_f^{\circ 2}}{l_f}\right)\left(\frac{n_B}{W_A}\right)$$

When $W_A = 10^3$ g $\Rightarrow n_B = m$ (molality)

$$\Delta T_f = \frac{RT_f^{\circ 2}}{l_f}\left(\frac{m}{10^3}\right)$$

K_f = Cryoscopic Constant. $= \dfrac{RT_f^{\circ 2}}{10^3 lf}$

It is the depression in freezing point for 1 molal solution.

'K_f' is also called Molal Depression Constant.

Units of $K_f \rightarrow K\ Kg\ mol^{-1}$

The phenomenon of boiling point elevation is analogous to freezing point depression. However, the magnitude of the freezing point depression is larger than the boiling point elevation for the same solvent and the same concentration of a solute. Because of these two phenomena, the liquid range of a solvent is increased in the presence of a solute.

The extent of freezing-point depression can be calculated by applying the Clausius-Clapeyron relation and Raoult's law together with the assumption of the non-solubility of the solute in the solid solvent. The result is that in dilute ideal solutions, the extent of freezing-point depression is directly proportional to the molal concentration of the solution according to the equation[1]

$$\Delta T_f = i\, K_f \cdot m_B$$

where

- ΔT_f, the freezing point depression, is defined as $T_{f\,(pure\ solvent)} - T_{f\,(solution)}$, the difference between the freezing point of the pure solvent and the solution. It is defined to assume positive values when the freezing point depression takes place.
- K_f, the cryoscopic constant, which is dependent on the properties of the solvent. It can be calculated as $K_f = RT_m^2 M/\Delta H_f$, where R is the gas constant, T_m is the melting point of the pure solvent in kelvin, M is the molar mass of the solvent, and ΔH_f is the heat of fusion per mole of the solvent.

  For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86$$

- m_B is the molality of the solution, calculated by taking dissociation into account since the freezing point depression is a colligative property, dependent on the number of particles in solution. This is most easily done by using the van 't Hoff factor i as $m_B = m_{solute} \cdot i$. The factor i accounts for the number of individual particles (typically ions) formed by a compound in solution. Examples:
  - i = 1 for sugar in water
  - i = 2 for sodium chloride in water, due to dissociation of NaCl into Na^+ and Cl^-
  - i = 3 for calcium chloride in water, due to dissociation of $CaCl_2$ into Ca^{2+} and 2 Cl^-
  - i = 2 for hydrogen chloride in water, due to complete dissociation of HCl into H^+ and Cl^-
  - i = 1 for hydrogen chloride in benzene, due to no dissociation of HCl in a non-polar solvent



Worked-out Examples

24. The elements X and Y form compounds having molecular formula XY_2 and XY_4. When dissolved in 20 g of benzene, 1 g XY_2 lowers the freezing point by 2.3°C, whereas 1 g of XY_4 lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.

Solution Let the atomic mass of X = a

and the atomic mass of Y = b

For compared XY_2

Mol. wt. = a + 2b

$$\therefore \text{ mole of } XY_2 = \frac{1}{a + 2b}$$

As we know that

$$\Delta T_f = K_f \times \text{number of moles of solute per 1000 g solvent}$$

or, $$\Delta T_f = k_f \times \frac{1}{a+2b} \times \frac{1000}{20}$$

or, $$2.3 = 5.1 \times \frac{1}{a+2b} \times \frac{1000}{20}$$

$\because$ $a + 2b = 110.869$ ...(1)

Similarly, for compound XY_4

$m = \text{mol. wt} = a + 4b$

$\because$ $$\Delta T_f = K_f \times \frac{w}{m} \times \frac{1000}{W}$$

$$1.3 = 5.1 \times \frac{1000}{20} \times \frac{1}{(a+4b)} \quad \therefore \; a + 4b = 196.153 \qquad \ldots(2)$$

$m = 196.153$

Solving equation (i) and (ii), **a = 25.60**

$b = 42.60$

25. Find Ka, the ionization constant of a monobasic acid AH if a 0.025 molal aqueous solution of acid freezes at –0.060°C (assumine molality = molality). Kf = 1.86 kg mol–1 K.

Solution Assuming that the tartaric acid be a monobasic as AH. It ionizes as

AH	$\rightleftharpoons$	A	+	H^+
Initially conc.	C	0		0
Con. After dissociation	C(1–α)	Cα		Cα,

Here, $i = \frac{C(1-\alpha) + C\alpha + C\alpha}{C}$, where α = degree of dissociation

$$= \frac{C(1+\alpha)}{C} = 1+\alpha$$

Molal concentration = 0.1

$$\Delta T_f = K_f \times C_m \times i$$

$$0.06 = 1.86 \times 0.025 \times (1+\alpha)$$

$\therefore$ $\alpha = 0.29$

$$K_a = \frac{[A^-][H^+]}{[AH]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{\alpha^2 C}{1-\alpha}$$

$$K = \frac{0.025 \times 0.29^2}{1-0.29}$$

$\therefore$ $K_a = 3 \times 10^{-3}$

26. In a 0.2 molal aqueous solution of weak acid HX, (the degree of dissociation 0.3) the freezing point is (given K_f = 1.85 K molality^{-1}): **[AIEEE-2003]**

(a) –0.26°C (b) + 0.48°C

(c) –0.48°C (d) –0.36°C

Solution (c) $\Delta T = K_f \times \text{molality} \times (1 + \alpha) = 1.85 \times 0.2\ (1 + 0.3) = 0.48$

$\therefore$ f.pt. = 0–0.48 = –0.48°C

27. Freezing point of an aqueous solution is –0.186°C. Elevation of boiling point of the same solution is ..... if Kb = 0.512 K molality–1 and Kf = 1.86 K molality–1: **[AIEEE-2002]**

(a) 0.186°C (b) 0.0512°C

(c) 0.092°C (d) 0.237°C

Solution (b) $\Delta T_f = \frac{1000.K_f.w}{W.m}$ and $\Delta T_b = \frac{1000.K_b.w}{W.m}$

$\therefore \quad \frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b} \text{ or } \frac{0.186}{\Delta T_b} = \frac{1.86}{0.512}$ $\quad \therefore \Delta T_b = 0.0512^oC$

28. Equimolar solutions of two non-electrolytes in the same solvent have: **[AIEEE-2005]**

(a) Same b.pt. but different f.pt.

(b) Same f.pt. but different b.pt.

(c) Same b.pt. and same f.pt.

(d) Different b.pt. and different f.pt.

Solution (c) $\Delta T_f = K_f \times$ molality

$\Delta T_b = K_b \times$ molality

Thus ΔT_f and ΔT_b for different non electrolytes is same as K_f and K_b are constant.

29. Given that ΔTf is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m, the quantity $\underset{m\to 0}{Lt}(\Delta T_f / m)$ is equal to……

Solution Kf: depression in freezing point, ΔTf = Kf. m, where Kf is the molar depression constant or cryoscopic constant and m is the molality of the solution given by moles of solute per 1000 g of the solvent.

30. 0.2 molal acid HX is 20% ionized in solution. K_f= 1.86 K molality^{-1}. The freezing point of the solution is: **[IIT-1995]**

(a) –0.45 (b) –0.90 (c) –0.31 (d) –0.53

Solution (a) Depression in freezing point, ΔTf = i × Kf × m

Van't Hoff factor, $i = \frac{1-\alpha+n\alpha}{1}$, where n = number of ions produced by comlete dissociation of 1 mole of HX.

$HX \rightleftharpoons H^+ + X^- \Rightarrow n = 2$

$\therefore \quad i = \frac{1-0.2+2\times 0.2}{1} = 1.2$

$\therefore \quad \Delta T_f = 1.2 \times 1.86 \times 0.2 = 0.45$

31. During depression of freezing point in a solution the following are in equilibrium: **[IIT-2003]**

(a) liquid solvent, solid solvent

(b) liquid solvent, solid solute

(c) liquid solute, solid solute

(d) liquid solute, solid solvent

Solution (a) At the freezing point liquid and solid remain in equilibrium. If a solution of a non-volatile solute is cooled to a temperature below the freezing point of solution, some of liquid solvent will separate as a solid solvent and thus the concentration of solution will increase.

32. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 Kg mol^{-1}), a freezing pint depression of 2K is observed. The Van't Hoff factor (i) is **[IIT-2007]**

(a) 0.5 (b) 1

(c) 2 (d) 3

Solution (a) Molecular weight of naphthoic acid

$C_{11}H_8O_2$ = 172 $gmol^{-1}$

The theoretical value of depression in freezing point = k_f ×molality = $1.72 \times \frac{20 \times 1000}{172 \times 50} = 4K$

Van't Hoff factor,

$$i = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}} = \frac{2}{4} = 0.5.$$

33. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to: **[IIT-1996]**

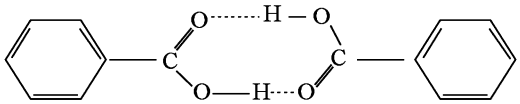
(a) ionization of benzoic acid

(b) dimerization of benzoic acid

(c) trimerization of benzoic acid

(d) solvation of benzoic acid

Solution (b) **Benzoic acid exists as dimmer in benzene.**



34. In the depression of freezing point experiment, it is found that the

(a) vapour pressure of the solution is less than that of pure solvent

(b) vapour pressure of the solution is more than that of pure solvent

(c) only solute molecules solidify at the freezing point

(d) only solvent molecules solidify at the freezing point

Solution (a, d) The freezing point of a solvent depresses as a nonvolatile solute is added to solvent. According to Raoult's law, when a non-volatile solute is added to a solvent the vapour pressure of the solvent decreases. At the freezing point it will be only the solvent molecules which will solidify.

PASSAGE (35-37) **[IIT-2008]**

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given: Freezing point depression constant of water (K_f^{water}) = 1.86 K kg mol^{-1}

Freezing point depression constant of ethanol ($K_f^{ethanol}$) = 2.0 K kg mol^{-1}

Boiling point elevation constant of water (K_d^{water}) = 0.52 K kg mol^{-1}

Boiling point elevation constant of ethanol ($K_b^{ethanol}$) = 1.2 K kg mol^{-1}

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol^{-1}

Molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

35. The freezing point of the solution M is

(a) 268.7 K (b) 268.5 K

(c) 234.2 K (d) 150.9 K

Solution (d)

Let total moles be 1, then

$$N_{ethanol} = 0.9$$

mass of ethanol = 41.4 g = 41.4×10^{-3} kg

$$n_{water} = 0.1$$

$$\text{molality, } m = \frac{0.1}{41.4} \times 10^3 = 2.4 \text{ mol/kg.}$$

$$\Delta T_f = k_{f^m} = 2 \times 2.4 = 4.8$$

$$T_f \text{(ethanol)} = 155.7 - 4.8 = 150.9 \text{ K}$$

36. The vapour pressure of the solution M is

(a) 39.3 mm Hg (b) 36.0 mm Hg

(c) 29.5 mm Hg (d) 28.8 mm Hg

Solution (b)

$$\frac{40 - P_s}{40} = 0.1$$

$$P_s = 36 \text{ mm of Hg.}$$

37. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

(a) 380.4 K (b) 376.2 K

(c) 375.5 K (d) 354.7 K

Solution (b)

Let no of moles be 1

$$nH_2O = 0.9 \; n_{ethanol} = 0.1$$

mass of $H_2O = 0.9 \times 18$ g = 16.2 g = 0.0162 kg

$$\text{molality} = \frac{0.1}{0.0162} \text{mol/kg} = 06.17 \text{ mol/kg}$$

$$\Delta Tb = kb.m$$

$$0.52 \times 6.17 = 3.2$$

Boiling point of solution = 373 + 3.2 = 376.2 K



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Osmotic Pressure

One of the simplest ways that you can set up an osmosis experiment is shown in figure (8.34). The liquid level in the tube rises. This shows that water from the beaker passes through the cellophane into the sugar solution. If you were to test the water in the beaker you would find that it is free of sugar. The cellophane allows some molecules to pass through it but not others; it is called a semipermeable membrane (Figure 8.35), or sometimes a perm-selective membrane. The result of the experiment looks as if there were pressure acting on the water in the beaker which pushes it through the membrane into the solution. This pressure is due to the process of osmosis. One of the key things to remember in osmosis is that:

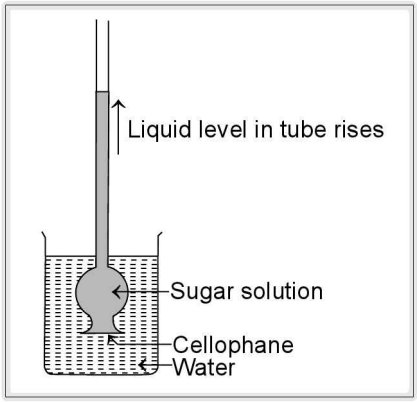


Fig. 8.34 A simple osmosis experiment. Water passes into the sugar solution, causing the liquid level in the tube to rise

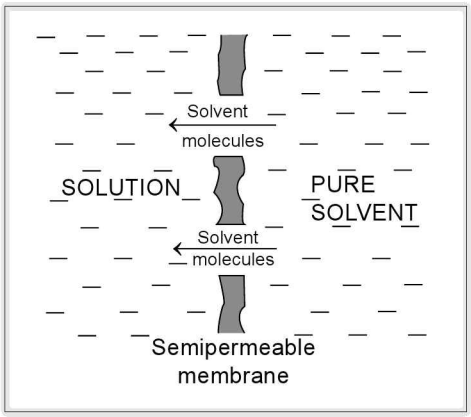


Fig. 8.35 In osmosis, solvent molecules always pass from the less concentrated to the more concentrated solution. Often the movement is from pure solvent to solution

The solvent will pass through a semipermeable membrane from the less concentrated to the more concentrated solution.

How might we explain osmosis?

One of the first explanations of osmotic pressure was due to van't Hoff in 1886. He suggested, correctly, that solvent molecules in the solution and the pure solvent bombarded the semipermeable membrane. Likewise, he pointed out that, on average, there were more solvent molecules bombarding the membrane on the solvent side than on the solution side. According to van't Hoff, we can draw the analogy with a gas and say that the solvent side has the higher 'pressure', so the solvent molecules will travel into the low

pressure (solution) side. However, the theory does not work out in detail. (This is in spite of the fact that some of the equations for osmotic pressure are very similar to the gas laws.) In practice solvent molecules interact with the solute particles in a solution. This interaction makes the situation significantly different to the behaviour of gases. A different explanation of why osmosis is linked to pressure, and why it is a colligative property, makes use of our knowledge of vapour pressures

We know that the vapour pressure of a solvent will be greater than that of a solution. The difference in vapour pressures within the narrow pores of the semipermeable membrane means that solvent molecules will travel from the solvent surface and join the solution. The osmotic pressure will depend on the difference between the two vapour pressures, which in turn depends on the number of solute particles in the solution.

You should not think that this is the correct explanation of osmosis. Osmosis is very complicated, and a full account of it would have to include details about the effects of the size of the solute and solvent particles, and about the nature of the membrane itself (some of them contain ions, some are covalent).

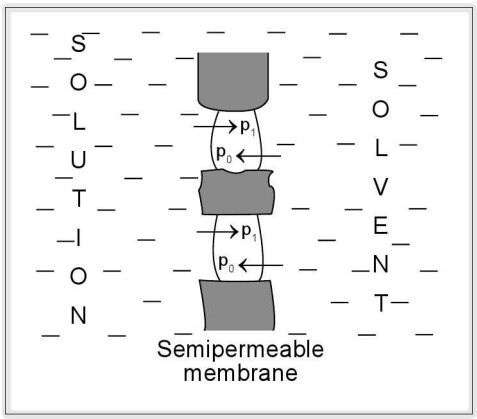


Fig. 8.36 One explanation of osmosis says there are channels through the semipermeable membrane where solvent and solution surfaces come close together. Because the vapour pressure of the solvent, P_0, is greater than that of the solution, P_1, solvent molecules transfer across the gap from the solvent to the solution

Some Examples of Osmosis

Osmotic pressure (π):

It is the movement of the solvent molecules through the semipermeable membrane from the solvent side to solution side or from less concentrated solution to more concentrates solution.

For dilute solutions $\pi = CRT = h\rho g$

Where C is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and ρ is the density of the solution in the column. On the basis of osmotic pressure, the solutions can be classified in three classes

Isotonic solutions: Two solutions having same osmotic pressures at same temperature. (This implies $C_1 = C_2$).

Hypertonic and Hypotonic Solution: When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic. The solution with lower osmotic pressure is termed as hypotonic.

Osmotic pressures can be determined quite accurately, hence it is used in the determination molecular weights of large proteins and similar substances.

Reverse Osmosis: If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

How to calculate molar masses from osmotic pressure experiments

We have said that a simple explanation of osmosis in terms of treating the solvent and solution as if they were gases is not strictly correct. However, some analogy with a gas is possible. Especially, from thermodynamics, it is possible to prove that the osmotic pressure, n, of a solution is given by

$$\Pi = \frac{nRT}{V}$$

where T is the Kelvin temperature, R the gas constant and there are n mol of solute in a volume V of solution. This equation is like the ideal gas equation, and we can use it in a similar way. Now look at example 1.



Worked-out Examples

38. 1.1 g of a protein were dissolved in 100cm³ (100 x 10^{-6}m³) of solution. The osmotic pressure at 25°C was measured as 1.15kPa, i.e., 1150N m^{-2}. What was the molar mass of the protein?

Solution We need to discover the value of n, so we start by rearranging the equation:

$$n = \frac{\Pi V}{RT}$$

$$= \frac{1150\,N\,m^{-2} \times 100 \times 10^{-6}\,m^3}{8.314\,J\,K^{-1}\,mol^{-1} \times 298\,K}$$

$$= 4.64 \times 10^{-5}\ mol$$

This represents our 1.1g of protein. Hence, the molar mass of the protein is

$$\frac{1.1\,g}{4.64 \times 10^{-5}\,mol} = 23\,700\,g\ mol^{-1}$$

This is a fairly typical value for a protein.

The results of osmosis experiments are subject to the same conditions that apply to the two other colligative properties of solutions, i.e., the solutions must be dilute, and the solute should not change its nature by dissociating or associating. In the case of proteins the molecules are so large and liable to interact with one another that strictly our equation $\Pi V = nRT$ is only true in the limit of infinite dilution.

39. A tube of uniform cross sectional area 1 cm² is closed at one end with semi permiable membrane. A solution having 5 g glucose per 100 ml is placed inside the tube and dipped in pure water at 27°C. When the equilibrium is established, what will be the osmotic pressure, height developed in vertical column. Also calculate molality and molarity of the solution. Density of glucose solution is 1 gm/ml.

Solution $\pi V = nRT$

$$\pi \times 0.1 = \frac{5}{180} \times 0.0821 \times 300$$

$$\pi = 6.841\ atm$$

$$\pi = h \times d \times g$$

$6.841 \times 76 \times 13.6 \times 981 = h \times 1 \times 981$

$h = 7070.85 \text{ cm} = 70.7 \text{ metre}$

$$M = \frac{W_B \times 1000}{M_B \times V} = \frac{5 \times 1000}{180 \times 100} = 0.277$$

Weight of solution = 100×1 g = 100 g

$W_B = 5$ g

$W_A = 100 - 5 = 95$ g

$$m = \frac{W_B \times 1000}{m_B \times W_A} = \frac{5 \times 1000}{180 \times 95} = 0.29$$

40. A solution of polystyrene in benzene contains 10 gm/L. The equilibrium height of the column of solution (density 0.88 gm/mL) in osmometer corrected for capillary rise is 11.6 an at 25°C what is the number average molar mass of the polystyrene, assuming solution to be ideal?

Solution $p = h\rho g$

$= 0.116 \text{ m} \times 0.88 \times 10^3 \text{ kg m}^{-3} \times 9.8 \text{ ms}^{-2} = 1000 \text{ Pa}$

$$\pi = \frac{mRT}{MV}$$

$$M = \frac{mRT}{\pi V}$$

$$M = \frac{109 \times 8.314 \text{JK}^{-1}\text{mol}^{-1} \times 298\text{K}}{10^3 \text{Pa} \times 10^{-3} \text{m}^3} = 2.7 \times 10^5 \text{ kg/mol}$$

41. What would be the concentration in gm/litre of a solution of non-electrolyte which is isotonic with decinormal solution of NaCl assuming degree of dissociation of NaCl to be 0.85?

Solution For NaCl solution $\pi = (1 + \alpha) \times 0.1 \times RT$

For given solute $\pi = C\,RT = \frac{w}{180} RT$

[W is weight of solute present in one litre]

$$\frac{w}{180} \times RT = (1 + \alpha) \times 0.1 \times RT$$

or $$\frac{w}{180} \times RT = (1 + 0.85) \times 0.1 \times RT$$

$\therefore$ $w = 33.3$ gm/lit.

42. Which statement is false? **[AIEEE-2004]**

(a) Two sucrose solutions of same molality prepared in different solvents have same ΔT_f

(b) Osmotic pressure, $\pi = MRT$

(c) Osmotic pressure for 0.01M aqueous solution: $BaCl_2 > KCl > CH_3COOH >$ Sucrose

(d) The vapour pressure of a component over a solution is proportional to its mole fraction

Solution (a) K_f of solvent is altogether different.

43. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be **[AIEEE-2007]**

(a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}
(c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1}

Solution (a) Osmotic pressure (π) of isotonic solutions are equal. For solution of unknown substance ($\pi = CRT$)

$$C_1 = \frac{5.25/M}{V}$$

For solution of urea, C_2(concentration) = $\frac{1.5/60}{V}$

Given, $\pi_1 = \pi_2$ $\because \pi = CRT$

$\therefore$ $C_1RT = C_2RT$ or $C_1 = C_2$ or $\frac{5.25/M}{V} = \frac{1.8/60}{V}$ $\therefore$ M = 210 g/mol

ONE CORRECT OPTION TYPE QUESTIONS

1. An aqueous solution containing a non-volatile solute has vapour presure of 750 mm Hg at 100°C. The mole fraction of he solute in that solution is

(a) 75/76 (b) 1/4

(c) 1/76 (d) can't be predicted

2. An aqueous solution containing nomolatile solute boils at 101° C. Its vapour pressure at 100°C.

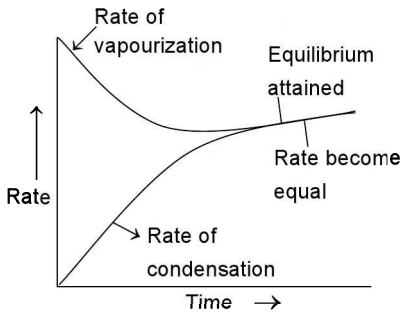
Given: latent heat of vapourization of water = 540 cal g^{-1}

(a) 760 mmHg (b) 766 mm Hg

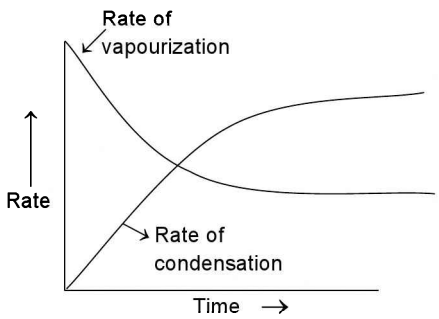
(c) 733.4 mm Hg (d) 750.4 mm Hg

3. Which of the following plots in correctly representing the variation in rate of evaporation and rate of condensation with time? (for liquid in a closed container)

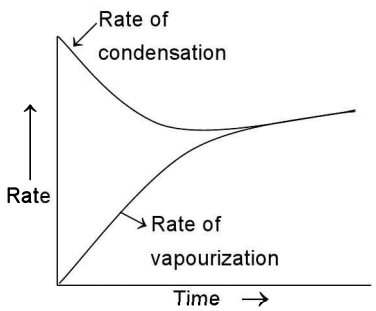
(a)



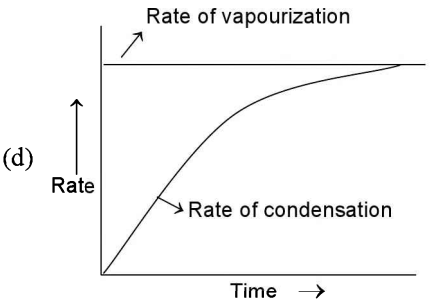
(b)



(c)



(d)



4. The freezing point of aqueous solution contains 5% by mass urea, 1.0% by mass KCl and 10% by mass of glucose is: ($K_{f_{H_2O}}$ = 1.86 K molality^{-1})

(a) 290.2 K (b) 285.5 K

(c) 269.93 K (d) 250 K

5. A solution of 18 g of glucose in 1000 g of water is cooled to – 0.2°C. The amount of ice separating out from this solution is (K_f, H_2O = 1.86 K molal^{-1})

(a) 70g (b) 140g

(c) 90g (d) 210g

6. An aqueous solution containing a weak monobasic acid boils at100.52°C. 100 ml of the solution requires 50 ml 1.5M NaOH for complete neutrilization. The value of α (degree of dissociation of weak acid)

100

(a) 1 (b) 1/3

(c) 1/4 (d) 0.5

7. An aqueous solution of a sparingly soluble salt MX_3 has vapour pressure 75 cm Hg at 100°C. Calculate the solubility product of MX_3 at 100°C.

(a) 1.62 (b) 2.53×10^{-2}

(c) 0.185 (d) 6.33×10^{-3}

8. pH of a 0.1M monobasic acid is found to be 2. Hence its osmotic pressure at a given temperature TK is

(a) 0.1 RT (b) 0.11RT

(c) 1.1RT (d) 0.01RT

9. If relative decrease in VP is 0.4 for a solution containing 1 mol NaCl in 3 mol of H_2O, the degree of ionization of NaCl is

(a) 60% (b) 50%

(c) 100% (d) 40%

10. 1.2 % (mass/volume) solution of NaCl is isotonic with 7.2% (mass/volume) solution of glucose. The degree of ionization of NaCl is (molar mass of NaCl = 58.5 molar mass of glucose = 180)

(a) 5% (b) 95%

(c) 50% (d) 90%

11. 1.2 % (mass/volume) solution of NaCl is isotonic with 7.2% (mass/volume) solution of glucose. The degree of ionization of NaCl is (molar mass of NaCl = 58.5 molar mass of glucose = 180)

(a) 5% (b) 95%

(c) 50% (d) 90%

12. Two liquids A and B are mixed at temperature T in a certain ratio to form an ideal solution. If it is found that the partial vapour pressure of A, i.e., p_A is equal to p_B, the vapour pressure of B for the liquid mixture. What is the total vapour pressure of the liquid mixture in terms of p_A^0 and p_B^0?

(a) $\frac{p_A^0 p_B^0}{p_A^0 + p_B^0}$ (b) $\frac{2p_A^0 p_B^0}{p_A^0 + p_B^0}$

(c) $\frac{p_A^0}{p_A^0 + p_B^0}$ (d) $\frac{2p_B^0}{p_A^0 + p_B^0}$

13. A complex of iron and cyanide ions is 100% ionized at 1 molal. If its elevation in boiling point is 2.08°, then the complex is (Given: $K_b = 0.52°C\ mol^{-1}\ kg$)

(a) $Fe^{III}_4[Fe^{II}(CN)_6]_3$ (b) $K_3[Fe^{III}(CN)_6]$

(c) $K_4[Fe^{III}(CN)_6]$ (d) $Fe^{III}_3[Fe^{III}(CN)_6]_2$

14. Depression in freezing point of 0.01 molal aqueous CH_3COOH solution is 0.02046°.1 molal urea solution freezes at –1.86°C. Assuming molality of solution equal to its molarity, pH of CH_3COOH solution would be

(a) 2 (b) 3

(c) 3.2 (d) 4.2

15. A weak electrolyte, AB, is 5% dissociated in aqueous solution. What is the freezing point of a 0.100 molal aqueous solution of AB? K_f for water is 1.86 deg/molal.

(a) –3.8°C (b) –0.1953°C

(c) –1.7°C (d) – 0.78°C

16. Calculate the boiling point of a one molar aqueous solution (density = 1.04 g mL^{-1}) of potassium chloride, K_b for water = 0.52 kg mol^{-1}. Atomic masses of K = 39, Cl = 35.5

(a) 107.28°C (b) 103.68°C

(c) 101.078°C (d) None of these

17. Y g of non-volatile organic substance of molecular mass M is dissolved in 250 g benzene. Molal elevation constant of benzene is K_b. Elevation in its boiling point is given by

(a) $\frac{M}{K_b Y}$ (b) $\frac{4K_b Y}{M}$

(c) $\frac{K_b Y}{4M}$ (d) $\frac{K_b Y}{M}$

18. The values of observed and calculated molecular weights of silver nitrate are 92.64 and 170 respectively. The degree of dissociation of silver nitrate is

(a) 60% (b) 83.5%

(c) 46.7% (d) 60.23%

19. The vapour pressures of ethanol and methanol are 42.0 mm and 88.5 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 46.0 g of ethanol with 16.0 g of methanol. The mole fraction of methanol in the vapour is:

(a) 0.467 (b) 0.502

(c) 0.513 (d) 0.556

20. For a binary ideal liquid solution, the total pressure of the solution is given as

(a) $P_{total} = P_A^* + (P_A^* - P_B^*)X_A$

(b) $P_{total} = P_B^* + (P_A^* - P_B^*)X_A$

(c) $P_{total} = P_A^* + (P_B^* - P_A^*)X_A$

(d) $P_{total} = P_B^* + (P_B^* - P_A^*)X_A$

21. Which of the following plots represents the behaviour of an ideal binary liquid solution?

(a) Plot of P_{total} vs Y_A (mol-fraction of A in vapour phase) is linear

(b) Plot of P_{total} vs Y_B is linear

(c) Plot of $1/P_{total}$ vs Y_A is linear

(d) Plot of $1/P_{total-}$ vs Y_B is non-linear

22. If the total vapour pressure of the liquid mixture A and B is given by the equation: $P = 180\ X_A + 90$ then the ratio of the vapour pressure of the pure liquids A and B is given by

(a) 3:2 (b) 4:1

(c) 3:1 (d) 6:2

23. Which one of the following pairs of solution will be isotonic at the same temperature?

(a) 1 M NaCl and 2 M – Urea

(b) 1 M $CaCl_2$ and 1.5 M – KCl

(c) 1.5 M $AlCl_3$ and 2 M Na_2SO_4

(d) 2.5 M KCl and 1 M – $Al_2(SO_4)_3$

24. NaCl is added to 1 litre water to such an extent that $\Delta T_f/K_f$ becomes to $\frac{1}{500}$, the wt. of NaCl added is

(a) 5.85 g (b) 0.585 g
(c) 0.0585 g (d) None

25. The vapour pressures of ethanol and methanol are 44.5mm and 88.7mm Hg respectively at the same temperature. An ideal solution is formed by mixing 60g of ethanol and 40g of methanol. The mole fraction of methanol in the vapour phase is

(a) 0.66 (b) 0.55
(c) 0.11 (d) 0.33

26. The degree of dissociation of $Ca(NO_3)_2$ in dilute aueous solution, containing 7 g of the salt per 100g of water at 100° C is 70%. If the vapor-pressure of water at 100° C is 760mm Hg. The vapour pressure of the solution is

(a) 746.3 mm Hg
(b) 1492.6 mm Hg
(c) 373.2 mm Hg
(d) 74.63 mm Hg

27. An aqueous solution of glucose boils at 100.01°C. The molal elevation constant for water is 0.5 K mol^{-1} kg. The number of molecules of glucose in the solution containing 100 g of water is

(a) 6.023×10^{23}
(b) 6.023×10^{22}
(c) 12.046×10^{20}
(d) 12.046×10^{23}

28. Addition of 0.643 g of a Compound to 50 ml of benzne (density = 0.879 g mol^{-1}) lowers the freezing point from 50.51°C to 50.03°C. If K_f for benzene is 5.12, the molecule of the compound is

(a) 156.00 (b) 312.00
(c) 78.00 (d) 468.000

29. During depression of freezing point in a solution the following are in equilibrium

(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent

30. The plot of $1/x_A$ versus $1/y_A$ (where x_A and y_A are the mole fractions of A in liquid and vapour phases respectively) is linear whose slope and intercept respectively are given as

(a) p°_A/p°_B,$(p^\circ_A - p^\circ_B)/p^\circ_B$
(b) p°_A/p°_B, $(p^\circ_B - p^\circ_A)/p^\circ_B$
(c) p°_B/p°_A, $(p^\circ_A - p^\circ_B)/p^\circ_B$
(d) p°_B/p°_A, $(p^\circ_B - p^\circ_A)/p^\circ_B$

31. Select incorrect statement:

(a) Higher the value of k_H (Henry's law constant) at a given pressure, the lower is the solubility of the gas in the liquid.
(b) Solubility of a gas in a liquid decreases with increase in temperature and pressure.
(c) To minimize the painful effects accompanying the decomposition of deep sea divers, O_2 diluted with less soluble He gas is used as breathing gas.
(d) The solubility of a gas in a liquid is governed by Henry's law.

32. 100 ml of a liquid A was mixed with 25 ml of a liquid B to give a non-ideal solution of A-B mixture. The volume of this mixture will be

(a) 75 ml
(b) 125 ml exact
(c) fluctuating between 75 ml and 125 ml
(d) close to 125 ml

33. For an ideal solution containing two components A and B, the Gibb's free energy of mixing is minimum when, the mole fraction of A and B (i.e., x_A and x_B) are

(a) $x_A = x_B = \frac{1}{2}$ (b) $x_A = x_B = 1$
(c) $x_A = x_B = \frac{3}{4}$ (d) $x_A = \frac{1}{2}; x_B = \frac{2}{3}$

34. One mol of a pure n-hexane and two mol of n-heptane are mixed at 27°C to form an ideal binary solution. The Δ_{mix} G and Δ_{mix} S are respectively

(a) –1585.38 J and 5.28 JK^{-1}
(b) 1585.38 J and –5.28 JK^{-1}
(c) –158.4 J and 52.8 JK^{-1}
(d) 158.4 J and –52.8 JK^{-1}

35. Organic liquids A and B have vapour pressures, p_1° and p_2° as pure liquids at 80°C. A mixture of the two behaving ideally and boiling at 80°C has mole fraction of A = 0.16. If $(p_2^\circ - p_1^\circ) = 472$ mm, what is the value of p_1°? (in mm)

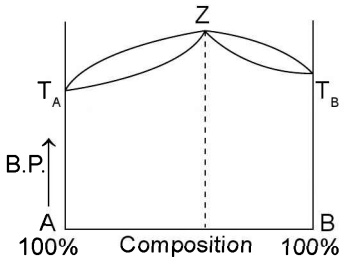
(a) 536.3 (b) 635.3
(c) 363.5 (d) 335.6

36. The freezing point of a solution of 0.1965 mole of KCN in a kg of water is $(\Delta T_f)_1$. After adding to the solution, 0.095 mole of $Hg(CN)_2$, the freezing point is $(\Delta T_f)_2$. Complex formation occurs according to the equation,

$Hg(CN)_2(s) + \underset{(\text{in soltuion})}{m\,CN^-} \longrightarrow [Hg(CN)_{m+2}]^{m-}$. If the ratio $\frac{(\Delta T_f)_1}{(\Delta T_f)_2} \simeq 1.32$, calculate the vale of m.

(a) 4 (b) 3
(c) 1 (d) 2

37. A liquid mixture having composition corresponding to point Z in the figure shown is subjected to distillation at constant pressure. Which of the following statement is correct about the process?



(a) The composition of distillate differs from the mixture
(b) The boiling point goes on changing
(c) The mixture has highest vapour pressure than for any other composition
(d) Composition of an azeotrope alters on changing the external pressure

38. The total vapour pressure of a 4 mole % solution of NH_3 in water at 293 K is 50.0 torr, the vapour pressure of pure water is 17.0 torr at this temperature. Applying Henry's and Raoult's laws, calculate the total vapour pressure for a 5 mole % solution:

(a) 58.25 torr (b) 33 torr
(c) 42.1 torr (d) 52.25 torr

39. The vapour pressure of two pure liquids A and B, that form an ideal solution are 100 and 900 torr respectively at temperature T. This liquid solution of A and B is composed of 1 mole of A and 1 mole of B. What will be the pressure, when 1 mole of mixture has been vaporized?

(a) 800 torr (b) 500 torr
(c) 300 torr (d) None of these

40. 1.0 g of a monobasic acid HA in 100 g water lowers the freezing point by 0.155 K. If 0.75 g, 0.2 g of same acid requires 15 ml of N/5 NaOH solution for complete neutralisation then %, degree of ionization of acid is (K_f of H_2O = 1.86 K kg mol^{-1}):

(a) 20% (b) 25%
(c) 40% (d) 50%

ANSWER KEYS

1. (c)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (b)	**7.** (b)	**8.** (b)	**9.** (c)	**10.** (d)
11. (d)	**12.** (b)	**13.** (b)	**14.** (b)	**15.** (b)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (c)	**20.** (b)
21. (c)	**22.** (c)	**23.** (a)	**24.** (c)	**25.** (a)	**26.** (a)	**27.** (c)	**28.** (a)	**29.** (a)	**30.** (b)
31. (b)	**32.** (d)	**33.** (a)	**34.** (a)	**35** (c)	**36.** (d)	**37.** (d)	**38.** (a)	**39.** (c)	**40.** (b)

HINTS AND EXPLANATIONS

1. (c) We know that water boils at 100° C (normal boiling point)

Hence $P^\circ_A = P^\circ_{H_2O}$ = 1 atm = 760 mm Hg

P_s = 750 mm Hg = $P^\circ_A X_A = P^\circ_{H_2O} X_{H_2O}$

= $780\, X_{H_2O}$

X_{H_2O} = 75/76

Hence X_B = Mole fraction of solute = $1 - X_{H_2O}$

= 1 – 75/76

= 1/76

2. (c) $\Delta T_b = T_b - T^\circ_b = \frac{RT_b^2}{\Delta \overline{H}^\circ_{vap}} X_B$

$1K = \frac{(2\,Cal\,mol^{-1}K^{-1})\,(373K)^2}{(18\,g\,mol^{-1})(540\,Cal\,g^{-1})} X_B$

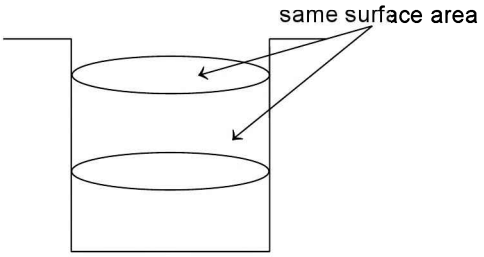
$$X_B = \frac{18 \times 540}{(373)^2 \times 2} \approx 0.035$$

Hence $X_A = X_{H_2O} = (1 - X_B) = 0.965$

$$P_{\underset{(at\,100^\circ C)}{solu}} = P^\circ_{H_2O} X_{H_2O} = 760\,(0.965)\text{ mm Hg}$$

$$= 733.4\text{ mmHg}$$

3. (d) The rate of condensation increases with the increase in the number of molecules going into the vapour phase. Hence it increases with time but the rate of vapourization depends only on the surface area which remains the same with time.



4. (c) $\Delta T_f = \Delta T_f$ for glucose + ΔT_f for KCl + ΔT_f for urea

$$= \frac{1000 \times 1.86 \times 10}{100 \times 80} + \frac{1000 \times 1.86 \times 1 \times 2}{74.5 \times 100} + \frac{1000 \times 1.86 \times 5}{100 \times 60}$$

$= 3.069^\circ$

$\therefore$ Freezing point = 273 – 3.069 = 269.93 K

5. (a) $\Delta T_f = iK_f m_f = 0.2 = (1.86)\,(0.1)\,m$

$$m_f = \frac{0.2}{1.86} = 0.1075$$

$m_i = 0.1$

$$\frac{0.1}{W_A(kg)} = 0.1075 \Rightarrow W_A(g) = \frac{100}{0.1075} = 930.23\text{ g}$$

Hence, amount of water separated out (1000 – 930.23) g $\approx$ 70 g

6. (b) $\Delta T_b = iK_b m = (1 + \alpha)\,(0.52)\,m = 0.52\,c(1 + \alpha) = 1$

100 ml of the solution requires 50 ml 1.5 M NaOH for complete neutralization

$100 \times M = 50 \times 1.5$

$M = 1.5/2 = 5/4$

$5/4\,(1 + \alpha) = 1 \Rightarrow 1 + \alpha = 4/3$

$\alpha = 4/3 - 1 = 1/3$

7. (**b**) $X_B = \frac{1}{76} = \left(\frac{4S}{55.5 + 4S}\right)$

$(76 \times 4S - 4S) = 55.55$

$$S = \left(\frac{55.55}{75 \times 4}\right) = 0.185\text{ mol litre}^{-1}$$

$K_{sp} = 4\,S^3 = 2.53 \times 10^{-2}$

8. (b) pH = 2

$(H^+) = 0.01\text{ M} = Cx = 0.1x$

$x = 0.1;\ i = 1 + x = 1.1$

$$P = \frac{n}{v}RT(i) = MRT\,i = 0.11RT$$

9. (c) NaCl is binary solute

$$\frac{\Delta P}{P^0} = \frac{n_1 i}{n_1 i + n_2}$$

$$0.4 = \frac{i}{i + 3}$$

$i = z = (1 + x)$ hence $x = 1$

10. (d) 1.2 g of NaCl is 100 ml of solution $\Rightarrow$ 1 litre = 12 g = $\frac{12}{58.5}$ M

7.2 g of glucose is 100 ml of solution $\Rightarrow$ 1 litre = 72 g = $\frac{72}{180}$

NaCl	Glucose
$i_1 = 1 + \alpha$	$i_2 = 1$
$C_1 = \left(\frac{12}{58.5}\right)$	$C_2 = \frac{72}{180}$ $i_1C_1 = i_2C_2$
	$(1 + \alpha)\left(\frac{12}{58.5}\right) = \frac{72}{180}$
	$\alpha = \frac{58.5}{30} - 1 = 0.95.$

11. (d) 1.2 g of NaCl is 100 ml of solution $\Rightarrow$ 1 litre = 12 g = $\frac{12}{58.5}$ M

7.2 g of glucose is 100 ml of solution $\Rightarrow$ 1 litre = 72 g = $\frac{72}{180}$

NaCl	Glucose
$i_1 = 1 + \alpha$	$i_2 = 1$
$C_1 = \left(\frac{12}{58.5}\right)$	$C_2 = \frac{72}{180}$ $i_1C_1 = i_2C_2$

$$(1+\alpha)\left(\frac{12}{58.5}\right)=\frac{72}{180}$$

$$\alpha=\frac{58.5}{30}-1=0.95.$$

12. (b) $P_A = P_A^\circ X_A$

$$P_B = P_B^\circ X_B = P_B^\circ[1-X_A]$$

For $P_A = P_B$; $X_A = \dfrac{P_B^\circ}{P_A^\circ + P_B^\circ}$

$$P_{Total} = P_A + P_B = 2P_A = \frac{2P_A^\circ \times P_B^\circ}{P_A^\circ + P_B^\circ}$$

$$P_{Total} = \frac{2P_A^\circ P_B^\circ}{P_A^\circ + P_B^\circ}$$

13. (b) For urea solution,

$$\Delta T_f = K_f \times m$$

$$\therefore \quad K_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86^\circ C \text{ molal}^{-1}$$

For acetic acid solution,

$$\Delta T'_f = K_f \times m \times i$$

$$\therefore \quad i = \frac{\Delta T_f}{K_f \times m} = \frac{0.02046}{1.86 \times 0.01} = 1.1$$

CH_3CO_2H in water ionizes as

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$$

$(1-\alpha)$ α α

$i = 1-\alpha+\alpha+\alpha = 1+\alpha = 1.1$

$\therefore \quad \alpha = 0.1$

$\therefore \quad [H^+] = C\alpha = 0.01 \times 0.1 = 10^{-3}$ M

$\therefore$ pH of CH_3CO_2H solution = 3

14. (b) The elevation in boiling point is given by

$$\Delta T_b = K_b \times m \times i$$

$2.08 = 0.52 \times 1 \times i \qquad \therefore i = 4$

This implies that the salt on dissociation gives 4 ions. Thus, the salt that gives four ions is $K_3[Fe^{III}(CN)_6]$

15. (b) Degree of dissociation, α, AB $= \dfrac{5}{100} = 0.05$

	AB	$\rightarrow$	A^+	+	B^-
Number of moles dissolved	m		0		0
Number of moles after dissociation	$m(1-\alpha)$		$m\alpha$		$m\alpha$
After dissociation	$0.1(1-0.05)$		0.1×0.05		0.1×0.05

Total moles = Molality

$= 0.1(1-0.05) + 0.1 \times 0.05 + 0.1 \times 0.05$

$= 0.095 + 0.005 + 0.005 = 0.105$m

$\Delta T_f = K_f m$ or $T_f^0 - T_f = 1.86$ K/m $\times$ 0.105m

$= 0.1953$ deg

$T_f = 0^\circ C - 0.1953 = -1953^\circ C$

16. (c) Volume of solution = 1000,

Mass of the solution = V $\times$ d = 1000 ml $\times$ 1.04 g/mL = 1040g

Amount of solute in 1000 ml solution = 1 M

= 1 M $\times$ Molecular Mass = 1M $\times$ 74.5g/mol = 74.5g

Mass of water = Mass of solution – Mass of KCl

= 1040g – 74.5g = 965.5g

Molality of the solution

$$= m = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{1 \text{ mol}}{(965.5/1000)\text{kg}} = 1.0357$$

$\Delta T_b = i.K_b.m = 2 \times 0.52$ K kg mol^{-1} $\times$ 1.0357

$= 1.078^\circ C$

Boiling point of the solution = 100°C + 1.078°C

= 101.078°C

17. (b) $\Delta T = \dfrac{1000 \times K_b \times Y}{250 \times M} = \dfrac{4K_bY}{M}$

18. (b) i for $AgNO_3 = \dfrac{\text{Normal mol.wt}}{\text{Observed mol.wt.}} = 1+\alpha$

$$\alpha = \frac{170}{92.64} - 1 = 0.835 = 83.5\,\%$$

19. (c) $P_m = P^0_{MeOH} X^0_{MeOH} + P^0_{EtOH}, X_{EtOH}$

$$\text{Thus } P_M = 88.5 \times \left[\frac{\frac{16}{32}}{\frac{16}{32}+\frac{46}{46}}\right] + 42X; \left[\frac{\frac{46}{46}}{\frac{16}{32}+\frac{46}{46}}\right] = 57.5$$

Now $P'_{MeOH} = P^\circ_{MeOH} \cdot X_{MeOH(l)} = P_m \cdot X_{MeOH(g)}$

$$\therefore \quad 88.5 \times \left[\frac{\frac{16}{32}}{\frac{16}{32}+\frac{46}{46}}\right] = 57.5X_{MeOH(g)}$$

$$\therefore \quad X_{MeOH} = 0.513,$$

20. (b) Since we know

$$P_T = P_A^* X_A + P_B^* X_B$$

$$= P_A^* X_A + P_B^*(1 - X_A)$$

$$P_{total} = P_B^* + (P_A^* - P_B^*)X_A$$

21. (c) $Y_A = \frac{P_A^\circ . X_A}{P_{total}}$

Graph of Y_A Vs $\frac{1}{P_{total}}$ is linear

22. (c) As we know

$$P_T = P_A^\circ X_S + P_B^\circ X_A$$

$$= \frac{P_A^\circ . X_A}{P_{total}} = (P_A^\circ - P_B^\circ) X_A + P_B^\circ \qquad \ldots(1)$$

But from question, $P_T = 180\, X_A + 90$ $\qquad \ldots(2)$

Equating equation (1) and (2)

$$\therefore \quad P_A^\circ - P_B^\circ = 180$$

$$P_B^\circ = 90\,; \; P_A^\circ = 180 + 90 = 270$$

$$\frac{P_A^\circ}{P_B^\circ} = \frac{270}{90} = 3:1$$

23. For

(a) 1M NaCl solution $(i \times Cm) = 2 \times 1M$
$= Cm = $ Molarity

2M orea solution $(i \times Cm) = 2M$

1M $CaCl_2$ solution $(i \times Cm) = 3 \times 1M = 3M$

1.5 M KCl solution $(i \times Cm) = 2 \times 1.5M = 3M$

Similarly, for 1.5 M $AlCl_3$ and 2M Na_2SO_4

The value of $i \times Cm$ be 6 and 2.5 M KCl and 1M $Al_2(SO_4)_3$ has 5 M each.

So, the each pair of solution

A,B,C and D have same concentration so, all pairs of solution be isotomic,

$\therefore$ A,B,C and D

24. (c) For NaCl, i = 2

$$\therefore \quad \Delta T_f = K_f \times i \times C_m$$

$$\therefore \quad \frac{\Delta T_f}{K_f} = 2 \times C_m$$

or, $\quad \frac{1}{500} = 2 \times$ molality

or molality $= \frac{1}{1000}$

i.e., $\quad \frac{1}{1000}$ moles Kg^{-1} water

i.e., $\quad \frac{1}{1000}$ moles per litre water

$$= \frac{1}{1000} \times 58.5 \text{ g NaCl} = 0.0585 \text{ g NaCl}$$

25. (a) Mole of $CH_3CH = \frac{40}{32} = 1.25$

Mole of $CH_3CH_2OH = \frac{60}{46} = 1.304$

Let $CH_3CH \rightarrow A$, $C_2H_5OH \rightarrow B$

$$X_A = \frac{n_A}{n_A + n_B} = \frac{1.25}{1.25 + 1.304} = 0.49$$

$$\therefore \quad X_B = 0.51$$

$$\therefore \quad P_T = P_A^\circ X_A + P_B^\circ X_B = 88.7 \times 0.49 + 44.5 \times 0.51$$

$$P_T = 43.480 + 2.695 = 66.175$$

$$\therefore \quad P_A = 43.48; \; \therefore X_A = \frac{P_A}{P_T} = \frac{43.48}{66.175} = 0.66$$

26. (a) Total mole $Ca(NO_3)_2$

$$N = (1 + 2 \times 0.7) \times \frac{7}{168} = 0.1$$

Mole-weight of $Ca(NO_3)_2 = 168$

Moles of solvent $(H_2O) = \frac{100}{18}$

From Raoult's law

$$\frac{P^\circ - P_S}{P^\circ} = \frac{n}{n+N} \text{ or, } \frac{P_A^\circ . X_A}{P_{total}} = \frac{0.1}{0.1 + \frac{100}{18}}$$

$$\therefore \quad P_S = 746.3 \text{ mm Hg}$$

27. (c) $\therefore \Delta T_b = K_b \times C_m$

Or $\quad C_m = \frac{0.01}{0.5} = 0.02$ mole Kg^{-1} solvent

$$\therefore \text{ number of moles in 100 g water} = \frac{0.02 \times 100}{1000}$$

$= 0.002$ moles of glucose

$= 0.002 \times 6.023 \times 10^{23}$ molecules of glucose

$= 2 \times 6.023 \times 10^{20}$ glucose moles

28. (a) Weight of benzene = V ×d
= 50 × 0.879 g
W = 43.95 g

Weight of compound = 0.643 g
$\Delta T_f = 50.51 - 50.03 = 0.48$

$$\therefore \quad \Delta T_f = K_f \times \frac{w}{m} \times \frac{1000}{w}$$

$$0.48 = 5.12 \times \frac{0.643}{m} \times \frac{1000}{43.95}$$

$$\therefore \quad m = 156.05$$

30. (b) $p_A = x_A p^\circ_A$, $p_B = x_B p^\circ_B$

$$y_A = \frac{p_A}{p_A + p_B} = \frac{x_A p^\circ_A}{x_A p^\circ_A + x_B p^\circ_B} = \frac{x_A p^\circ_A}{x_A p^\circ_A + (1 - x_A) p^\circ_B}$$

$$= \frac{x_A p^\circ_A}{x_A (p^\circ_A - p^\circ_B) + p^\circ_B}$$

or $$\frac{1}{y_A} = \frac{x_A (p^\circ_A - p^\circ_B) + p^\circ_B}{x_A p^\circ_A}$$

or $$\frac{1}{y_A} = \frac{p^\circ_A - p^\circ_B}{p^\circ_A} + \frac{p^\circ_B}{p^\circ_A} \frac{1}{x_A}$$

or $$\frac{1}{x_A} = \frac{p^\circ_A}{p^\circ_B} \frac{1}{y_A} + \frac{p^\circ_B - p^\circ_a}{p^\circ_B}$$

Hence plot of $\frac{1}{x_A}$ vs $\frac{1}{y_A}$ will be linear with slope $= p^\circ_A / p^\circ_B$ and intercept $= (p^\circ_B / p^\circ_A) / p^\circ_B$

32. (d) For non-ideal solution, 100 ml + 25 ml is nearly 125 ml but not exactly 125 ml.

33. (a) Since $x_A + x_B = 1$, equation (1) (in the passage) becomes

$$\Delta_{mix} G = RT(x_A \ell n\, x_A + x_B \ell n\, x_B)$$

$$\frac{\Delta_{mix} G}{RT} = x_A \ell n\, x_A + x_B \ell n\, x_B$$

For Δ_{mix} G to be minimum at a given T and p

$$\left(\frac{\partial(\Delta_{mix} G)}{\partial x_A}\right)_{T,p} = 0$$

Thus $$\frac{\partial}{\partial x_A}(x_A \ell n\, x_A + (1 - x_A) \ell n\, (1 - x_A)) = 0 \text{ or}$$

$$X_A \left(\frac{1}{x_A}\right) + \ell n\, x_A + (1 - x_A) \times \left(\frac{1}{1 - x_A}\right) + \ell n$$

$$(1 - x_A)(-1) = 0$$

(or) $1 - \ell n\, x_A - 1 - \ell n\, (1 - x_A) = 0$

$$\ell n \left(\frac{x_A}{1 - x_A}\right) = 0 \; ; \; \frac{x_A}{1 - x_A} = 1 \text{ or } x_A = \frac{1}{2}; \; x_B = \frac{1}{2}$$

34. (a) $\Delta_{mix} G = RT(x_A \ell n\, x_A + x_B \ell n\, x_B)$ $x_A = \frac{1}{3} = 0.334$;
$x_B = 1 - 0.334 = 0.666$

$= 8.314 \times 300 \{(0.334 \ell n\, 0.334) + 0.666 \ell n\, 0.666\} = -1585.38$ J

$$\Delta_{mix} S = -\frac{\Delta_{mix} G}{T} = \frac{-(-1585.38)}{300} = 5.28 \text{ JK}^{-1}$$

35. (c) $p_1 + p_2 = p^1_o x + p^2_o (1 - x) = p^\circ_1 (0.16) + p^\circ_2 (0.84)$
= 760 mm

$p^\circ_2 - p^\circ_1 = 472$ mm $\therefore$ $p^\circ_2 = (p^\circ_1 + 472)$ mm

$\therefore$ $p^\circ_1 (0.16) + (p^\circ_1 + 472)\, 0.84 = 760$

$\therefore$ $p^\circ_{1mm} = 760 - (0.84 \times 472)$

$p^\circ_1 = 363.5$ mm

36. (d) Assuming complete ionization of KCN, $(\Delta T_1)_1 = K_f \times [2 \times 0.1965]$

$(\Delta T_f)_2 = K_f [2 \times 0.1965) - (m - 1) 0.095]$

(since one mole of $Hg(CN)_2$. removes m moles of $\bar{C}N$ ions and yields one mole of the complex)

$$\therefore \quad \frac{(\Delta T_f)_1}{(\Delta T_f)_2} = \frac{0.393}{0.393 - (m - 1)(0.095)} = 1.32 = \frac{4}{3}$$

$\therefore$ $3\,(0.393) = 4(0.393) - 4\,(m-1)(0.095)$

$\therefore$ $(m - 1) \times 4 \times (0.095) = 0.393$

i.e., $m - 1 \simeq \frac{0.393}{0.38} \simeq 1$ $\quad \therefore m = 2$

38. (a) The given data are $P_{water} = 17.0$ torr; P_{total} (4 mole % solution)

$= P_{NH_3} + P_{water} = 50.0$ torr $x_{NH_3} = 0.04$ and $x_{water} = 0.96$

Now according to Raoult's law;

$P_{water} = x_{water} P^\circ_{water} = 0.96 \times 17.0$ torr $= 16.32$ torr

Now Henry's law constant for ammonia is

$$K_H(NH_3) = \frac{P_{NH_3}}{x_{NH_3}} = \frac{33.68 \text{ torr}}{0.04} = 842 \text{ torr}$$

Hence, for 5 mole % solution, we have

$P_{NH_3} = K_H(NH_3)\, x_{NH_3} = (842 \text{ torr})\ (0.05)$

$= 42.1$ torr

$P_{water} = P^\circ_{water}\ x_{water} = (17 \text{ torr})\ (0.95) = 16.15$ torr

Thus, P_{total} (5 mole % solution) $= P_{NH_3} + P_{water}$

$= 42.1 + 16.15 = 58.25$ torr

39. (c) Let n_B mole of B present in 1 mole of mixture that has been vaporized. Thus, $y_B = \frac{n_B}{1}$

Mole fraction of B in the remaining liquid phase will be $x_B = \frac{1 - n_B}{1}$

$$x_B = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ} \quad \text{....(1)}$$

$$[\because P = P_T^\circ + (P_B^\circ - P_T^\circ)\, x_B]$$

and $y_B = \frac{P_B}{P} \Rightarrow \frac{P_B^\circ x_B}{P}$ .... (2)

After substitution of values of x_B and y_B in (1) and (2)

we get $1 - n_B = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ}$ .... (3)

and $n_B = \frac{(1 - n_B)P_B^\circ}{P}$ .... (4)

or $n_B = \frac{P_B^\circ}{P + P_B}$ so

$$1 - \frac{P_B^\circ}{P + P_B} = \frac{P - P_T^\circ}{P_B^\circ - P_T^\circ}$$

$\Rightarrow P = \sqrt{P_B^\circ . P_T^\circ} = \sqrt{100 \times 900}$

$\Rightarrow 300$ torr

40. (b) $\Delta T_f = K_f \times \frac{w_{acid}}{M_{acid} \times W_{H_2O}} \times 1000;$

$\therefore$ M_{acid} (observed) = 120

Normal molecular mass of acid can calculate as milli-equivalents of acid = milli-equivalents of base

(for HA and NaOH, N = M) $\frac{0.75}{M_{acid}} \times 1000 = 15 \times \frac{1}{5}$

$\Rightarrow M_{acid(Normal)} = 150$

$\therefore \quad i = \frac{150}{120}$

$\Rightarrow \quad 1.25\, i = 1 + \alpha \Rightarrow 0.25 \therefore \% \alpha = 25$

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. 1 mole of benzene ($P^\circ_{Benzene}$ = 42 mm) and 2 mole of toluene ($P^\circ_{toluene}$ = 36 mm) will have
(a) positive deviation from Raults' law
(b) negative deviation from Raults' law
(c) total vapour pressure 38 mm
(d) mole fraction of vapours of toluene above liquid mixture is 12/19

2. Which of the following condition are correct for a binary solution, in which the solute as well as the solvent are liquid?
(a) C_6H_6 and $C_6H_5CH_3$ $\Delta H_{solution} > 0$; $\Delta V_{solution} = 0$
(b) CH_3COCH_3 and $CHCl_3$ $\Delta H_{solution} < 0$; $\Delta V_{solution} < 0$
(c) H_2O and HCl $\Delta H_{solution} > 0$; $\Delta V_{solution} < 0$
(d) H_2O and C_2H_5OH $\Delta H_{solution} > 0$; $\Delta V_{solution} > 0$.

3. A and B form an ideal solution and both are volatile. If $P^\circ_A > P^\circ_B$ which of the following relation must be correct?
(a) $X_A > X_B$ (b) $Y_A > X_A$
(c) $Y_A > Y_B$ (d) $Y_B > X_B$

4. Calculate the boiling point of a one molar aqueous solution (density = 1.04 g mL^{-1}) of potassium chloride, K_b for water = 0.52 kg mol^{-1}. Atomic masses of K = 39, Cl = 35.5
(a) 107.28°C (b) 103.68°C
(c) 101.078°C (d) None of these

5. When mercuric iodide is added to an aqueous solution of potassium iodide then
(a) Freezing point is raised
(b) Freezing point is lowered

(c) Freezing point does not change
(d) Boiling point is lowered.

6. If P^0 and P_s be the vapour pressure of solvent and its solution respectively and N_1 and N_2 be the mole-fractions of solvent and solute respectively, then:

(a) $P_S = P^0.N_2$ (b) $P^0 = P_s = P \cdot N_2$

(c) $P_S = P^0 N_1$ (d) $\frac{P^0 - P_s}{P_s} = \frac{N_1}{N_1 + N_2}$

ANSWER KEYS

1. (c,d) **2.** (b,d) **3.** (b) **4.** (c) **5.** (a,d) **6.** (a,b)

HINTS AND EXPLANATIONS

1. Benzene and toulene form ideal solution.

$$P_{solution} = P^{\circ}_B X_B + P^{\circ}_T X_T$$

$$= [42\left(\frac{1}{3}\right) + 36(\frac{2}{3})] \text{ mm Hg}$$

$$= (14 + 24) \text{ mm Hg} = 38 \text{ mm Hg}$$

$$y_T = \frac{P^{\circ}_T X_T}{P_T} = \frac{24}{38} = \frac{12}{19}$$

2. Factual

3. $P_A = P^{\circ}_A X_A$ (Roult's lawof vapour pressure) $= Y_A P_T$ (Dalton's law of partial pressure)

$$\Rightarrow Y_A = \frac{P^{\circ}_A X_A}{P_T} = \frac{P^{\circ}_A X_A}{P^{\circ}_A X_A + P^{\circ}_B X_B}$$

P_T = pressure of the solution

As $P^{\circ}_A > P^{\circ}_B \Rightarrow P^{\circ}_A > P_T > P^{\circ}_B$

Hence, $\frac{P^{\circ}_A}{P_T} = \frac{Y_A}{X_A} > 1 \Rightarrow Y_A > X_A$ (always correct when $P^{\circ}_A > P^{\circ}_B$)

4. Volume of solution = 1000,

Mass of the solution = V × d = 1000 ml × 1.04 g/mL
= 1040 g

Amount of solute in 1000 ml solution = 1 M

= 1 M × Molecular Mass = 1 M × 74.5 g/mol = 74.5 g

Mass of water = Mass of solution – Mass of
KCl = 1040 g – 74.5 g = 965.5 g

Molality of the solution =

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} = \frac{1 \text{mol}}{(965.5/1000) \text{kg}} = 1.0357$$

$$\Delta T_b = i \,.\, K_b.m = 2 \times 0.52 \text{ K kg mol}^{-1} \times 1.0357$$
$$= 1.078^{\circ}C$$

Boiling pint of the solution = 100°C + 1.078°C
= 101.078°C

5. C.P. $\propto$ i, where C.P. $\rightarrow$ colligative property and 'i' van't Hoff factor.

6. According to Raoult's Laws

Vapour pressure of solution = V.P. of solvent X solvent

$$W_1 P_S = P^{\circ}$$

$$\therefore \quad P_S = P^{\circ} (1 - N_2) \quad \therefore N_1 + N_2 = 1$$

$$W_1 P^{\circ} - P_S = P_S N_2$$

$\therefore$ (a) and (b)

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

This comprehension is expected to be read, understood, and the associated questions answered within the stipulated time limit.

When a liquid is completely miscible with another liquid, a homogeneous solution consisting of a single phase is formed. If such a solution is placed in a closed evacuated vessel, the total pressure exerted by the vapour, after the system attained equilibrium will be equal to the sum of partial pressures of the constituents. A solution is said to be ideal if its constituents follow Raoult's law under all conditions of concentrations. i.e., the partial pressures of each and every constituent is given by

$$p_i = x_i p_i^\circ$$

where p_i is the partial pressure of the constituent I, whose amount fraction in the solution is x_i and p_i° is the corresponding vapour pressure of the pure constituent.

The changes in the thermodynamic functions when an ideal solution is formed by mixing pure components is given by the following expressions.

$$\Delta_{mix} G = \sum_i n_i RT \ell n\, x_i = n_{total} RT \sum_i x_i \ell n\, x_i \quad ....(1)$$

where n_{total} is the total amount of all the constituents present in the solution.

$$\Delta_{mix} S = -n_{total} R \sum_i x_i \ell n\, x_i \quad ....(2)$$

$$\Delta_{mix} H = n_{total} RT \sum_i x_i \ell n\, x_i - n_{total} R \sum_i x_i \ell n\, x_i = 0 \quad ...(3)$$

$$\Delta_{mix} U = 0 \quad ....(4)$$

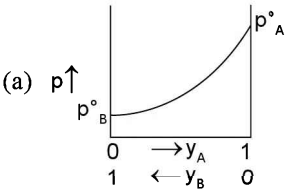
Since both the components of an ideal binary liquid system follow Raoult's law over the entire range of the composition, the partial pressure exerted by the vapours of these constituents over the solution will be given by

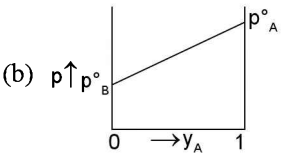
$$p_A = x_A p_A^\circ \quad ...(5)$$

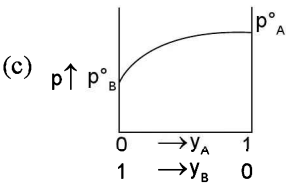
$$p_B = x_B p_B^\circ \quad ...(6)$$

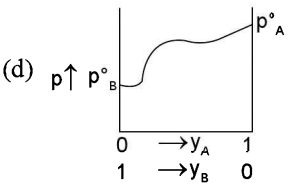
where x_A and x_B are the amount fractions of the two constituents in the liquid phase and p_A° and p_B° are the respective vapour pressures of the pure constituents. The total pressure (p) over the solution will be the sum of the partial pressures. The composition of the vapour phase (y_A) can be determined with the help of Dalton's law of partial pressures.

1. For an ideal solution in which $p_A^\circ > p_B^\circ$, the plot of total pressure (p) verses the mole fraction of A at constant temperature in the vapour phase is

(a) 

(b) 

(c) 

(d) 

2. Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution in 600 torr, the amount fraction of A in the vapour phase is 0.35 and in the liquid phase 0.70. The vapoure pressures of pure B and A are

(a) 800 torr; 1300 torr (b) 1300 torr; 300 torr
(c) 300 torr; 1300 torr (d) 300 torr; 800 torr

3. 1 mole of liquid 'C' is added to an ideal liquid solution containing 1 mole of A and 1 mole of B. The entropy change due to the mixing of 'C' is (Assume the solutions are ideal in nature) [R = Gas constant]

(a) R ℓn 4 (b) R ℓn 3
(c) ℓn (27/4) (d) ℓn(9/4)

COMPREHENSION-II

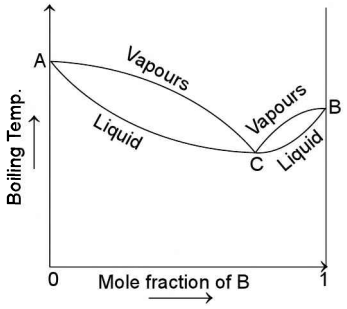
Azoetropes are constant boiling mixtures, which like a pure chemical compound boils at a constant temperature

and distils over completely at die same temperature without change in composition. There may be two type of binary solution which gives azeotropic mixture

Type-1: Mixture which shows a minimum in "Boiling point-Composition curve".

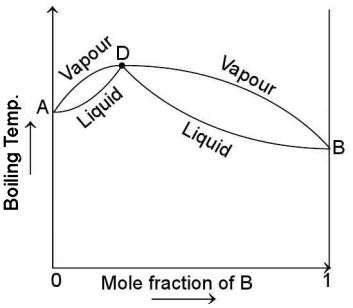
Type-II: Mixture which shows a maximum in "Boiling point-Composition curve".

Both types are shown below:



(a)

Figure "Boiling Temperature – Composition" curve for liquid and vapour phases in binary solution of Type – I.



(b)

Figure "Boiling Temperature – Composition" curve liquid and vapour phases in binary solution of Type-II

In Figure (a) point 'C' represents azeotropic composition and in Figure (b).

Point 'D' represents azeotropic composition 'A' and 'B' shows boiling temperature of pure liquids 'A' and 'B' respectively.

4. For Fig. (a) and (b) predict which of the component (i.e., A and B) is more volatile?
(a) liquid A
(b) Liquid B
(c) Both have equal volatility
(d) Can't predict

5. Which of the type above (i.e., Type-I or Type-II) shows negative deviation from Raoult's law?
(a) Solution of Type-I
(b) Solution of Type-II
(c) Both Type-I and Type-II
(d) None of the above

6. Let the solution of "water-ethanol" corresponds to Type-I and at point 'C', it had a composition of 95.6% of by weight in vapour phase". If this solution is boiled at 78.13°C then find out the % by wt. of water in 'liquid phase' (Given T_C (temperature at point C) = 78.13°C
(a) 95.6 %
(b) 4.4%
(c) 72.4%
(d) 63%

ANSWER KEYS

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

[redacted]TS AND EXPLANATIONS

COMPREHENSION-I

1. (a) The composition of the vapour (y_A)

$$= \frac{\text{partial pressure (A)}}{\text{total pressure (p)}}$$

$$= \frac{p_A}{p} = \frac{x_A p_A^\circ}{p_B^\circ + (p_A^\circ + P_B^\circ)x_A} \quad \ldots.(1)$$

and $y_B = \frac{p_B}{p} = 1 - y_A = \frac{x_B p_B^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ)x_A}$ ....(2)

To express the total vapour pressure in terms of composition of the vapour phase, rearrange equation (1)

$$x_A = \frac{y_A p_B^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ)y_A} \quad \ldots.(3)$$

The total pressure over the solution is given by

$$p = p_B^\circ + (p_A^\circ - p_B^\circ)x_A$$

Substitute x_A in the above equation

$$p = p_B^\circ + (p_A^\circ + p_B^\circ)\frac{y_A p_B^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ)y_A}$$

i.e., $p = \frac{p_B^\circ p_A^\circ}{p_A^\circ + (p_B^\circ - p_A^\circ)y_A}$ ....(4)

The plot of p verses y_A for a solution in which $p_A^\circ > p_B^\circ$ is (a), i.e., as the composition of y_A increases, the total pressure decreases.

2. (b) Given $x_A = 0.70$; $y_A = 0.35$; $p = 600$ torr

$p_A^\circ = ?$ $p_B^\circ = ?$

$$y_A = \frac{p_A}{p} = \frac{x_A^\circ p_A^\circ}{p} \quad \therefore p_A^\circ$$

$$= \frac{y_A p}{x_A} = \frac{0.35 \times 600}{0.70} = 300 \text{ torr}$$

Similarly, $p_B^\circ = \frac{y_B p}{x_B} = \frac{0.65 \times 600}{0.30} = 1300$ torr

3. (c) $\Delta_{mix}S = -n_{total}\ R \sum_i x_i \ell n\ x_i$

ΔS_{1mix} (of initial solution) $= -2\ R\ (\frac{1}{2}\ell n\frac{1}{2} + \frac{1}{2}\ell n\frac{1}{2})$

$$= -2\ R\ \ell n\left(\frac{1}{2}\right)$$

$$= 2\ R\ \ell n\ 2 = R\ \ell n\ 4$$

ΔS_{2mix} (of final solution) $= -3\ R\ (\times\frac{1}{3}\ell n\frac{1}{3})$

$$= 3\ R\ \ell n\ 3$$

Hence ΔS_{mix} (due to mixing of 'C') $= \Delta S_{2mix} - \Delta S_{1mix}$

$= R\ \ell n\ 3^3 - R\ \ell n\ 4 = R\ \ell n\ (27/4)$

COMPREHENSION-II

4. (b) Component having lower boiling point is more volatile.

5. (b) Solution which shows maximum in boiling point.

6. (b) Composition will remain same after boiling also.

MATCH THE COLUMN TYPE QUESTIONS

1. Column I contains concentration of aqueous solutions and Column II contains Colligative propesties of aqueous solution (Matrix type).

	Column-I		**Column-II**
(a)	5.555 molal aqueous solution of glucose	(p)	The boiling point of the solution is 101.04°C
(b)	26.47 mass% aqueous solution of glucose	(q)	Relative lowering in vapour pressure is $\frac{1}{11}$
(c)	1.5 molal aqueous solution of NaCl which is 95% ionized.	(r)	Osmotic pressure at 27°C is more than 1 atm
(d)	2 molal aqueous solution of glucose	(s)	The vapour pressure at 100°C is 691 mm Hg

Molar mass of glucose = 180

Given $K_b(H_2O) = 0.52$ K Kg mol^{-1} Assume non-volatile solute and ideal (molal elevation solution constant)

2. A liquid mixture of benzene and toluene is composed of 1 mol of benzene and 1 mol of toluene the pressure over the mixture at 300 K is reduced,

Column-I

(i) at what pressure does the first vapour form? (P_T° = 32.05 mm Hg, P_B° = 103 mm Hg

(ii) What is the composition of the first trace of vapour formed.

(iii) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?

(iv) What is the composition of the last trace of liquid?

Column-II

(a) mole fraction of one Toluene(X_T) = 0.76

(b) 67.52 mm Hg

(c) $X_B = 0.76$ $X_T = 0.24$

(d) 49.01 mm Hg

ANSWER KEYS

1. (a); (q, s, r) (d); (p, r) (b); (p, r) (c); (r) **2.** (a); (s) (b); (p) (c); (q) (d); (r)

HINTS AND EXPLANATIONS

1. $X_B = \dfrac{n_B}{n_{H_2O} + n_B} = \dfrac{5.555}{55.55 + 5.555} = \dfrac{1}{11}$

$P_S = P_{H_2O}\, X_{H_2O} = 760 \times \dfrac{10}{11}$

$\Delta T_b = 1.04 = i\, K_b\, m = 0.52\, m$

$m = 2$

360 g glucose in 10^3 g solvent

or

$\dfrac{360}{1360} \times 100\% = 26.4\ \%$

$2 \times 0.0821 \times 300$ atm

2.

(p) $P_{Total} = P_B^\circ X_B + P_T^\circ X_T$

$= (1.03 \times \dfrac{1}{2} + 32.05 \times \dfrac{1}{2})$ mm

Hg = 67.52

(q) $Y_B = \dfrac{P_B^\circ X_B}{P_{Total}} = \dfrac{103 \times \frac{1}{2}}{67.52} = 0.76$

$\Rightarrow$ mole fraction of benzene in the first formed vapour.

(r) composition of vapour (final) = Initial composition of liquid (neglecting the initial vapour present)

(s) $Y_B = X_B^\circ$ (initial solution) = 0.5

Hence $Y_B = \dfrac{P_B^\circ X_B}{P_B^\circ X_B + P_A^\circ (1 - X_B)} = 0.5$

$= \dfrac{103 X_B}{103 X_B + 32.05(1 - X_B)}$

$X_B = 0.24$

$P_T = P_B^\circ X_B + P_T^\circ X_T$

$= (103 \times 0.24 + 32.05 \times 0.76)$ mm Hg

$= 49.01$ mm Hg

ASSERTION/REASON TYPE QUESTIONS

In each of the following questions, two statements are given, one labelled as the Assertion (A) and the other labelled as the Reason (R). Examine these statements carefully and mark the correct choice as per following instructions.

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not a correct explanation of A

(c) A is true but R is false

(d) A is false but R is true

SUBJECTIVE QUESTIONS

1. Mixture of two liquids A and B is placed in cylinder containing piston. Piston is pulled out isothermally so that volume of liquid decreases but that of vapour increases. When negligibly small amount of liquid was remaining, the mole fraction of A in vapour is 0.4. Given $P_A^\circ = 0.4$ atm and $P_B^\circ = 1.2$ atm at the experimental temperature. Calculate the total pressure at which the liquid has almost evaporated. (Assume ideal behaviour).

2. A dilute solution contains m mol of solute A in 1 kg of a solvent with molal elevation constant K_b; The solute dimerises in solution as $2A \rightleftharpoons A_2$. Show that equilibrium constant for this dimer formation is $K = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$, where ΔT_b is the elevation in boiling point for the given solution. (Assume molarity = molality).

3. When 3.24 g of $Hg(NO_3)_2$ is dissolved in 1 kg of water the freezing point of solution is found to be –0.0558°C when 10.84 g of $HgCl_2$ is dissolved in 1 kg of water the freezing point of solution is –0.0744°C. Find out the whether these salts dissociate into ions in aqueous solution? (K_f for water = 1.86°C/m)

4. River water is found to contain 11.7% NaCl, 9.5% $MgCl_2$, and 8.4%. $NaHCO_3$ by weight of solution. Calculate its normal boiling point assuming 90% ionization of NaCl, 70% ionization of $MgCl_2$ and 50% ionization of $NaHCO_3$ (K_b for water = 0.52)

5. The freezing point depression of a 0.109 M aq. solution of formic acid is –0.21°C. Calculate the equilibrium constant for the reaction,

   $HCOOH\ (aq) \rightleftharpoons H^+\ (aq) + HCOO^-\ (aq)$.

   K_f for water = 1.86 kg mol^{-1} K.

HINTS AND EXPLANATIONS

1. From Raoult's law

$$P = P_A^0 \cdot X_A + P_B^0 \cdot X_B$$

or, $P = 0.4 \cdot X_A + 1.2\, X_B$ ... (i)

i.e., $Y_a = 0.4,\ \therefore\ Y_B = 0.6$

or, $0.4 = Y_A = \frac{0.4 \cdot X_A}{P}$ ...(ii)

$$Y_B = 0.6 = \frac{1.2 \cdot X_B}{P} \quad \text{... (iii)}$$

$X_A + X_B = 1$ ... (iv)

From equation (ii), (iii) and (iv), wet get

$$X_A = \frac{2}{3},\ X_B = \frac{1}{3}$$

Substituting the values of X_A and X_B in equation (i)

We get

$P = 0.4 \times 2/3 + 1.2 \times 1/3$

$= 0.268 + 0.396$

$= 0.664$ atm

2. Let the degree of dimer formation be α. The reaction occurs as under

	$2A$	$\rightleftharpoons$	$(A)_2$
Initially	m		0
after dimer formation	m-mα		$\frac{m\alpha}{2}$

where m = molality = molarity (as also given)

Due to dimer formation, the resultant

$$\text{Molality will be} = (m - m\alpha) + \frac{m\alpha}{2}$$

$$\text{Vont Hoff's factor, } i = \frac{(m - m\alpha) + \frac{m\alpha}{2}}{m}$$

$$i = \frac{m\left(1 - \frac{\alpha}{2}\right)}{m}$$

$$i = 1 - \frac{\alpha}{2}$$

As we know the elevation in boiling point,

$\Rightarrow \Delta T_b = K_b \times i \times C_m$,

$\Rightarrow \Delta T_b = K_b \times \left(1 - \frac{\alpha}{2}\right) \times m$, here $C_m = m$

$$\Rightarrow \quad \alpha = \frac{2(K_b m - \Delta T_b)}{K_b m}$$

The equilibrium constant for dimer formations

$$K_{eq} = \frac{[A_2]}{[A]^2} = \frac{m\frac{\alpha}{2}}{\{m(1-\alpha)\}^2} = \frac{m\frac{\alpha}{2}}{m^2(1-\alpha)^2}$$

$$K_{eq} = \frac{\alpha}{2m(1-\alpha)^2} \qquad \ldots(1)$$

Putting the value of α in equation (1)

$$\therefore \quad K_{eq} = \frac{\frac{2(K_b m - \Delta T_b)}{K_b m}}{2m\left\{1 - \frac{2(K_b m - \Delta T_b)^2}{K_b m}\right\}}$$

or, $$K_{equ} = \frac{K_{eq}(Kbm - \Delta Tb)}{(2\Delta Tb - Kbm)^2}$$

3. $\Delta T_f = K_f \times m$ [where m = molality]

$0.0558 = 1.86 \times m$

$$\therefore \quad m = \frac{0.0558}{1.86} = 0.03 \text{ m}$$

But the number of moles of $Hg(NO_3)_2$ in 1 kg of water was,

$$\text{Moles of } Hg(NO_3)_2 = \frac{3.24}{324} = 0.01 \text{ mol}$$

$\therefore$ $Hg(NO_3)_2$ dissociates into one Hg^{2+} and two NO_3^- ions in aqueous solution

Similarly, for $HgCl_2$

$$\Delta T_f = K_f \times m$$

$$0.0744 = 1.86 \times m$$

$$\therefore \quad m = \frac{0.0744}{1.86} = 0.04$$

The number of moles of $HgCl_2$ dissolved in 1000 g of solvent is

$$\text{Moles of } HgCl_2 = \frac{10.84}{271} = 0.04$$

$\therefore$ $HgCl_2$ remains as undissociated molecules in aqueous solution confirming $HgCl_2$ to be a weak electrolyte.

4. $$n_{NaCl} = \frac{11.7}{58.5} = 0.2$$

$$n_{MgCl_2} = \frac{9.5}{95} = 0.1$$

$$n_{NaHCO_3} = \frac{8.4}{84} = 0.1$$

$$i_{NaCl} = 1 + \alpha = 1 + 0.9 = 1.9$$

$$i_{MgCl_2} = 1 + 2\alpha = 1 + 0.7 \times 2 = 2.4$$

$$i_{NaHCO_3} = 1 + 2\alpha = 1 + 0.5 \times 2 = 2.0$$

Weight of the solvent = 100 – (11.7 + 9.5 + 8.4) = 70.4 g

$\Delta T_b =$

$$\frac{(i_{NaCl} \times n_{NaCl} + i_{MgCl_2} \times n_{MgCl_2} + i_{NaHCO_3} \times n_{NaHCO_3}) \times K_b \times 1000}{\text{Weight of solvent}}$$

$$= \frac{(1.9 \times 0.2 + 2.4 \times 0.1 + 2 \times 0.1) \times 0.52 \times 1000}{70.4}$$

$= 5.94°C$

$\therefore$ Boiling point of solution = 100 + 5.94 = 105.95°C

5. From the question

$\Delta T_f = 0.21°C$

Molality of solution = 0.109 m

The reaction is

	$HCOOH$ (aq) $\rightleftharpoons$	H^+(aq) +	$HCOO^-$ (aq)
Initially moles	C	0	0
Moles after dissociation	αC	αC	
$(1-\alpha)C$			

$$i = \frac{(1-\alpha) \times C + \alpha \times C + \alpha \times C}{1 \times C} = 1 + \alpha, \text{ where } \alpha$$

= degree of dissociation

As we know,

$$\Delta T_f = K_f \times i \times C_m$$

$0.21 = 1.86 \times (1+\alpha) \times 0.109$ (in very dilute solution molarity and molality can be taken as same)

$$\therefore \quad 1+\alpha = \frac{0.21}{1.86 \times 0.109} = 1.0358$$

or, $\alpha = 0.0358 = 0.036$

$\therefore$ $[HCOOH] = (1-\alpha) \times C = (1-0.036) \times C$

$= 0.964 \times C$

$[H^+] = \alpha \times C = 0.036 \times C$, $[HCOO^-] = 0.036 \times C$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{0.036 \times C \times 0.036 \times C}{0.964 \times C}$$

$= 1.34 \times 10^{-3} \times C$ mol lit^{-1}

$= 1.34 \times 10^{-3} \times 0.109$

$K_a = 1.46 \times 10^{-4}$

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

1. Select the correct statement:
(a) The semipermeable membrane is the cause of osmotic pressure.
(b) Osmosis results from decrease in entropy
(c) Osmotic pressure depends on temperature and concentration but is independent of the nature of the membrane.
(d) The passage of solvent molecules occur only in one direction through a semipermeable membrane.

2. The incorrect statement is
(a) Vapour pressure of a liquid always increases by increasing temperature.
(b) Vapour pressure only depends on temperature and not on the nature of substance.
(c) Vapour pressure does not depend on the quantity of the liquid taken and the surface area of the liquid.
(d) Vapour pressure is not a colligative property & is independent of the concentration of the liquid.

3. Which of the following has been arranged in order of decreasing freezing point?
(a) 0.05 M KNO_3 > 0.04 M $CaCl_2$ > 0.140 M sugar > 0.075 M CuSO4
(b) 0.04 M $BaCl_2$ > 0.140 M sucrose > 0.075 M $CuSO_4$ > 0.05 M KNO_3
(c) 0.075 M $CuSO_4$ > 0.140 M sucrose > 0.04 M $BaCl_2$ > 0.05 M KNO_3
(d) 0.075 M $CuSO_4$> 0.05 M $NaNO_3$> 0.140 M sucrose > 0.04 M $BaCl_2$

4. An ideal mixture of liquids A and B with 2 moles of A and 2 moles of B has a total vapour pressure of 1 atm at a certain temperature. Another mixture with 1 mole of A and 3 moles of B has a vapour pressure greater than 1 atm. But if 4 moles of C are added to the second mixture, the vapour pressure comes down to 1 atm. Vapour pressure of C, P_c° = 0.8 atm. Calculate the vapour pressures of pure A and pure B.
(a) P_A° = 1.4 atm, P_B° = 0.7 atm
(b) PA = 1.2 atm, P_B° = 0.6 atm
(c) PA = 1.4 atm, P_B° = 0.6 atm
(d) P_A° = 0.6 atm, P_BC = 1.4 atm

5. Available solutions are 1L of 0.1 M NaCI and 2L of 0.2 M $CaCl_2$. Using **only these two solutions,** what maximum volume of a solution can be prepared having $[Cl^-]$ = 0.34 M exactly. Both electrolytes are strong
(a) 2.5 L (b) 2.4 L
(c) 2.3 L (d) None of these

6. The vapour pressures of benzene, toluene and a xylene are 75 Torr, 22 Torr and 10 Torr at 20°C. Which of the following is not a possible value of the vapour pressure of an equimolar binary/ternary solution of these at 20°C? Assume all form ideal solution with each other.
(a) $48\frac{1}{2}$ (b) 16
(c) $35\frac{2}{3}$ (d) $53\frac{1}{2}$

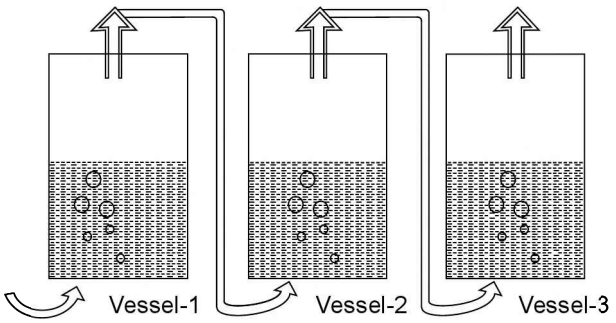
7. 3.24 g of $Hg(NO_3)_2$ (molar mass = 324) dissolved in 1000 g of water constitutes a solution having a freezing point of –0.0558°C while 21.68 g of $HgC1_2$ (molar mass = 271) in 2000 g of water constitutes a solution with a freezing point of –0.0744°C. The K_f for water is 1.86 $\frac{k-kg}{Mol}$. About the state of ionization of these two solids in water it can be inferred that:
(a) $Hg(NO_3)_2$ and $HgC1_2$ both are completely ionized
(b) $Hg(NO_3)_2$ is fully ionized but $HgC1_2$ is fully unionized
(c) $Hg(NO_3)_2$ and $HgC1_2$ both are completely unionized
(d) $Hg(NO_3)_2$ is fully unionized but $HgC1_2$ is fully ionized

8. For a solution of 0.849 g of mercurous chloride in 50 g of $HgC1_2$(f) the freezing point depression is 1.24°C. K_f for $HgC1_2$ is 34.3. What is the state of mercurous chloride in $HgC1_2$? (Hg – 200, CI – 35.5)

(a) as Hg_2Cl_2 molecules
(b) as HgCI molecules
(c) as Ng+ and Cl^- ions
(d) as Hg_2^{2+} and Cl^- ions

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

9. Dry air is slowly passed through three solutions of different concentrations, c, c_2 and c_3; each containing (non volatile) NaCI as solute and water as solvent, as shown in the figure. If the vessel 2 gains weight and the vessel 3 loses weight, then



(a) $c_1 > c_2$ (b) $c_1 < c_2$
(c) $c_1 < c_3$ (d) $c_2 >$

10. In which of the following pairs of solutions will the values of the van't Hoff factor be the same?
(a) 0.05 M $K_4[Fe(CN)_6]$ and 0.10 M $FeSO_4$
(b) 0.10 M $K_4[Fe(CN)_6]$ and 0.05 M $FeSO_4(NH_4)_2SO_4 \cdot 6H_20$
(c) 0.20 M NaCI and 0.10 M $BaCl_2$
(d) 0.05 M $FeSO_4(NH_4)_2SO_4$ $6H_20$ and 0.02 M KCI. $MgC1_2 \cdot 6H_20$

11. Vapour pressure of solution containing 6 g of a non-volatile solute in 180 g water is 20.0 Torr. If 1 mole water is further added vapour pressure increases by 0.02 Torr. Which of the following is true?
(a) The molecular weight of solute is 54g mol^{-1}
(b) The vapour pressure of pure water is 20.22 Torr
(c) Addition of more water in the solution will further raise the vapour pressure of solution
(d) The vapour pressure of pure water is 22.22 Torr

12. Two liquids Aand B form an ideal solution. The solution has a vapour pressure of 700 Torr at 80°C. It is distilled till 2/3°' of the solution is collected as condensate. The composition of the condensate is x'_A= 0.75 and that of the residue is x''_A= 0.30. If the vapour pressure of the residue at 80°C is 600 Tom, which of the following is/are true?
(a) Tile composition of the original liquid was x_A = 0.6.
(b) The composition of the original liquid was x_A = 0.4.
(c) $P_A° = \frac{2500}{3}$ Torr.
(d) $P_B° = 500$ Torr.

ASSERTION/REASON TYPE QUESTIONS

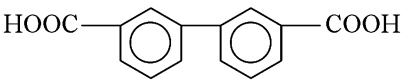
13. **Statement-1:** Perfectly ideal solution is not possible with respect to binary solution of two liquids.
Statement-2: No two substances can have exactly the same nature of intermolecular forces & also of the same magnitude.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

14. **Statement-1:** When a cell is placed in hypertonic solution, it shrinks.
Statement-2: Reverse osmosis is used for desalination of water.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

15. **Statement-1:** The difference in the boiling points of equimolar solution of HCI and HF decreases as their molarity is decreased.
Statement-2: The extent of dissociation decreases steadily with increasing dilution.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(c) Statement -1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

16. **Statement-1:** The molar mass obtained for benzoic acid in benzene is found to be nearly
Statement-2: Benzoic acid has the formula



(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

17. **Statement-1:** When 'a' mL of a 0.1 molal urea solution is mixed with another 'b' mL of 0.1 molal glucose solution, the boiling point of the solution is no different from the boiling points of the samples prior to mixing but if 'a' mL of 0.1 molal urea is mixed with 'b' mL of 0.1 molal HF the boiling point of the mixture is different from the boiling points of the separate samples.
Statement-2: HF is an electrolyte (weak) whereas glucose is a non electrolyte.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

TRUE AND FALSE TYPE QUESTIONS

18. The lowering of vapour pressure of a solvent is equal to mole fraction of the solute.

19. Van's Hoff factor $= \dfrac{\text{Normal Colligative Property}}{\text{Observed Colligative Property}}$

20. Vapour pressure of a solvent decreases with decreasing temperature.

21. Vapour pressure is a colligative property.

22. Freezing point of a solution is always lower than that of the pure solvent.

23. Acetic acid undergoes association in benzene. Themolar mass of acetic acid, determined by elevation of boiling point is always higher than its normal molar mass.

24. A plant cell swells when placed in a hypertonic solution.

25. Osmotic pressure measurements can be used for determination of molar mass of polymers.

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

IDEAL SOLUTION FIXED TEMPERATURE

Consider two liquids 'B' and 'C' that form an ideal solutlion. We hold the temperature fixed at some value T that is above the freezing points of 'B' and 'C'. We shall plot the system's pressure P and against X_B, the **overall mole fraction** of B in the system:

$$x_B = \frac{n_{B.total}}{n_{total}} = \frac{n_B^{\ell} + n_B^{v}}{n_B^{v} + n_B^{\ell} + n_c^{\ell} + n_B^{\ell}}$$

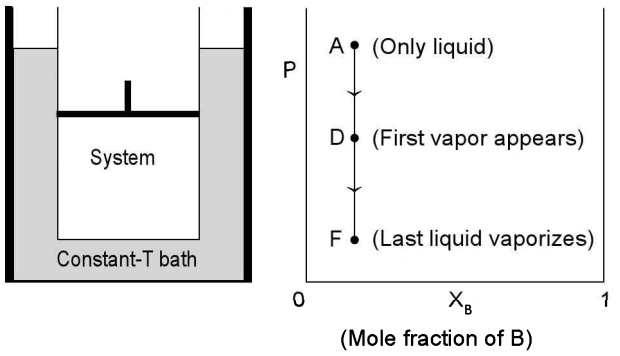
Where, n_B^{ℓ} and n_B^{v} are the number of moles of B in the liquid and vapour phases, respectively. For a close system x_B, is fixed, although n_B^{ℓ} and n_B^{v} may vary.

Let the system be enclosed in a cylinder fitted with a piston and immersed in a constant-temperature bath.To see

what the P-versus-x_B phase diagram looks like, let us initially set the external pressure on the piston high enough for the system to be entirely liquid (point A in figure). As the pressure is lowered below that at A, the system eventually reaches a pressure where the liquid just begins to vaporizes (point D). At point D, the liquid has composition x_B^{ℓ} where, x_B^{ℓ} at D is equal to the overall mole fraction x_B since only an infinitesimal amount of liquid has vapourized. What is the composition of the first vapour that comes off ? Raoult's law, $P_B \equiv x_B^v P_B^0$ relates the vapour-phase mole fractions to the liquid composition as follows:

$$x_B^v = \frac{x_B^{\ell} p_B^0}{P} \text{ and } x_C^v = \frac{x_C^{\ell} p_c^0}{P} \quad \ldots\ldots\ldots\ldots (i)$$

Where, P_B^0 and P_C^0 are the vapour pressures of pure 'B' and pure 'C' at T, where the system's pressure P equals the sum $P_B + P_c$ of the partial pressures, where $x_B^{\ell} = \frac{n_B^{\ell}}{\left(n_B^{\ell} + n_C^{\ell}\right)}$, and the vapour is assumed ideal.

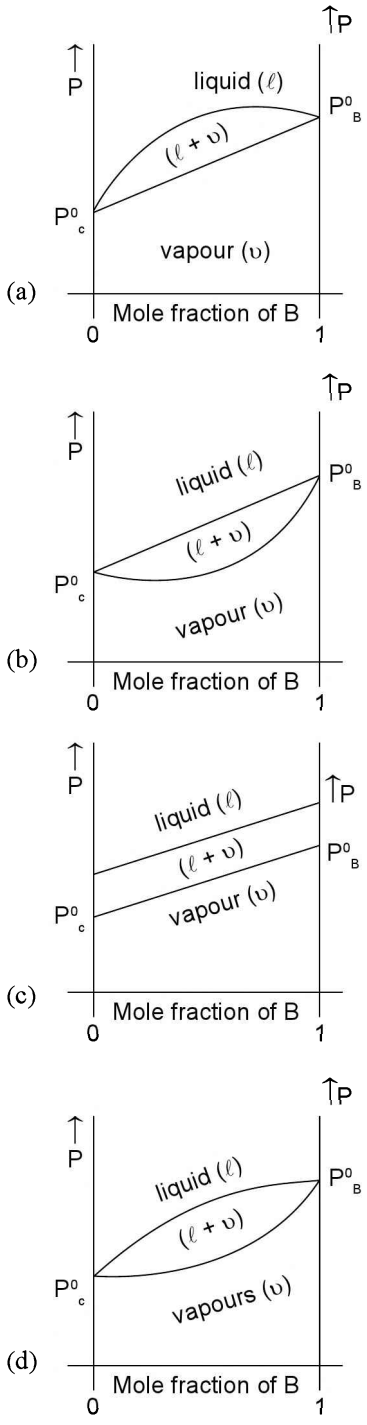


$$\frac{x_B^c}{x_c^v} = \frac{x_B^{\ell} p_B^*}{x_C^{\ell} p_C^*} \quad \text{ideal solution} \quad \ldots\ldots\ldots\ldots (2)$$

Let B be the more volatile component, meaning that $P_B^0 > P_C^0$ Above equation then shows that $x_B^v / x_c^v > x_B^{\ell} / x_C^{\ell}$. The vapour above an ideal solution is richer than the liquid in the more volatile component. Equations (1) and (2) apply at any pressure where liquid-vapour equilibrium exists, not just at point D.

Now, let us isothermally lower the pressure below point D, causing more liquid to vaporize. Eventually, we reach point F in figure, where the last drop of liquid vaporizes. Below F, we have only vapour. For any point or the line between D and F liquid and vapour phases coexist in equilibrium.

26. If the above process is repeated for all other compositions of mixture of C and B. If all the points where vapours start converting into liquid are connected and all the points where vapours get completely converted into liquid are connected then obtained graph will look like.



27. The equation of the curve obtained by connecting all those points where the vapours of above mixture (all mixtures of different composition are taken) just start forming will be

(a) $P = P_C^0 + (P^0{}_C - P^0{}_C)X^{\ell}_B$

(b) $P = P^0{}_B + (P^0{}_B - P^0{}_C)X^{\ell}_B$

(c) $P = \dfrac{P_B^0 P_C^0}{X_B^0(P_C^0 - P_B^0) + P_B^0}$

(d) $P = \dfrac{P_B^0 C_C^0}{X_B^{\ell}(P_C^0 - P_B^0) + P_B^0}$

28. Two liquids A and B have the same molecular weight and form an ideal solution. The solution has a vapour pressure of 700 Torrs at 80°C. It is distilled till 2/3rd of the solution (2/3rd moles out of total moles) is collected as condensate.The composition of the condensate is $x'_A = 0.75$ and that of the residue is $X''_A = 0.30$. If the vapour pressure of the residue at 80°C is 600 Torrs, find the original composition of the liquid.

(a) $X_A = 0.5$
(b) $X_B = 0.6$
(c) $X_A = 0.6$
(d) $X_B = 0.3$

COMPERHENSION-2

The pressure of two pure liquid A and B which form an ideal solution are 400 mm Hg and 800 mm Hg respectively at temperature T. A liquid containing 3 : 1 molar composition of A and B present in a cylinder closed by a piston on which pressure can be varied. The solution is slowly vaporized at temperature T by decreasing the applied pressure starting with a pressure of 760 mm Hg. A pressure gauge (in mm) Hg is connected which given the reading of pressure applied.

29. The reading of pressure Gauge at which only liquid phase exists.

(a) 499 (b) 399
(c) 299 (d) None

30. The reading of pressure Gauge at bubble point is

(a) 500 (b) 600
(c) 700 (d) None

31. The reading of pressure Gauge at which only vapour phase exists is

(a) 501 (b) 457.14
(c) 425 (d) 525

COMPREHENSION-3

Colligative property measurement is one of the techniques used in the measurement of chemical quantities with reasonable accuracy.

If a 40.65 gm sample of K_2SO_4 and $BaSO_4$ is dissolved in 900 gm of pure water to form a solution 'A' at 57°C, its vapour pressure is found to be 39.6 torr while vapour pressure of pure water at 57°C is 40 torr. Density of solution A is 1.24 gm/ml.T

In a different experiment when small amount of pure $BaSO_4$ is mixed with water at 57°C it gives the osmotic rise of 4.05×10^{-5} atm. (R = 0.082 Lt.-atm/mol-K; K = 39, Ba = 137, S = 32, 0 = 16)

32. Percentage of K_2SO_4 in the sample is:

(a) 65.75% (b) 71.34%
(c) 60.35% (d) 78.74%

33. Solubility product of $BaSO_4$ in water at 57°C is:

(a) 5×10^{-15} (b) 3.125×10^{-13}
(c) 5.625×10^{43} (d) $2.25 - 10^{-12}$

34. Concentration of Ba^{2+} ions in solution 'A' is:

(a) $3.5 \times 10^{-}$" M
(b) 4.7×10^{-15} M
(c) $2.3 \times 10^{43}1111$
(d) 3.9×10^{-12} M

35. Boiling point of solution A is (K_b water = 0.54 K-kg/mol):

(a) 0.3 K (b) 0.1 K
(c) 0.04 K (d) 0.05 K

COMPREHENSION-4

A system of greater disorder of molecules is more probable. The disorder of molecules is reflected by the entropy of the system. A liquid vaporizes to form a more disordered gas. When a solulte is present, there is additional contribution to the entropy of the liquid due to increase randomness. As the entropy of solution is higher than that of pure liquid, there is weaker tendency to form the gas. Thus, a solute (non volatile) lowers the vapour pressure of a liquid, and hence a higher booing point of the solution.

Similarly, the greater randomness of the solution opposes the tendency to freeze. In consequence, a lower the temperature must be reached for achieving the equilibrium between the solid (frozen solvent) and the solution. Elevation of B.Pt. (ΔT_b) and depression of F.Pt. (ΔT_f) of a solution are the colligative properties which depend only on the concentration of particles of the solute, not their identity. For dilute solutions, ΔT_b and ΔT_f are proportional to the molality of the solute in the solution.

$\Delta T_b = K_b m$ $\quad K_b$ = Ebullioscopic constant

$$= \frac{RT_b^{0^2}M}{1000\Delta H_{vap}}$$

And $\Delta T_f = K_f m$ K_f = Cryoscopic constant

$$= \frac{RT_f^{0^2}}{1000\Delta H_{fus}}$$

(M = molecular mass of the solvent)

The vaues of K_b and K_f do depend on the properties of the solvent. For liquids, $\frac{\Delta H_{vap}}{T_b^0}$ is almost constant.

[**Troutan's Rule,** this constant for most of the **Unassociated liquids** (not having any strong bonding like Hydrogen bonding in the liquid state) is equal to 90 J/mol.]

For solutes undergoing change of molecular state is solution (ionization or association), the observed ΔT values differ from the calculate ones using the above relations. In such situations, the relationships are modified as $\Delta T_b = iK_b m$; $\Delta T_f = iK_f m$

Where i = Van't-Hoff factor, greater than unity for ionization and smaller than unity for association of the solute molecules.

36. Depression of freezing point of which of the following solutions does represent the cryoscopic constant of water?
- (a) 6% by mass of urea is aqueous solution
- (b) 100 g of aqueous solution containing 18 g of glucose
- (c) 59 g of aqueous solution containing 9 g of glucose
- (d) 1 M KCl solution in water

37. Dissolution of a non-volatile solute into a liquid leads to the
- (a) decrease of entropy
- (b) increase in tendency of the liquid to freeze
- (c) increases in tendency to pass into the vapour phase.
- (d) decrease in tendency of the liquid to freeze

38. To aqueous solution of Nal, increasing amounts of solid HgI_2 is added. The vapour pressure of the solution
- (a) decreases to a constant value
- (b) increases to a constant value
- (c) increases first and then decreases
- (d) remains constant because HgI_2 is sparingly soluble in water.

39. A liquid possessing which of the following characteristics will be most suitable for determining the molecular mass of a compound by cryoscopic measurements?
- (a) That having low freezing point and small enthalpy of freezing
- (b) That having high freezing point and small enthalpy of freezing
- (c) That having high freezing point and small enthalpy of vaporization
- (d) That having large surface tension

40. A mixture of two immiscible liquids at a constant pressure of 1 atm boils at a temperature
- (a) equal to the normal boiling point of more volatile liquid.
- (b) equal to the mean of the normal boiling points of the two liquids.
- (c) greater than the normal boiling point of either of the liquid.
- (d) smaller than the normal boiling point of either of the liquid.

MATCH THE COLUMN TYPE QUESTIONS

41.

Column-I	Column-II
(a) Acetone + $CHCI_3$	(p) $AS_{nu.} > 0$
(b) Ethanol + Water	(q) > 0
(c) $C_2H_5Br + C_2H_5I$	(r) $AH_m < 0$
(d) Acetone + Benzene	(s) Maximum boiling azeotropes
	(t) Minimum boiling azeotropes

42.

Assuming all the solutes are non volatile and all solutions are ideal.

Column-1	Column-II
(a) 10 ml 0.1 M NaOH aqueous solution is added to 10 ml 0.1 M HCI aqueous solution	(p) Osmotic pressure of solution increases
(b) 10 ml 0,1 M NaOH aqueous solution is added to 10 ml 0.1M CH_3COOH aqueous solution	(q) Vapour pressure of solution increases

(c) 10 ml 0.1 M HCI aqueous solution is added to 10 ml 0.1 M NH_3 aqueous solution — (r) Boiling point of solution increases

(d) 10 ml 0.1 M HCI aqueous solution to 10 ml 0.1 M KOH aqueous solution — (s) Freezing point of solution increases

43. For a binary liquid solution of A and B. p^{0}_{A} = pure vapour pressure of A. p^{0}_{B} = pure vapour pressure of B. X_A = mole fraction of A in liquid phase. Y_A = mole fraction of A in vapour phase.

Column-I	Column-II
(a) p2 > pa [Ideal liquid solution]	(p) $X_A\ Y_A$
(b) Azeotropic mixture	(q) $X_A < Y_A$
(c) Equimolar ideal mixture of A & B with $P^0_A < P^0_B$	(r) $X_B < Y_B$
(d) Equimolar ideal mixture of A & B with $P^0_A = P^0_B$	(S) $Y_B > Y_A$

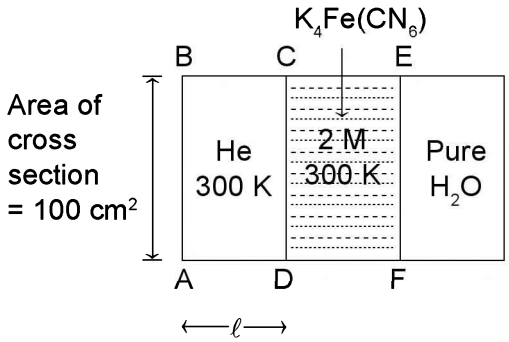
SUBJECTIVE TYPE QUESTIONS

SHORT SUBJECTIVE

44. 0.0125 mol of sucrose is dissolved in 100 gm of water and it undergo pmealliavalsion according to the following equation

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6l - 1_{12}O_6 + C_6H1_2O_6$$

If elevation in boiling point of solution is 0.104°C calculate $\frac{1}{10}$ mol percentage of sugar inverted ($K_{b,\ H_2O}$ = 0.5 2).



45. 25 ml of FeC_2O_4 dissolved in 186 gm of water calculate depression inflecting point if 10 mid of same FeC_2O_4 titrated with 30 ml of 0.4 M $KMnO_4$ in acidic medium (k_f for H_2O = 1.86i, Assme 100% ionization of FeC_2O_4).

46. CD: Fixed wall, EF: SPM, Fixed wall: allows the pressure transfer but no mass transfer.

If 16 gm Helium present in ABCD chamber calculate the length of this chamber in cm if no osmosis takes place through SPM EF. Assume 75% ionization of $K_4Fe(CN)_6$.

47. In 10^3 Litre sample of hard water $CaSO_4$ and $MgSO_4$ present If elevation in Boiling point is 0.000052°C. Calculate the degree of Hardness of hard water. (K_b for H_2O = 0.52)

ANSWER KEYS

1. (c)	**2.** (b)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (a)	**9.** (b, d)	
10. (b, d)	**11.** (a, b, c)	**12.** (a, c, d)	**13.** (a)	**14.** (b)	**15.** (c)	**16.** (c)	**17.** (a)	**18.** False	
19. False	**20.** True	**21.** False	**22.** True	**23.** True	**24.** False	**25.** True	**26.** (b)	**27.** (a)	**28.** (c)
29. (d)	**30.** (a)	**31.** (c)	**32.** (b)	**33.** (c)	**34.** (d)	**35.** (a)	**36.** (c)	**37.** (d)	**38.** (b)
39. (b)	**40.** (d)	**41.** (a – p, s, r), (b – p, q, t), (c – p), (d – p, q, t)				**42.** (a – q, s), ; (b – q, s), (c – q, s), (d – q, s)			
43. (a – q), (b – p), (c – r, s) (d – p)									

HINTS AND EXPLANATIONS

3. (a) Higher freezing point
$\Rightarrow$ lesser ΔT_f
$\Rightarrow$ lesser molality
$\Rightarrow$ lesser number of particles

4. (d) $\frac{P_A^0}{2}+\frac{P_B^0}{2} = 1$ atm $\Rightarrow$ $P_A° + P_B° = 2$ atm

$\frac{p_A^0}{4}+\frac{3P_B^0}{4} > 1$ atm $\Rightarrow$ $P_A° + 3P_B° > 4$ atm

& $\frac{P_A^0}{8}+\frac{3P_B^0}{8}+\frac{4P_C^0}{8} = 1$ at

$\Rightarrow$ $P_A° + 3P_B° + 4P_C° = 8$ atm

So, $P_A° + 3P_B° = (8 - 4 \times 0.8)$ atm $= 4.8$ atm

Hence, $P_B° = 1.4$ atm

$P_B° = 0.6$ atm

5. (a) Let volumes taken to be 'x' & 'y' litres,

so $\frac{0.1x+0.4y}{x+y} = 0.34$ & Vg = (x + y) (to be maximized)

so y = 4x so for maximum volume

y = 2L & × = $\frac{1}{2}$L.

6. (d) $P_T = \frac{1}{2}(75 + 22) = 48.5$ torr

$P_T = \frac{1}{2}(75 + 10) = 42.5$ torr

$P_T = \frac{1}{2}(22 + 10) = 16$ torr

$P_T = \frac{1}{3}(75 + 22 + 10) = 35\frac{2}{3}$ torr

7. (b) $0.0558 = i \times \frac{3.24}{324} \times 1.86$

$\Rightarrow$ i = 3 (100% dissociated)

$0.0744 = i = \times \frac{21.68}{271} \times \frac{1000}{2000} \times 1.86$

$\Rightarrow$ $i \approx 1$ (almost undissociated)

8. (a) $1.24 = 34.3\left[\frac{\frac{0.849}{M}}{0.050}\right]$ $\Rightarrow$ M = 469.68

10. (b, d)
Number of particles from $K_4[Fe(CN)_6] = 5$
Number of particles from $FeSO_4(NH_4)_2SO_4 . 6H_2O = 5$
Number of particles from KCl. $MgCl_2 . 8H_2O = 5$

11. (a, b, c)

$\frac{P-20}{20} = \frac{6}{m} \times \frac{18}{180} = \frac{6}{m} \times \frac{1}{10}$

$\frac{P-20.02}{20.02} = \frac{6}{m} \times \frac{18}{198} = \frac{6}{m} \times \frac{1}{11}$

calculation gives $m \simeq 54$ gm/mole
$p = 20.22$ torr
and on dilution ΔP decreases (lowering) so net pressure increases.

12. (a, c, d)
$x_A P_A° + x_B P_B° = 700$ ... (i)
$xA" PA° + x_B" P_B° = 0.30 P_A° + 0.70 P_B° = 600$ .... (ii)
if moles of A & B initially are x & y then

$x = 0.75 \times \frac{2}{3}(x+y) + 0.30 \times \frac{1}{3}(x+y)$

& $x_A = \frac{x}{x+y}$ or $x_B = \frac{y}{x+y}$

solving gives

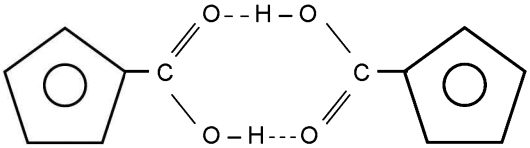
$x_A = 0.6$, $x_B = 0.4$, $P_A° = \frac{2500}{3}$ torr
and $P_B° = 500$ torr

13. (a) S-1 is true, S-2 is true & S-2 is the correct explanation of the S-1.

14. (b) 'S-1' is correct because fluids present inside the cell come out due to higher vapour pressure inside the cell than outside the cell.
'S-2' is correct because in reverse osmosis, solvent from saline water enters the pure solvent through semi-permeable memberane.

15. (c) Extent of dissociated increases steadily with increasing dilution.

16. (c) The benzoic acids forms a dimer due to H-bonding as



17. (a) As degree of dissociation of HF gets changed on dilution.

18. **False** Relative lowering = X_{solute}

19. **False** $i = \frac{\text{observed colligative properly}}{\text{normal colligative properly}}$

21. **False** $\frac{\Delta P}{P}$ is a Colligative property.

24. **False** it shrinks

26. (b) When liquid just starts forming vapours, we have Roult's law valid with X_b & X_c as mole fraction in liquid state so equation of curve obtained by collecting such points will be

$$P = X_B^{\ell} P_B^{\circ} + X_C^{\ell} P_C^0 = X_B^{\ell} P_B^{\circ} + \left(1 - X_B^{\ell}\right) P_C^0 + P_C^0 + (P_B^{\circ} - P_C^{\circ})\ X_B^{\ell} = P_C^{\circ} + (P_B^{\circ} - P_C^{\circ})\ X_B$$

The second curve will not be a straight line having equation

$$P = \frac{P_B^{\circ} - P_C^{\circ}}{X_B^{\ell}(P_C^{\circ} - P_B^{\circ}) + P_B^{\circ}}$$

27. (a) Form solution of above question

28. (c) If initially liquid there are x moles of A and y moles of B then $X_A = \frac{x}{x+y}, X_B = \frac{y}{(x+y)}$

we have, $700 = X_A P_A^{\circ} + X_B P_B^{\circ}$ ..... (1)

$600 = X_A$ "$P_A^{\circ} + X_B$" P_B° ..... (2)

Also $x = \frac{1}{3}(x+y) \times \frac{3}{10} + \frac{2}{3}(x+y) \times \frac{3}{4}$

Which gives $\frac{x}{x+y} = 0.6$

29. to 31.

$x_A = 0.75$ $x_B = 0.05$ above 500 mm Hg only liquid phase exists.

P_{bubble} point $= x_A P_A^{\circ} + x_B P_B^{\circ}$

$P_{\text{cqycqfyr fcUnq}} = x_A P_A^{\circ} + x_B P_B^{\circ}$

$= 0.75 \times 400 + 0.25 \times 800 = 500$ mm.

$y_A = 0.75,$ $y_B = 0.5$

At dew point

$$\frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0} \Rightarrow \frac{1}{P_T} = \frac{0.75}{400} + \frac{0.25}{800} = \frac{1.5+0.25}{800}$$

$$\Rightarrow P_T = \frac{800}{1.75} = 457.14 \text{ mm Hg}$$

Below dew point only vapour phase exists.

36. (c) Cryoscopic constant $K_f = \Delta T_f$ of solution having unit molality of normal solutes

Molality of glucose solution in (c)

$$= \frac{9 \times 1000}{(59-9) \times 180} = 1$$

37. (d) Since the solution has greater entropy (disorder) than the pure liquid, so former has lesser tendency to freeze i.e., the temperature has to be lowered to freeze the solution.

38. (b) $2N^{a+}$ (aq) + $2I^-$ (aq) + HgI_2(s) $\rightarrow$ $2N^{a+}$ (aq) + HgI_4^{2-} (aq)

The number of mole particle decreases from 4 ($2N^{a+} + 2I^-$) to 3 ($2N^{a+} + HgI_4^{2-}$). Hence, the Colligative property will decrease or, the vapour pressure will increase to a constant value until NaI is completely consumed.

39. (b) $K_f = \frac{RT_f^{02}M}{1000\Delta H_{fus}}$ would be larger for larger value of $T°_f$ and smaller value of the enthalpy of fusion of the solid solvent.

40. (d) The vapour pressure of a mixture of two immiscible liquids is the sum o their vapour pressure in the pure states, independent of their relative amounts. Hence, Boiling Point of the mixture will be less than that of either of the liquids, remaining constant throughout.

40. (a – p, s, r), (b – p, q, t), (c – p), (d – p, q, t)

(a) Acetone + $CHCl_3$ –ve deviation from Raoult's law $\Delta S > 0$

$\Delta H < 0$ $\Delta V < 0$

Maximum Boiling Azeotropes.

(b) Ethanol + Water + ve Deviation from Raoult's law $\Delta S > 0$

$\Delta H > 0$ $\Delta V > 0$ Minimum Boiling Azeotropes

(c) $C_2H_5Br + C_2H_5I$ Ideal solution no Azeotropes

$\Delta H = 0$ $\Delta V = 0$

Acetone + Benzene

$\Delta H > 0$ $\Delta V > 0$ $\Delta S > 0$

Minimum Boiling Azeotropes

42. (a – q, s), (b – q, s), (c – q, s), (d – q, s)

43. (a – q), (b – p), (c – r, s) (d – p)

(a) $P_A^0 > P_B^0$ means A is more volatile than B and therefore, A will be richer in vapour phase. [or $Y_A = X_A \frac{P_A^0}{PT}$]

(b) For Azeotropes, composition of vapour phase and liquid phase is same

(c) For $P_A^0 < P_B^0$, $< X_B < Y_B$ and $Y_B > Y_A$ for an equimolar ratio.

(d) For $P_A^0 = P_B^0$, $X_A = Y_A$ for an equimolar ratio.

44.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

mol	0.0125	0	0
	0.0125 – x	x	x

$$\Delta T_b = m_1K_b + m_2K_b + m_3K_b$$

$$m_1 + m_2 + m_3 = \frac{0.104}{0.52} = 0.2$$

$$\frac{0.125 - x + x + x}{100} \times 100 = 0.2$$

$$x = 0.0075$$

$$\text{mol \%} = \frac{0.0075}{0.0125} \times 100 = 60$$

$$\frac{1}{10}\text{th of mol\%} = \frac{60}{10} = 6.$$

45. $x_{FeC_2O_4} = x_{KMnO_4}$ a $FeC_2O_4 \longrightarrow Fe^{+2} + C_2O_4^{-2}$

$$x_{Fe^{+2}} + x_{C_2O_4^{-2}} = x_{KMnO_4} \qquad n_{FeC_2O_4} = \frac{MV}{1000}$$

$$1 \times n + 2 \times n = \frac{0.4 \times 5 \times 30}{1000} \qquad 0.02 = \frac{M \times 10}{1000}$$

$$n = \frac{2 \times 10}{1000} = 0.02 \qquad M = 2$$

$$\Delta T_F = mK_f i = \frac{25 \times 2}{1000} \times \frac{1000}{186} \times 1.86 \times 2 = \frac{100}{100} = 1$$

46. $\pi = MRTi$ $\qquad i = 1 + (y - 1)\,\alpha$

$\pi = 2 \times 0.0821 \times 300 \times 4$ $\qquad i = 1 + (5 - 10)0.75$

For He $PV = nRT$ $\qquad i = 1 + 3$

$\pi V = nRT$ $\qquad i = 4$

$$2 \times 0.0821 \times 300 \times 4 \times 100 \times \ell \times 10^{-3} = \frac{16}{4} \times 0.0821 \times 300$$

$$\ell = \frac{4}{8 \times 10^{-1}} = \frac{40}{8} = 5$$

47. $\Delta T_b = \Delta T_1 + \Delta T_2$

$\Delta T_b = 0.0000104 = (m_{1i}i_1 + m_2i_2) \times k_b$

$CaSO_4$	$MgSO_4$
$i = i1$	$i' = i_2$
$n = n_1$	$n' = n_2$

$$0.000052 = \frac{(n_1 + n_2) \times 0.52 \times 2}{10^6} \times 1000$$

n1 + n2 = 0.05

for degree of Hardness

$n_{CaSO_4} + n_{MgSO_4} = n_{CaCO_3}$

$n_{CaCO_3} = 0.05$

$m_{CaCO_3} = 0.05 \times 10^6 = 5$ ppm

SUBJECTIVE ANSWER TYPE QUESTIONS

18. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

Sol. For initial solution, $\because \pi = \frac{500}{760}$ atm, $T = 283$ K

$$\frac{500}{760} \times V_1 = n \times S \times 283 \qquad \ldots. (1)$$

After dilution, let volume becomes V_2 and temperature is raised to 25°C, i.e., 298 K.

$$\pi = \frac{105.3}{760} \text{ atm}$$

$$\frac{105.3}{760} \times V_2 = n \times S \times 298 \qquad \ldots. (2)$$

$\therefore$ By Eqs. (1) and (2), we get

$$\frac{V_1}{V_2} = \frac{283}{298} \times \frac{105.3}{500} \qquad \frac{V_1}{V_2} = \frac{1}{5} \qquad \therefore \quad V_2 = 5V_1$$

i.e., Solution was diluted to 5 times.

19. A mixture of two immiscible liquids nitrobenzene and water boiling at 99°C has a partial vapour pressure of water 733 mm and that of nitrobenzene 27 mm. Calculate the ratio of the weights of nitrobenzene to the water in distillate.

Sol. $P' = P_M \cdot X_A$

where, X_A is mole fraction in gaseous phase

$$\therefore \quad 27 = 760. \frac{\frac{w_2}{123}}{\frac{w_1}{18}+\frac{w_2}{123}} \qquad \text{(for nitrobenzene)}$$

and $\quad 733 = 760. \dfrac{w_1/18}{\frac{w_1}{18}+\frac{w_2}{123}}$ (for water) $\quad \therefore \dfrac{w_1}{w_2} = 4$

20. A certain mass of substance when dissolved in 100 g C_6H_6 lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100 g of water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely dissociation in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and 5.12 K mol^{-1} kg respectively.

Sol. $\because \quad \Delta T = \dfrac{1000 \times K_f' \times w}{W \times m}$

In C_6H_6: $1.28 = \dfrac{1000 \times 5.12 \times w}{m_N \times 100}$ ... (1)

In H_2O: $1.40 = \dfrac{1000 \times 1.86 \times w}{m_{exp} \times 100}$ ... (2)

(Since given that solute behaves as normal in C_6H_6 and dissociates in water.)

By Eqs. (1) and (2),

$$\frac{m_N}{m_{exp}} = \frac{1.40}{1.28} \times \frac{5.12}{1.86} = 3.01$$

$\therefore \quad i = 3.01 \approx 3.0$

Since solute is 100% ionized, i.e., $\alpha = 1$

Let solute be A_xB_y

$$A_xB_y \rightleftharpoons xA^+ + yB^-$$

1	0	0
$(1-\alpha)$	$x\alpha$	$y\alpha$

$\therefore \quad i = 1 - \alpha + x\alpha + y\alpha$

$\because \quad i = 3$ and $\alpha = 1$

$\therefore \quad x + y = 3$ or No. of ions given = 3

21. A solution containing 28 g phosphorus in 315 g CS_2 (b.pt.46.3°C) boils at 47.98°C. K_b' for CS_2 is 2.34 K mol^{-1} kg. Calculate m.wt. of phosphorus and deduce its molecular formula. Assume its complete association.

Sol. $\Delta T = \dfrac{1000 \times K_b' \times w}{m \times W}$

$$1.68 = \frac{1000 \times 2.34 \times 28}{m \times 315} \qquad \therefore \ m_{exp} = 123.80$$

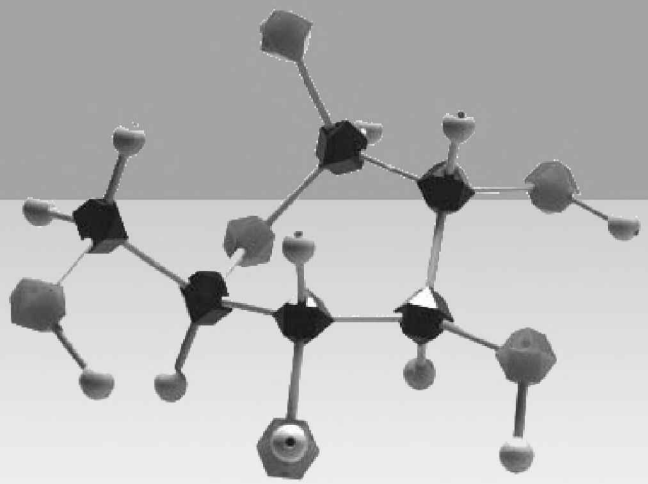
$$\frac{m_N}{m_{exp}} = 1 - \alpha + \frac{\alpha}{n}$$

$\because \quad \alpha = 1$

$$\therefore \quad \frac{m_N}{e_{exp}} = \frac{1}{n} (m_N \text{ of } P = 31)$$

$$\therefore \quad \frac{31}{123.80} = \frac{1}{n} \qquad \therefore \ n \approx 4, \text{ i.e., } P_4$$

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CHAPTER 9

Electrochemistry

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry which deals with the relationship between electrical energy and chemical energy.

You must have heard of chemical energy. What is it?

As you know, that every chemical reaction is associated with a change in free energy which we represented as ΔG. This ΔG associated with a chemical reaction is what we mean by Chemical energy.

In case of a spontaneous reaction, the value of ΔG is negative and that for a non-spontaneous reaction is positive. When the free energy decreases in a spontaneous reaction,the amount of energy decreased has to be converted to any other form of energy (as we can expect from the 'law of conservation of energy'). One simple choice is its conversion to electrical energy.

On the other hand, there can be non-spontaneous reactions which increase demand in the free energy.The required free energy can be supplied from other form of energy. One choice is electrical energy.

But the desired transformation cannot be achieved without a 'device'.The 'device' Which is used for the interconversion of chemical energy and electrical energy is known as electrochemical cell.

Electrochemical Cells

An electrochemical cell is a device capable of either deriving electrical energy from chemical reactions, or facilitating chemical reactions through the introduction of electrical energy. A common example of an electrochemical cell is a standard 1.5-volt "battery". (Actually, a single "Galvanic cell"; a battery properly consists of multiple cells.)

Electrochemical cells can be broadly classified into two categories, viz., electrolytic cells and galvanic (or voltaic) cells.

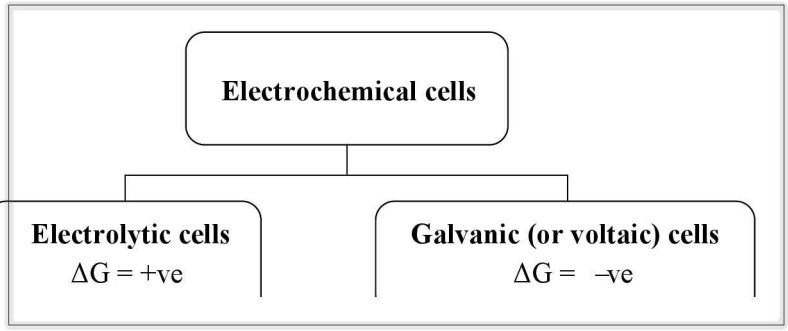


Fig. 9.1

In an electrolytic cell, the reaction that occurs is a non-spontaneous one.Therefore, it is used to convert the electrical energy to the chemical energy. In fact, a chemical reaction (more precisely electrolysis) is carried out with the help of an electrical current.

In a galvanic cell, the reaction that occurs is spontaneous. So it is used to transform the chemical energy to the electrical energy. In fact, an electrical current is produced as a result of some spontaneous chemical reaction.

Finally, we can conclude that electrolytic cell is a device to convert electrical energy into chemical energy whereas in the galvanic cell, the reverse of this process takes place.

Electrolytic cell

Consider an electrolytic cell involving the electrolysis of molten sodium chloride using platinum electrodes as shown in figure

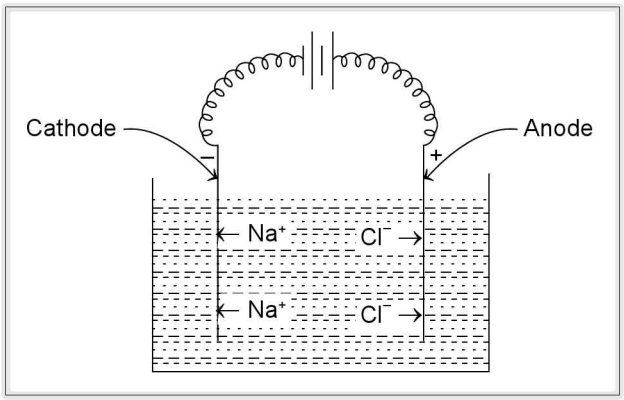


Fig. 9.2 Electrolysis of molten sodium chloride

The left-side electrode is connected to the negative terminal of an external battery which supplies electrons to this electrode. It is because of this, the left-side electrode becomes negatively charged. Electrons are being sucked out of the right-side electrode by the positive terminal of the battery and thus this electrode acquires a positive charge. Within the solution, electricity is carried out by the movements of ions. The positive ions (i.e., cations) are attracted towards the negative electrode and the negative ions (i.e., anions) towards the positive electrode. Since cations are attracted towards the negative electrode, the latter is known as the cathode. Similarly, the positive electrode is known as the anode. **Electrode reactions involve reduction at the cathode and oxidation at the anode.** Thus in the present case, we have,

$$\text{At cathode } Na^+ + e^- \rightarrow Na$$

$$\text{At anode } \quad Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$$

The overall transformation is

$$Na^+ + Cl^- \rightarrow Na + \frac{1}{2} Cl_2 \quad \Delta G = +ve$$

Remember:

- The entire assembly except that of the external battery is known as the electrolytic cell. It is because the battery itself is a galvanic cell.
- The electrode on which oxidation takes place is called ***anode*** (or +ve pole in electrolytic cell) and the electrode on which reduction takes place is called ***cathode*** (or –ve pole in electrolytic cell).
- Free electron cannot be present in solution. So, oxidation and reduction take place at the surface of the electrodes only.
- When electrodes are placed in an electrolyte and a voltage is applied, the electrolyte will conduct electricity. Lone electrons normally cannot pass through the electrolyte; instead, a chemical reaction occurs at the cathode consuming electrons from the anode, and another reaction occurs at the anode producing electrons to be taken up by the cathode. As a result, a negative charge cloud develops in the electrolyte around the cathode, and a positive charge develops around the anode. The ions in the electrolyte move to neutralize these charges so that the reactions can continue and the electrons can keep flowing

Energy changes during electrolysis

The amount of electrical energy that must be added equals the change in Gibbs free energy of the reaction plus the losses in the system. The losses can (in theory) be arbitrarily close to zero, so the maximum thermodynamic efficiency equals the enthalpy change divided by the free energy change of the reaction. In most cases, the electric input is larger than the enthalpy change of the reaction, so some energy is released in the form of heat. In some cases, for instance, in the electrolysis of steam into hydrogen and oxygen at high temperature, the opposite is true. Heat is absorbed from the surroundings, and the heating value of the produced hydrogen is higher than the electric input

Galvanic cell

As stated above, in the galvanic cell, electric current is generated as a result of some spontaneous chemical reaction that takes place in the cell.

Working of Daniell Cell

To understand how electric current is generated, let us consider an example of Daniell cell where the following reaction is produced:

$$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$$

or, in ionic form

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$

This reaction occurs at a very fast speed, i.e., the moment zinc is added in copper sulphate solution, copper is immediately formed. In this reaction, we have basically the following two partial reactions:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \text{ (oxidation)}$$

and $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (reduction)

If the two partial reactions are carried out in two physically separate places, the electrons will have to flow from a place where oxidation occurs to a place where reduction occurs through an external wire. This flow of electrons constitutes a current, which can be used to drive a motor, lift a mass, or do any other work.

Formulation of Daniell Cell

The most obvious way to separate the partial reactions occurring in Daniell cell is to insert the Zn electrode into a solution containing Zn^{2+} ions (but not Cu^{2+} ions) and the Cu electrode (or some unreactive metal) into a solution containing Cu^{2+} ions as shown in the figure. from Zn electrode, a minute amount of Zn can go into the solution as Zn^{2+} ions leaving a negative charge on the electrode (because of electrons left behind) and a positive charge in the solution. These charges stop the ionization process of zinc almost immediately; for every Zn^{2+} ion entering the solution, it or another ion will be driven back to the Zn electrode by the attraction of the negative electrode and the repulsion of the positive solution. Similarly, on the Cu electrode a few Cu^{2+} ions from the solution may be deposited as Cu atoms. This process will make the electrode positive and the solution negative and thus, the deposition process is stopped. However, these processes at the two electrodes, namely, oxidation at Zn electrode an reduction at Cu electrode, can be resumed provided we connect the two electrodes by a wire to allow the electrons to flow from Zn electrode to the electron-deficient Cu electrode and bring the two solutions into contact through a porous lug or a salt bridge so as to neutralize the charges of the two solutions and prevent a direct flow of Cu^{2+} ions towards Zn electrode.

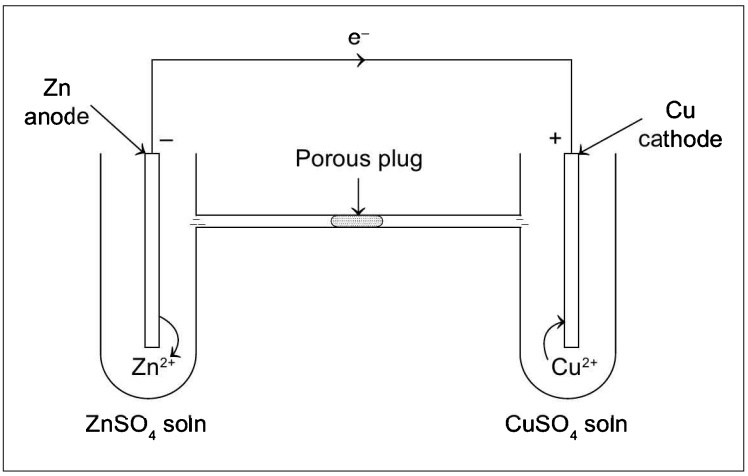


Fig. 9.3 Daniell cell

Sign and Nomenclature of Electrodes

In the cell shown in fig., the Zn electrode becomes negatively charged as the electrons released in the oxidation reaction ($Zn \rightarrow Zn^{2+} + 2e^-$) reside at his electrode. Similarly, the Cu electrode becomes positively charged as the electrons are taken out of this electrode for the reduction reaction ($Cu^{2+} + 2e^- \rightarrow Cu$) which takes place at this electrode. As in the electrolytic cell, the electrode at which oxidation reaction takes place is known as the anode and that where reduction reaction occurs is known as the cathode. Thus, the negative electrode of the galvanic cell is known as anode and the positive one as the cathode.

Galvanic Cell Without a Salt Bridge

In the above example of Daniell cell, we have two solutions which have to be connected so that no intermixing takes place. An example in which this difficulty does not arise is due to the following spontaneous reaction:

$$Zn(s) + 2AgCl(s) \rightarrow 2Ag(s) + Zn^{2+}(aq) + 2Cl^{-}(aq)$$

If the two solids Zn and AgCl are brought into contact, the reaction will take place very slowly owing to the difficulty of establishing sufficient intimate contact between them. But the reaction has a strong tendency to take place and can be carried out by using the cell shown in the figure

The reaction at the Zn electrode is

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$

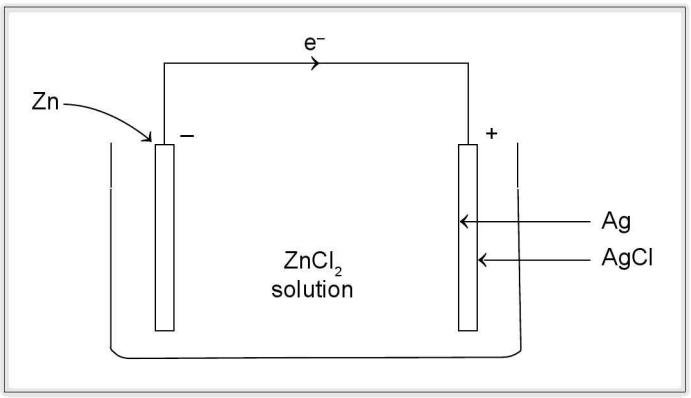


Fig. 9.4

Resume of Sign Conventions

In a galvanic cell, electrons are fed into the anode by the oxidation reaction that takes place at the electrode. The anode pushes these electrons into the external circuit and is, therefore, regarded as the negative electrode-the source of negative charge. The cathode is an electron sink and is, therefore, called the positive electrode.

In an electrolytic cell, the cathode is still the electron sink, but, this time, we are forcibly feeding electrons into the cathode by connecting it to the negative terminal of a generator or a galvanic cell. It is because of this that the cathode of an electrolytic cell is a negative electrode. Since electrons are being sucked out of the anode by the positive terminal of the external battery, the anode is considered a positive electrode.

Oxidation takes place at anode and reduction at cathode in a cell of either type. The only difference is about the sign of the electrodes. Table gives the sign convention and electrode reactions in both cells.

	Anode		***Cathode***	
Cell	Sign	Type of reaction	Sign	Type of reaction
Galvanic	Negative	Oxidation	Positive	Reduction
Electrolytic	Positive	Oxidation	Negative	Reduction

Diagrammatic Distinction Between Galvanic and Electrolytic Cells

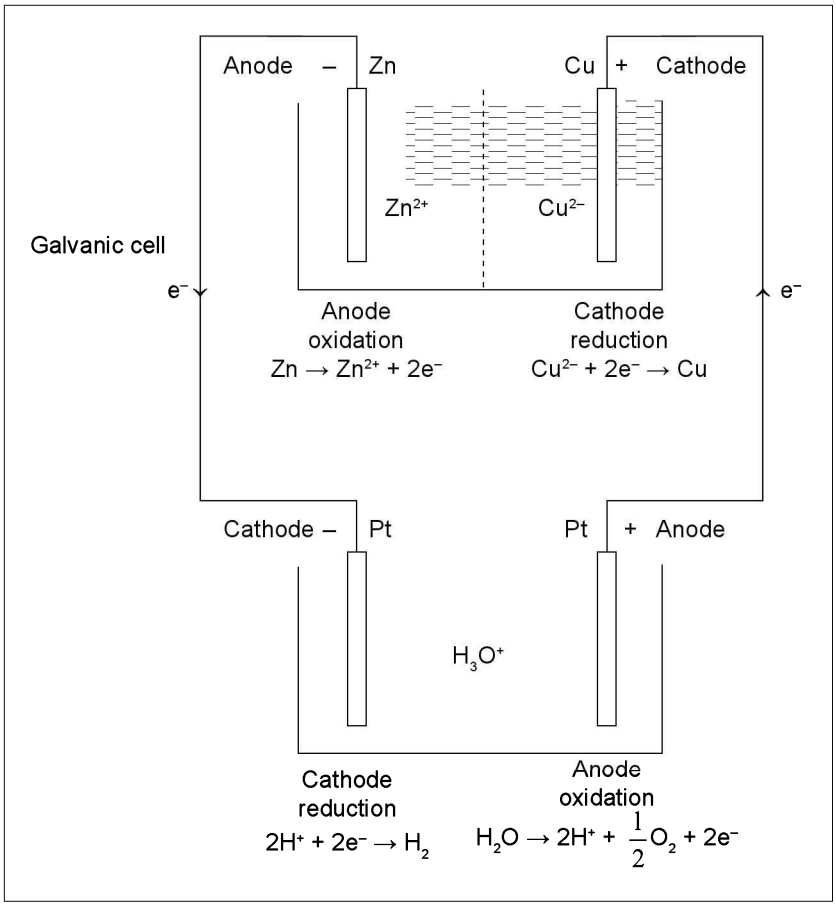


Fig. 9.5 Distinction between the sign conventions of the two types of cells

Electrolytic Cell and Electrolysis

Take the note of the following important points:

Electrolysis is the passage of an electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials.

The main components required to achieve electrolysis are:

- A liquid containing mobile ions-an electrolyte
- An external source of direct electric current
- Two solid rods or plates known as electrodes

The components perform the following roles in the electrolysis process:

- The mobile ions are the carriers of electrical current in the liquid (electrolyte). If the ions are not mobile, as in a solid salt then electrolysis cannot occur.
- The externally supplied direct electric current supplies the energy necessary to create or discharge the ions in the liquid or solution. Electric current is carried by electrons in the external circuit.
- The electrodes provide the physical interface between.
  - the electrical circuit providing the energy to achieve the electrolysis
  - the electrolyte containing the ionic materials that are to be separated.

The electrodes must be able to conduct electricity. Electrodes of metal, graphite and semiconductor material are widely used. Choice of suitable electrode depends on:

- Chemical reactivity between the electrode and electrolyte
- Cost of manufacture of the electrode

Ancillary practical components to achieve electrolysis include:

- Vessels to supply, contain and remove the reactants and products
- Electrical circuitry

The product of electrolysis depends on following factors:

1. Electrode Potential
2. Nature of Electrodes
3. Concentration

1. Electrode Potential

A potential difference develops between the electrode and the electrolyte is called electrode potential. Thus the tendency of an electrode to gain or lose electrons when it is in contact with its own ions in the solution is called electrode potential.

It is of two types:

(a) Oxidation potential: [Measure of tendency to loose electron]

The potential difference arise due to loss of electrons is called oxidation potential.

The half cell in which oxidation takes place is called anode and it has negative potential with respect to the solution.

For example:

$$Fe(s) \rightleftharpoons Fe^{2+}(aq) + 2e^{-}$$

(b) Reduction potential: [Measure of tendency to gain electron]

The potential difference arises due to gain of electron is called reduction potential.

The half cell in which reduction takes place is called cathode and its has positive potential with respect to the solution.

For example:

$$Cu^{+2}(aq.) + 2e^{-} \rightleftharpoons Cu(s)$$

Over voltage

For metals to be deposited on the cathode during electrolysis, the voltage required is almost the same as the standard electrode potential. However, for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential. The extra voltage thus required is called **over voltage** or **bubble voltage.** Its value depends on the particular ion, the particular electrode, and the particular way in which electrolysis is being carried out.

Discharge potential

The discharge potential of an ion at an electrode is equal to the electrode potential associated with the ion plus only overvoltage, i.e., it is the actual value of the minimum potential difference to be applied for the discharge of a particular ion.

Discharge potential = Electrode potential + Overvoltage of the electrode.

The magnitude of electrode potentials depends upon the following factors:

1. **Nature of the electrode**
2. **Concentration of the ions in solution**
3. **Temperature**

If electrolyte solution consist of more than two ions it is observed that all the ions are not discharged at the electrode simultaneously but certain ions are liberated at the electrode in preference to other. The product of electrolysis depends upon discharge potential of cation and anion. Those cations will be preferred to discharge at cathode which have high reduction potential (lower discharge potential). Example [measure of tendency to gain electron in solution]

(a) Electrolysis of NaCl(aq.) H^+ ions will discharge at cathode in preference to Na^+ because discharge potential of H^+ ions is low. Similarly, at anode Cl^- are discharged at anode in preference to OH^- so Na^+ and OH^- remain in solution as NaOH.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At Cathode	**At Anode**	
$H^+ + e^- \rightarrow H$	$Cl^- \rightarrow Cl + e^-$	Primary change
$2H \rightarrow H_2$	$2Cl \rightarrow Cl_2$	Secondary change

But H^+ are produced by ionization of water

$$H_2O \rightarrow H^+ + OH^-$$

Net reaction will be $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ ($E^\circ = -0.83$)

$Cl^- + \frac{1}{2} Cl_2 + e^-$ $E^\circ = 1.36$ V

$2H_2O + O_2(g) + 4H^+ + 4e^-$ $E^\circ = 1.23$ V

The reaction at anode with lower E° is preferred and therefore water should get oxidized in preference to $Cl^-_{(aq)}$. However, due to over potential of oxygen, Cl^- gets oxidized to give Cl_2

(b) Electrolysis of $CuSO_4$(aq.): Cu^{2+} will be preferred to discharge at cathode and OH^- at anode. SO_4^{2-} and H^+ ions will form H_2SO_4 in remaining solution so the solution will become acidic.

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At Cathode	**At Anode**
$Cu^{2+} + 2e^- \rightarrow Cu$	$2OH^- \rightarrow H_2O + O + 2e^-$

$O + O \rightarrow O_2$

or $2H_2O \rightarrow 4H^+ O_2 + 4e^-$

(c) Elecrolysis of Na_2SO_4(aq) will give H_2 and O_2 by discharge of H^+ and OH^- where as Na_2SO_4 will remain as such in solution.

Note: Decreasing order of discharge potential or increasing order of deposition of some ions are as under:

Selective discharge of ions during an electrolysis

At the cathode		*At the anode*
Na^+	Most difficul	F^-
Al^{3+}		SO_4^{2-}
Zn^{2+}		NO_3^-
Pb^{2+}		Cl^-
H^+		Br^-
Cu^{2+}		I^-
Ag^+	Least difficul	OH^-

↑ Discharge potential increases. Therefore, it will be more difficult to discharge that ion

Although, oxidation potential of H_2O is more than Cl^- ions, yet during the electrolysis of concentrated solution of NaCl, the Cl^- ions gets oxidized in preference to H_2O to give Cl_2 gas. Transfer of electron from H_2O is kinetically slow process as it requires relatively large activation energy. The slowness of electrode reaction creates some electrical resistance at electrode surface. Hence, extra potential is required to provide activation energy and to overcome resistance for oxidation of water. This extra voltage required is called overvoltage. Due to overvoltage Cl^- will be oxidized in preference to H_2O.

F^- will never discharge at electrode from aquears solution because of its high discharge potential.

Nature of electrode

There are two types of electrodes; non-attackable and attackable electrodes. The former are also called inert electrodes (example Pt, gold, Graphite).They simply act as carriers for the electrons, which are accepted at the cathode and released at the anode. These electrodes are in no way involved in any chemical reaction.

The attackable electrodes take part in the chemical reactions and influence the nature of the products. Thus, the products of electrolysis will not be the same when a particular electrolyte is subjected to electrolysis by using these two types of electrodes.

If electrode are made up of active metals, it will prefer to loose electron so no anion from solution will be allowed to discharge at anode. For example,

Electrolysis of $CuSO_4$(aq.) using copper electrode.

At Cathode **At Anode**

$Cu^{2+} + 2e^- \rightarrow Cu$ $Cu \rightarrow Cu^{2+} + 2e^-$

So there will be net transfer of copper from anode to cathode. This kind of electrolysis is really helpful to refine crude coppe . Chrome plating, bronzing and refining of coppe , all employ this process.

Note in **Castner-Kellner** cell when mercury electrode is used instead of H^+ ion, Na^+ will prefer to discharge.

Faraday's Laws of Electrolysis

Faraday's laws of electrolysis are quantitative relationships based on the electrochemical researches published by Michael Faraday in 1834.

Several versions of the laws can be found,the most common statements resemble the following:

Faraday's 1st Law of Electrolysis The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb, $W \propto Q$.

Where,

W = Mass of ions liberated in *gm,*

Q = Quantity of electricity passed in Coulombs

= Current in Amperes (I) × Time in second (t)

$\therefore \quad W \propto I \times t$ or $W = Z \times I \times t$

In case current efficiency (η) is given, then,

$$W = Z \times I \times t \times \frac{\eta}{100}$$

Where, Z = constant, known as ***electrochemical equivalent*** (ECE) of the ion deposited.

When a current of 1 Ampere is passed for 1 second (*i.e.*, Q = 1), then, W = Z

Thus, ***electrochemical equivalent*** (ECE) may be defined as "*the mass of the ion deposited by passing a current of one Ampere for one second (i.e., by passing Coulomb of electricity)*". It's unit is gram per coulomb.

Coulomb is the unit of electrical charge.

96500 Coulombs $= 6.023 \times 10^{23}$ *electrons* = 1 *mole electrons.*

$$1 \text{ Coulomb} = \frac{6.023 \times 10^{23}}{96500} = 6.28 \times 10^{18} \text{ electrons,}$$

or 1 electronic charge $= 1.6 \times 10^{-19}$ *Coulomb.*

Faraday's 2nd Law of Electrolysis For a given quantity of electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \text{ or } \frac{Z_1 It}{Z_2 It} = \frac{E_1}{E_2} \text{ or } \frac{Z_1}{Z_2} = \frac{E_1}{E_2} \qquad (\because W = ZIt)$$

Thus, the electrochemical equivalent (Z) of an element is directly proportional to its equivalent weight (E), *i.e.,*

$$E \propto Z \text{ or } E = FZ \text{ or } E = 96500 \times Z$$

Where, F = Faraday constant = $96500\,C\,mol^{-1}$

So, 1 Faraday = 1F =Electrical charge carried out by one mole of electrons.

Mathematical Form

Faraday's laws can be summarized by,

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

Where,

m is the mass of the substance altered at an electrode

Q is the total electric charge passed through the substance

F = 96,485 C mol^{-1} is the Faraday constant

M is the molar mass of the substance

z is the valency number of ions of the substance (electrons transferred per ion)

Note that M/z is the same as the equivalent weight of the substance altered.

For Faraday's first law, M, F, and z are constants, so that the larger the value of Q, the larger m will be.

For Faraday's second law, Q, F, and z are constants, so that the larger the value of M/z (equivalent weight), the larger m will be.

In the simple case of constant-current electrolysis, Q = It leading to

$$m = \left(\frac{It}{F}\right)\left(\frac{M}{z}\right)$$

and then to,

$$n = \left(\frac{It}{F}\right)\left(\frac{1}{z}\right)$$

Where,

n is the amount of substance ("number of moles") altered: n = m/M

t is the total time the constant current was applied.

In the more-complicated case of a variable electrical current, the total charge Q is the electric current I(τ) integrated over time τ:

$$Q = \int_0^t I \, d\tau$$

Here, t is the total electrolysis time. Please note that tau is used as the current I is a function of tau.

Assume that these three reactions are occurring in three separate electrolytic cells connected in series. When x moles of electrons are passed through the three cells, the mass of Na, Cu and Al deposited are 23x g, 31.75x g and 9x g respectively. We can see that 23, 31.75 and 9 g/eq are the chemical equivalent weights of the three elements.

$\therefore$ w = moles of electrons × E

The charge possessed by 1 mole of electrons = $1.6 \times 10^{-19} \times 6.023 \times 10^{23} \approx 96500$ C

This charge is called as **1 Faraday.**

If we pass one Faraday of charge, it means that we are passing one mole of electron and by passing 1 Faraday of charge 1g equivalent weight of the substance will be deposited or liberated.

$$\therefore \quad W = \frac{q}{96500} \times E$$

By combining the first and second la , we get

$$Z = \frac{E}{96500}$$

Current Efficiency

It is the fraction of the current that is virtually effective in electrolysing the solution.

number of coulombs = current in amps × time in seconds that the current flow

In shorthand, this is

coulombs = amps × time (in seconds)

For example, if we pass a current of 0.2 A for 30 min through silver nitrate solution, the number of coulombs transferred would be,

number of coulombs = 0.2 A X 30 × 60 s = 360 C
(Notice the conversion of the 30 min to seconds by multiplying by 60.)

We also know that the charge on one electron is 1.6×10^{-19} C, so the number of coulombs represented by 1 mol of electrons is $1.6 \times 10^{-19}\,C \times 6.02 \times 10^{23} mol^{-1} = 9.632 \times 10^{4}\,C\ mol^{-1}$. This is an important quantity of charge, which is sometimes known as the faraday of electricity. It represents the charge carried by a mole of electrons. The name is in honour of Michael Faraday who, in the 1870s and 1880s, was the first person to investigate electrolysis systematically. Often, the faraday is written as a round number, perhaps 96 500 C mol^{-1}, which is not an accurate value but handy in calculations.

In our example, we can now work out how many moles of electrons were transferred:

$$\text{number of moles of electrons} = \frac{360\,C}{9.632 \times 10^{4}\,C\,mol^{-1}}$$
$$= 3.74 \times 10^{-3}\,mol$$

The equation for the reaction tells us that 3.74×10^{-3}mol of electrons will produce 3.74×10^{-3}mol of silver. Thus, the mass of silver is 3.74×10^{-3}molx 108g mol^{-1}, or 0.40g.

Here, is another example. If a current of 0.1 A is passed for 10 hours through acidified water at room temperature, what volume of oxygen will be released? We shall take the faraday as 96 500 C mol^{-1}.

Stage 1 The equation:

At the anode,

$$4H_2O(1) - 4e^- \rightarrow 4H^+(aq) + O_2(g)$$
4 mol 4 mol 4 mol 24 dm^3 at room temp.

Thus, we know that 4 mol of electrons will release 24 dm^3 of oxygen.

Stage 2 The number of coulombs passed:

Number of coulombs = 0.1 A × 10 × 60 × 60s
= 3600 C

Stage 3 The number of moles of electrons:

$$\text{Number of moles of electrons} = \frac{3600\,C}{96500\,C\,mol^{-1}}$$
$$= 0.0373\ mol$$

Stage 4 The final answer

$$\text{Volume of oxygen released} = 24\ dm^3 \times \frac{0.0373\ mol}{4\ mol}$$
$$= 0.224\ dm^3$$



Worked-out Examples

Type–I: Amount of Electrolyte discharged at the cost of amount of charged passed.

1. Calculate the quantity of electricity that will be required to liberate 710 g of Cl_2 gas by electrolyzing a conc. solution of NaCl. What weight of NaOH and what volume of H_2 at 27°C and 1 atm pressure is obtained during this process?

Solution $w = \frac{E.i.t}{96500}$ $\qquad 2Cl^- \rightarrow Cl_2 + 2e$

$\because \quad Q = i.t \qquad \therefore \quad E_{Cl_2} = \frac{M.wt.}{2}3$

$\therefore \quad Q = \frac{96500w}{E}$

$= 1930000$ coulomb

$\because$ 1 F gives 1 g equation or 40 g NaOH

$\therefore$ 20 F gives 20 g equation or 40×20 g NaOH = 800 g NaOH

Also, 1 F gives 1 g equation or 1 g H_2

$\therefore$ 20 F gives 20 g equation or 20 g H_2

From $PV = \frac{w}{m}RT$

$1 \times V = \frac{20}{2} \times 0.0821 \times 300$

$\therefore \quad V_{H_2} = 246.3$ litre

2. Find out the volume of gases evolved by passing 0.965 A current for 1 h through an aqueous solution of CH_3COONa at 25°C and 1 atm.

Solution $2CH_3COONa(aq.) \xrightarrow{\text{eletrolysis}} \overset{\text{Anode}}{C_2H_6} + 2CO_2 + 2\overset{\text{Cathode}}{NaOH} + H_2$

$2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e$

$2H^+ \longrightarrow H_2 + 2e$

Equivalent $\left(\frac{W}{E}\right) = \frac{i.t}{96500} = \frac{0.965 \times 1 \times 60 \times 60}{96500} = 0.036$

Thus, total equivalent of $C_2H_6 + CO_2 + H_2 = 0.036 + 0.036 + 0.036$

$\therefore$ Total moles of gases (n) $= \frac{0.036}{2} + \frac{0.036}{1} + \frac{0.036}{2} = 0.072$

$\left[\because E_{C_2H_6} = \frac{M}{2}; \quad E_{H_2} = \frac{M}{2}; \quad E_{CO_2} = \frac{M}{1}\right]$

$\therefore \quad V = \frac{nRT}{P} = \frac{0.072 \times 0.0821 \times 298}{1} = 1.762$ litre

3. Copper sulphate solution (250 mL) was electrolysed using a platinum anode an a copper cathode. A constant current of 2 mA was passed for 16 minute. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. **[IIT-2000]**

Solution Equivalent of Cu^{2+} lost during electrolysis

$$= \frac{i \times t}{96500} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500}$$

$$= 1.989 \times 10^{-5}$$

or Mole of Cu^{2+} lost during electrolysis $= \frac{1.989 \times 10^{-5}}{2}$

This value is 50% of the initial concentration of solution

Thus, initial mole of $CuSO_4 = \frac{2 \times 1.989 \times 10^{-5}}{2} = 1.989 \times 10^{-5}$

Thus, initial concentration of $CuSO_4 = \frac{1.989 \times 10^{-5} \times 1000}{250}$

$[CuSO_4] = 7.95 \times 10^{-5}$ M

4. A Zn rod weighing 25 g was kept in 100 mL of 1 M $CuSO_4$ solution. After a certain time the molarity of Cu^{2+} in solution was 0.8. What was molarity of SO_4^{2-} ? What was the weight of Zn rod after cleaning? At. weight of Zn = 65.4.

Solution ∵ Meq. = N × V

Meq. of Cu^{2+} before reaction = 100 × 1 × 2 = 200

Meq. of Cu^{2+} after reaction = 100 × 0.8 × 2 = 160

∴ Meq. of Cu^{2+} lost = 200 – 160 = 40

∴ Meq. of Zn lost = 40

∴ $\frac{w}{65.4/2} \times 1000 = 40$

∴ Net weight of Zn rod = 25 – 1.308 g

= 23.692 g

Also the reactions are $Zn \rightarrow Zn^{2+} + 2e$

$Cu^{2+} + 2e \rightarrow Cu$

∴ No change in molarity of SO_4^{2-}

5. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per reaction,

$$Mn^{2+}(aq.) + 2H_2O \rightarrow MnO_2(s) + 2H^+(aq.) + H_2(g)$$

Passing a current of 27 A for 24 hour gives one kg of MnO_2. What is the value of current effi ciency? Write the reaction taking place at the cathode and at the anode.

[IIT-May 1997]

Solution $w = \frac{E.i.t}{96500}$

∴ $1000 = \frac{87 \times i \times 24 \times 60 \times 60}{2 \times 96500}$

i = 25.6 ampere

$\therefore$ Current efficiency $= \frac{25.6}{27} \times 100 = 94.8\%$

Reactions

Anode: $Mn^{2+} \rightarrow Mn^{4+} + 2e$

Cathode: $2H^+ + 2e \rightarrow H_2$

6. 50 mL of 0.1 M $CuSO_4$ solution is electrolysed using Pt electrodes with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate $[Cu^{2+}]$, $[H^+]$ and $[SO_4^{2-}]$ after electrolysis. What will be the concentration of each species if current is passed using Cu electrodes?

Solution Meq. of $CuSO_4 = 50 \times 0.1 \times 2 = 10$ (Meq. = N × V mL)

or Meq. of $Cu^{2+} = 10$

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e$

Cathode: $Cu^{2+} + 2e \rightarrow Cu$

Now $\frac{w}{E} = \frac{i.t}{96500}$

and Equivalent of Cu^{2+} lost = Equivalent of H^+ formed $= \frac{i.t.}{96500} = \frac{0.965 \times 1 \times 60}{96500} = 6 \times 10^{-4}$

$\therefore$ Meq. of Cu^{2+} lost = Meq. of H^+ formed = 0.6

$\therefore$ Meq. of Cu^{2+} left in solution or Meq. of $CuSO_4$ left in solution

$\therefore$ $[Cu^{2+}] = \frac{N_{Cu^{2+}}}{2} = \frac{9.4}{50 \times 2} = 0.094M$ $\left[\because N = \frac{\text{Meq.}}{\text{Volume (mL)}}\right]$

$[H^+] = \frac{N_{H^+}}{1} = \frac{0.6}{50} = \mathbf{0.012\ M}$

$[SO_4^{2-}] = 0.1$ M

Since, SO_4^{2-} does not take part in redox change.

Also if Cu electrodes are used, no change will be in the molarity of electrolyte, i.e., 0.1 M

Since the reactions are, $Cu^{2+} + 2e \rightarrow Cu$

$Cu \rightarrow Cu^{2+} + 2e$

7. In fuel cell H_2 and O_2 react to produce electricity. In the process, H_2 gas is oxidized at the anode and O_2 at cathode. If 67.2 litre of H_2 at S.T.P. reacts in 15 minute, what is average current produced? If the entire current is used for electro deposition of Cu from Cu^{+2}, how many g of Cu are deposited?

Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e$ **[IIT-1988]**

Solution Moles of H_2 reacting $= \frac{67.2}{22.4} = 3$

$\therefore$ Equation of H_2 used $= 3 \times 2 = 6$

Now, $\frac{w}{E} = \frac{i.t}{96500}$; $6 = \frac{i \times 15 \times 60}{96500}$

$\therefore$ $i = 643.33$ ampere

Also, Equation of H_2 = Equation of Cu formed

$\therefore$ Equation of Cu deposited = 6

$\therefore$ $w_{Cu} = 6 \times \frac{63.5}{2} = 190.5$ g

Weight of Cu deposited = 190.5 g

8. An aqueous solution of NaCl on electrolysis gives $H_{2(g)}$, $Cl_{2(g)}$ and NaOH according to reaction:

$$2Cl^-_{aq} + 2H_2O \rightarrow 2OH^-_{aq} + H_{2(g)} + Cl_{2(g)}$$

A direct current of 25 ampere with a current efficiency of 62% is passed through 20 litre of NaCl solution (20% by weight).

(a) Write down the reactions taking place at the electrodes.
(b) How long will it take to produce 1 kg of Cl_2?
(c) What will be the molarity of solution with respect to OH^-?

Assume no loss in volume due to evaporation. **[IIT-1992]**

Solution (a) Anode: $2Cl^- \rightarrow Cl_2 + 2e$

Cathode: $2e + 2H_2O \rightarrow 2OH^- + H_2$

(b) $w = \frac{E.i.t}{96500}$ $\because$ $W_{Cl_2} = 10^3$ g, $E_{Cl_2} = 35.5$

$10^3 = \frac{35.5 \times 25 \times 62 \times t}{100 \times 96500}$ $\because$ Current efficiency = 62

$t = 175374.83$ sec $\therefore$ $i = \frac{25 \times 62}{100}$ ampere

$\therefore$ $t = 48.71$ hr

(c) Equation of OH^- formed = Equation of Cl_2 formed = $\frac{10^3}{35.5} = 28.17$

$\therefore$ Mole of OH^- formed = 28.17 ($\because$ monovalent)

$\therefore$ $[OH^-] = \frac{\text{mole}}{\text{Volume in litre}} = \frac{28.17}{20} = 1.408$ mol litre^{-1}

9. A current of 1.70 A is passed through 300 mL of 0.160 M solution of $ZnSO_4$ for 230 sec with a current efficiency of 90%. Find the molarity of Zn^{+2} after the deposition of Zn. Assume the volume of the solution remains constant during electrolysis.

[IIT-1991]

Solution $i = \frac{1.70 \times 90}{100}$ ampere

$\therefore$ Equation of Zn^{+2} lost = $\frac{i.t}{96500} = \frac{1.70 \times 90 \times 230}{100 \times 96500} = 3.646 \times 10^{-3}$

$\therefore$ Meq. of Zn^{+2} lost = 3.646

Initial Meq. of $Zn^{+2} = 300 \times 0.160 \times 2$ [$\because$ M × 2 = N for Zn^{+2}

$= 48 \times 2 = 96$ Meq. = N × $V_{(in\ mL)}$]

$\therefore$ Meq. of Zn^{+2} left in solution = 96 – 3.646 = 92.354

$\therefore$ $[ZnSO_4] = \frac{92.354}{2 \times 300} = 0.154$ M

10. An acidic solution of Cu^{+2} salt containing 0.4 g of Cu^{+2} is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minute with the volume of solution kept at 100 mL and the current at 1.2 ampere. Calculate volume of gases evolved at N.T.P. during entire electrolysis. Atomic weight of Cu = 63.6.

[IIT-1989]

Solution For 1 part of electrolysis

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e$

Cathode: $Cu^{+2} + 2e \rightarrow Cu$

$\therefore$ Eq. of O_2 formed = Eq. of Cu = $\frac{0.4 \times 2}{63.6} = 12.58 \times 10^{-3}$

For II part of electrolysis: Since Cu^+ ions are discharged completely and thus, further passage of current through solution will lead the following changes.

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e$

Cahode: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

Eq. of H_2 = Eq. of $O_2 = \frac{i.t}{96500} = \frac{1.2 \times 7 \times 60}{96500} = 5.22 \times 10^{-3}$

$\therefore$ Total Eq. of O_2 Eq. of $H_2 = 5.22 \times 10^{-3}$

$= 5.22 \times 10^{-3} + 12.58 \times 10^{-3}$ 2Eq. of H_2 at NTP

$= 17.8 \times 10^{-3}$ = 22.4 litre

$\because$ 4 eq. O_2 at NTP = 22.4 litre $\therefore$ 5.22×10^{-3} Eq. at NTP

$\therefore$ 17.8×10^{-3} Eq. O_2 at NTP $= \frac{22.4 \times 5.22 \times 10^{-3}}{2}$ litre

$= \frac{22.4 \times 17.8 \times 10^{-3}}{4}$ litre = 58.46 mL

= 99.68 mL

$\therefore$ Total volume of $O_2 + H_2 = 99.68 + 58.46 = 158.14$ mL

Note: If Cu^{+2} is as $CuCl_2$, then Cl_2 will come out in I step and H_2 and O_2 in II step. Calculate their volumes.

11. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if current efficiency is 50%. If the potential drops across the cell is 3.0 volt, how much energy will be consumed? **[IIT-1990]**

Solution $C_6H_5NO_2 + 6H^+ + 6e \rightarrow C_6H_5NH_2 + 2H_2O$

$N^{+3} + 6e \rightarrow N^{-3}$

$\therefore$ Eq. wt. of nitrobenzene = $\frac{M}{6} = \frac{123}{6}$

$$\text{Now } w = \frac{E.i.t}{96500} \quad \text{Since current efficiency is 50}$$

$$12.3 = \frac{123 \times i \times t \times 50}{6 \times 100 \times 96500} \qquad \therefore i = \frac{50\, i_0}{100}$$

$$\therefore \quad i \times t = 115800 \text{ coulomb}$$

Now energy used = $Q \times V = 115800 \times 3 = 347.4$ kJ

12. How many grams of silver could be plated out on a serving tray by electrolysis of solution containing silver in +1 oxidation state for a period of 8.0 hour at a current of 8.46 ampere? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3.

[IIT-July 1997]

Solution $W_{Ag} = \frac{E.i.t}{96500} = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500} = 272.18$ g

Volume of Ag $= \frac{272.18}{10.5} = 25.92$ mL $\quad \therefore$ Surface area $= \frac{25.92}{0.00254} = 1.02 \times 10^4$ cm^2

Do it yourself

1. How long a current of 3 ampere has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with a thickness of 0.005 mm? Density of Ag is 10.5 g cm^{-3}.

[Ans. 125.09 second] **[IIT-1985]**

2. A current of 80 microampere is passed through a solution of $AgNO_3$ for 32 minute using Pt electrodes. A uniform single atom thick layer is deposited covering 86% of the cathode surface. If total surface area of cathode is 601.7 cm^2. Calculate area covered by one Ag atom.

[Ans. 5.4×10^{-16} cm^2]

3. A current of 15 ampere is used to plate Ni from $NiSO_4$ bath. Both H_2 and Ni are formed at cathode. The current efficiency of Ni formation is 60%.

(a) How many g of Ni is plated per hour?

(b) What is the thickness of plating if the cathode consists of a sheet of 4 cm^2 which is coated on both sides? The density of Ni is 8.9 g mL^{-1}.

(c) What volume of H_2 is formed per hour at STP?

(d) What volume of O_2 is formed per hour at STP?

[Ans. (a) 9.85 g, (b) 0.138 cm, (c) 2.51 litre, (d) 3.13 litre]

Hint: At cathode two reductions occur, i.e., of Ni^{2+} and H^+. Since current efficiency of Ni^{2+} is 60%, $\therefore$ current efficiency for H^+ is 40%.



Worked-out Examples

Type–II: Preferentially discharge of cation or anion

13. A 300 mL solution of NaCl was electrolysed for 6.00 min. If the pH of the final solution was 12.24, calculate the average current used.

PLAN NaCl (aq) on electrolysis is converted into NaOH and H_2 at cathode, and Cl_2 at anode. From the pH, amount of NaOH formed or NaCl reacted is determined, hence the average current.

Solution pH = 12.24

$\therefore$ pOH = 1.76 $\therefore$ $[NaOH] = 10^{-1.76} = 10^{-2}\, 10^{0.24} = 1.74 \times 10^{-2}$ M

$\therefore$ NaOH in 300 mL = $1.74 \times 10^{-2} \times 0.300 = 0.522 \times 10^{-2}$ mol

$\therefore$ $w = 0.522 \times 10^{-2} \times 40$ g NaOH

Also $w = zit = \dfrac{40}{1 \times 96500} \times 6 \times 60 \times i$

$$i = \frac{0.522 \times 10^{-2} \times 40 \times 96500}{40 \times 360} = 1.4 \text{ A}$$

14. A current is passed through 500 mL of a solution of CaI_2. The following electrode reactions occur:

Anode: $2I^- \rightarrow I_2 + 2e^-$

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

After sometime, analysis of the solution shows that 47.7 millimoles of I_2 have been formed.

(a) How many faradays of charge have passed through the solution?

(b) How many coulombs?

(c) What volume of dry H_2 at STP has been formed? What is the pH of the solution?

PLAN Number of equivalent of I_2 = Number of faradays

Mol of H_2 = Mol of I_2

Mol of OH^- = 2 × Mol of I_2

Thus, required values can be calculated.

Solution (a) I_2 = 47.7 millimol = 47.7×10^{-3} mol = $2 \times 47.7 \times 10^{-3}$ equivalent

$\therefore$ Number of faradays = 95.4×10^{-3} F

(b) Number of coulombs = $95.4 \times 10^{-3} \times 96500 = 9206.1$ coulombs

(c) Also from the reactions, $H_2 = I_2 = 47.7 \times 10^{-3}$ mol = $47.7 \times 10^{-3} \times 22.4$ L at STP

$= 1.0685$ L H_2

Also, $[OH^-] = 2 \times I_2 = 2 \times 47.7 \times 10^{-3}$ mol in 500 mL

$= 2 \times 47.7 \times 10^{-3} \times 2$ mol $L^{-1} = 0.1908$ M

$\therefore$ $pOH = -\log [OH^-] = -\log (0.1908) = 0.72$

$\therefore$ $pH = 14 - 0.72 = 13.28$

At the cathode

OH^- ions formed will combine with $H_2PO_4^-$ to form HPO_4^{2-}. Thus, $[HPO_4^{2-}]$ is increased and $[H_2PO_4^-]$ is decreased.

$$HPO_4^- + OH^- \rightleftharpoons HPO_4^{2-} + H_2O$$

initial	1.0 M		1.0 M
$[OH^-]$ formed			0.165 M
Change	–0.165 M	–0.165 M	+ 0.165 M
Net	0.835 M	0	1.165 M

$$pH = 2.15 + \log \frac{1.165}{0.835}$$

$$= 2.15 + 0.145 = 2.295$$

15. 2.00 L of a buffer solution is prepared that is 1.00 M NaH_2PO_4 and 1.00 M Na_2HPO_4. The solution is divided in half between the two compartments (each containing 1 L buffer) of an electrolysis cell. The electrodes used are Pt. Asume that the only reaction is the electrolysis of water. If electrolysis is carried out for 212 min with a constant current of 1.25 A, what will be the pH in each cell compartment at the end of the electrolysis? $[pK_a(H_2PO_4^-) = 2.15]$

PLAN On electrolysis, there is formation of H^+ ion at the anode and OH^-

Solution At the anode: $2H_2O(l) \rightarrow 4H^+ + O_2 + 4e^-$

At the cathode: $4H_2O(l) + 4e^- \rightarrow 4OH^- + 2H_2(g)$

Thus, there is formation of H^+ ion at the anode and OH^- ion at the cathode in equivalent part.

$[H^+] = [OH^-]$ at each electrode = izt

$$= 1.25 \times \frac{1}{96500} \times 212 \times 60 \quad = 0.165 \text{ M}$$

At the anode

H^+ ions formed will combine with HPO_4^{2-} to form $H_2PO_4^-$, thus. $[HPO_4^{2-}]$ is decreased and $[H_2PO_4^-]$ is increased.

HPO_4^{2-} +	H^+	$\rightleftharpoons$	$H_2PO_4^-$
initial	1.0 M		1.0 M
H^+ formed			0.165 M
Change –0.165 M		–0.165 M	+ 0.165 M
Net 0.835 M		0	1.165 M

Using the Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[Salt]}{[acid]}$$

$$= pK_a + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 2.15 + \log \left(\frac{0.835}{1.165}\right)$$

$$= 2.15 - 0.145 \quad = 2.005$$

At the cathode

OH^- ions formed will combine with $H_2PO_4^-$ to form HPO_4^{2-}. Thus, $[HPO_4^{2-}]$ is increased and $[H_2PO_4^-]$ is decreased.

HPO_4^- +	OH^-	$\rightleftharpoons$	$HPO_4^{2-} + H_2O$	initial	1.0 M	1.0 M
$[OH^-]$ formed					0.165 M	
Change	–0.165 M		–0.165 M		+ 0.165 M	
	0		1.165 M			

$$pH = 2.15 + \log \frac{1.165}{0.835}$$

$$= 2.15 + 0.145 = 2.295$$

16. Assume that impure copper contains only Fe, Au and Ag as impurities. After the passage of 140 amperes for 482.5 sec, the mass of the anode decreased by 22.26 gm., and that of the cathode increased by 22.011gm. Calculate the % of iron and copper originally present.

Solution There are certain assumptions to be done in solving this problems. First of all we must assume that the cathode is either a pure copper electrode or an inert electrode.

We must understand that the anode which is impure copper has the metals getting oxidised from it when electricity is passed. This assumption has to be made because we want to find the %

of copper and iron in the anode and this fact can be related to the mass increase of cathode only if the metal from the anode gets deposited in the cathode. Therefore, if the metals of the anode are going to be oxidised, then its Fe which will be oxidised first and then Cu. Once all copper oxidises, gold and silver which are just impurities will fall into the electrolyte as ***'anode mud'***.

There is another assumption to be made. This is with regard to the electrolyte. The electrolyte should not contain cu^{2+} ions. This is because if it contains cu^{2+} ions, then the mass increase of the cathode, during the oxidation of Fe to Fe^{2+}, would be the due to copper and the mass increase of the cathode, during the oxidation of copper would also be due to copper. Therefore, it would not be possible to calculate the % of Cu and Fe in the anode. Therefore, we assume the solution to be that of an acid with an anion having a low standard oxidation potential. This means that as Fe gets oxidised to Fe^{2+}, it is the H^+ of the solution which gets reduced at the cathode to give H_2. As H_2 is a gas, the mass of cathode does not increase. After Fe, it will be Cu which will get oxidised to cu^{2+} and at this time, it is Cu^{2+} which will be reduced and the mass of the cathode starts increasing.

$\therefore$ Mass increase of cathode = Mass of Cu in the anode = 22.011 gm.

Mass decrease of anode = Mass of Cu, Fe, Ag and Au = 22.26 gm

$\therefore$ percentage of Cu in the anode $= \dfrac{22.011 \times 100}{22.26}$

$= \mathbf{98.88\%}$

Moles of electrons passed $= \dfrac{482.5 \times 140}{96500} = 0.7$

Moles of electrons used for Cu $= \dfrac{22.011}{63.5} \times 2$

$= 0.693$

Moles of electrons used for Fe $= 0.7 - 0.693$

$= 7 \times 10^{-3}$

Moles of Fe $= \dfrac{7 \times 10^{-3}}{2}$ $= 3.5 \times 10^{-3}$

Percentage of Fe in the anode $= \dfrac{3.5 \times 10^{-3} \times 56}{22.26} \times 100$

$= \mathbf{0.88\%}$

Do it yourself

1. How long a current of 0.5 ampere be passed through 50 mL of a 0.10 M NaCl solution in order to make its pH 12, assuming no volume change?

   [Ans. 96.5 sec]

2. A current of 0.193 A is passed through 100 mL of 0.2 M NaCl for an hour. Calculate pH of solution after electrolysis if current efficiency is 90%. Assume no volume change.

   [Ans. 12.82]



Worked-out Examples

Electrolysis

17. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The products at the anode and cathode are:

(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na

(c) O_2, Na (d) $S_2O_8^{2-}$, H_2

Solution (a) H_2O is more readily reduced at cathode than Na^+. It is also more readily oxidized at anode than SO_4^{2-}. Hence, the electrode reactions are

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ [at cathode]}$$

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \text{ [at anode]}$$

18. In the electrolytic cell, flow of electrons is from **[IIT-JEE-2003]**

(a) Cathode to anode in solution

(b) Cathode to anode through external supply

(c) Cathode to anode through internal supply

(d) Anode to cathode through internal supply

Solution (c) In an electrolytic cell, electrons do not flow themselves. It is the migration of ions towards oppositely charged electrons that indirectly constitutes the flow of electrons from cathode to anode through internal supply.

19. When during electrolysis of a solution of $AgNO_3$, 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be: **[AIEEE-2003]**

(a) 1.08 g (b) 10.8 g

(c) 21.6 g (d) 108 g

Solution (b) $w = \frac{E.Q.}{96500} = \frac{108 \times 9650}{96500} = 10.8$ g

20. Aluminium oxide may be electrolysed at 1000°C to furnish Al metal (at. mass = 27 amu). The cathode reaction is: $Al^{3+} + 3e \longrightarrow Al$ **[AIEEE-2005]**

How much electricity is required to prepare 5.12 kg of Al by this method?

(a) 5.49×10^7 coulomb (b) 1.83×10^7 coulomb

(c) 5.49×10^4 coulomb (d) 5.49×10^{10} coulomb

Solution (a) $w = \frac{E.Q.}{96500}$ $\quad 5.12 \times 10^3 = \frac{27 \times Q}{3 \times 96500}$ $\quad \therefore Q = 5.49 \times 10^7$ C

21. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol^{-1}) **[IIT-2008]**

(a) 9.65×10^4 sec (b) 19.3×10^4 sec

(c) 28.95×10^4 sec (d) 38.6×10^4 sec

Solution (b) 0.01 mol of H_2 gas $\equiv 0.01 \times 2$ equiv H^+

$\therefore$ Current required $0.01 \times 2 \times 96500$ C

$$0.01 \times 2 \times 96500 = 10^{-3} \times 10 \times t$$

$$t = \frac{0.01 \times 2 \times 96500}{0.01} = 19.3 \times 10^4 \text{ s}$$

Galvanic cell

A **Galvanic cell**, named after Luigi Galvani, is an electrochemical cell that derives electrical energy from chemical reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane. It is sometimes called a "Voltaic cell", after Alessandro Volta, inventor of the voltaic pile, the first electrical battery. In common usage, the word "battery" has come to include a single Galvanic cell, but a battery properly consists of multiple cells.[1][2]

A Galvanic cell is a device capable of either deriving electrical energy from chemical reactions, or facilitating chemical reactions through the introduction of electrical energy. A common example of an electrochemical cell is a standard 1.5-volt "battery". (Actually, a single "Galvanic cell"; a battery properly consists of multiple cells.)

Half-cells

An electrochemical cell consists of two half-cells. Each *half-cell* consists of an electrode, and an electrolyte. The two half-cells may use the same electrolyte, or they may use different electrolytes. The chemical reactions in the cell may involve the electrolyte, the electrodes or an external substance (as in fuel cells which may use hydrogen gas as a reactant). In a full electrochemical cell, species from one half-cell lose electrons (oxidation) to their electrode while species from the other half-cell gain electrons (reduction) from their electrode. A *salt bridge* is often employed to provide ionic contact between two half-cells with different electrolytes—to prevent the solutions from mixing and causing unwanted side reactions. This can simply be a strip of filter paper soaked in saturated potassium nitrate solution. Other devices for achieving separation of solutions are porous pots and gelled solutions.

A standard half cell, used in electrochemistry, consists of a metal electrode in a 1 molar (1 mol/L) aqueous solution of the metal's salt, at 298 kelvin (25°C). The electrochemical series, which consists of standard electrode potentials and is closely related to the reactivity series, was generated by measuring the difference in potential between the metal half cell in a circuit with a standard hydrogen half cell, connected by a salt bridge.

The standard hydrogen half cell:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

The half cells of a Daniell cell:

Original equation,

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Half cell (anode) of Zn

$$Zn \rightarrow Zn^{2+} + 2e^-$$

Half cell (cathode) of Cu

$$Cu^{2+} + 2e^- \rightarrow Cu$$

IUPAC representation of galvanic cell

Direction of chemical change,

The galvanic cell mentioned above is represented in a short IUPAC cell notation as follows:

$$\underbrace{Zn \mid ZnSO_4 (C_1)}_{\text{Anode}} \,\|\, \underbrace{CuSO_4 \mid Cu\ (C_2)}_{\text{Cathode}}$$

Because SO_4^{2-} does not participate in the redox changes it can be represented as:

$$Zn(s) \mid Zn^{2+}(C_1) \,\|\, Cu^{2+}(C_2) \mid Cu(s)$$

Oxidation Reduction

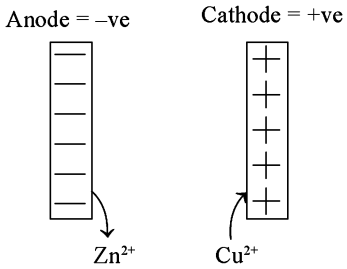
(i) Electrodes must be placed at the extreme ends of the representation
(ii) L.H.S of represents the anode where as RHS represents the cathode
R.H.S = Cathode = Reduction
(iii) Normally, cathode and anode are separated by a double slash (||) which represents the salt bridge (it is not necessary to be present)
(iv) The different components involved in half cell reaction are generally separated by a single slash when their phases are different. This single slash is called phase bar. If the physical states are same, comma(,) is used in classmate place of phase bar.
(v) Tthe electrolyte of the anode and cathode should be written with concentration. In this case, it is $ZnSO_4$ with concentration as C_1 and $CuSO_4$ with its concentration which is C_2. In case of the gas, its partial pressure is mentioned.

To represent the galvanic cell we need to be familiar with the types of half cells.

Types of Half Cell

1. *Metal Metal ion half cell*

The metallic rod is immersed in a solution containing own ion.



Elemental solid involved in half cell reaction generally forms the electrode.
An example of this is a metallic silver electrode in an $AgNO_3$ solution. The electrode is represented as $Ag \mid Ag^+$ (c) and the electrode reaction is $Ag^+ + e^- \rightarrow Ag$.

Note: Very active metals react directly with water itself and cannot be used for such electrodes.
The half cell reaction only involves the metal and the metal ion.

Example:

$Zn \rightarrow Zn^{2+} + 2e^-$ representation: Zn/Zn^{2+}

$Cu^{2+} + 2e^- \rightarrow Cu$ representation: Zn/Zn^{2+}

(iv) Amalgam Electrode: In a variation of the previous electrode, the metal is in the form of an amalgam, i.e., it is dissolved in mercury, rather than in the pure form. Electrical contact is made by a Pt wire dipping into the amalgam pool. The reaction is the same as in the metal–metal ion electrode, with the Hg playing no role. A sodium amalgam electrode is represented as,

Na [in Hg at C_1] | Na^+ (C_2).

(v) ***Metal Insoluble Salt Electrode:*** An example of this is $Ag \mid AgCl \mid Cl^-(C)$. The electrode process at such an electrode is,

$AgCl\ (s) \rightarrow Ag^+ + Cl^-$, $Ag^+ + e^- \rightarrow Ag.$, overall reaction is,

$AgCl\ (s) + e^- \rightarrow Ag + Cl^-$

The electrode reaction involves only the concentration of Cl^- as a as a variable in contrast with the $Ag \mid Ag^+$ electrode which has the Ag^+ concentration as the variable.

The most frequently used electrode of this type is the **calomel electrode** which consists of metallic Hg in contact with a chloride solution (fig 9.6) The electrode reaction is,

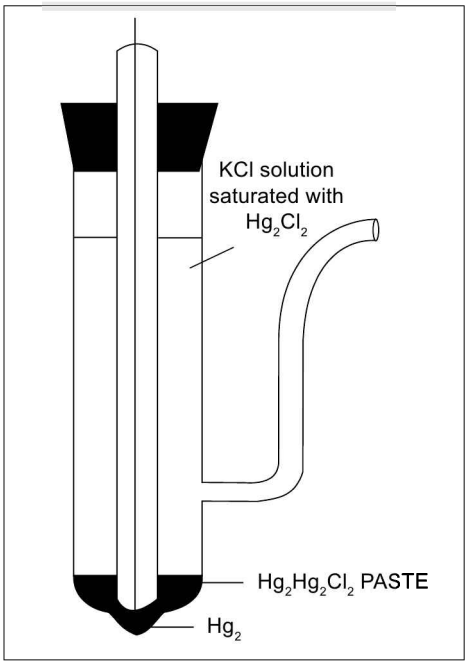


Fig. 9.6

$$\frac{1}{2}\,Hg_2Cl_2 \rightleftharpoons Hg^+ + Cl$$

$$Hg^+ + e^- \rightleftharpoons Hg$$

Overall reaction is,

$$\frac{1}{2}\,Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$$

The electrode is generally made with a chloride solution of 0.1 M, 1M, or saturated KCl. The saturated calomel electrode is the most common.

The calomel electrode is represented as Cl^- (1M) | Hg_2Cl_2, Hg.

2. *Gas ion half cell*

The gas and its ion (anion or cation) are involved in the half cell reaction. The gas can be introduced or the gas is evolved at the electrode. Let us consider the following reaction:

$$H_2(g) \xrightarrow[\text{anode}]{\text{oxidation}} 2H^+ + 2e^-$$

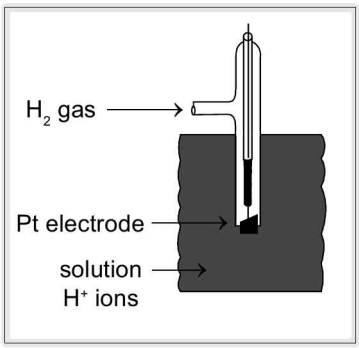


Fig. 9.7

The electrode is such that, on the surface of the inert metal (platinum) electrode, the reagent H_2 (which is being forced into the solution with the pressure), the H^+ ions go into the solution leaving the electrons on the electrode. Hence, the electrode becomes negatively charged and it is the anode. (note the reaction is oxidation)

The electrode assembly is written as Pt | H_2 (1 atm) | H^+ (1M).

To represent the gas ion electrode platinum or any inert metal is taken as the default electrode.

Let us consider one more reaction,

$$2e^- + Cl_2 \xrightarrow{\text{Reduction}} 2Cl^- (aq)$$

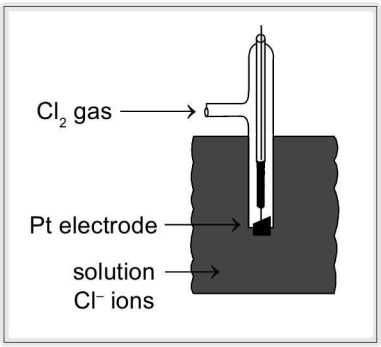


Fig. 9.8

The electrode is such that, on the surface of the inert metal (platinum) electrode, the reagent Cl_2 (which is being forced into the solution with the pressure), the electrons are taken up from the electrodes making the electrode positively charged. Since the process is reduction, the positively charged electrode is cathode. The Cl^- ions produced go into the solution.

If we combine the above two gas ion half cells, the following cell can be made,

$$Pt|H_2(g) \mid H^+ \| Cl^-(aq) \mid Cl_2 \mid Pt$$

or $Pt(H_2) \mid H^+ \| Cl^-(aq)(Cl_2)| Pt$

oxidation reduction

bracket because

H_2 gets adsorbed in it

The representation of cell does not necessarily correspond to direction of chemical change

This is not the direction of chemical change because the R.H.S. of the representation is the cathode and the reaction must represent reduction

oxidation ?

$$Pt \mid H_2(g)| H^+ \| Cl^-(aq) \mid Cl_2 \mid Pt$$

3. *Redox half cell*

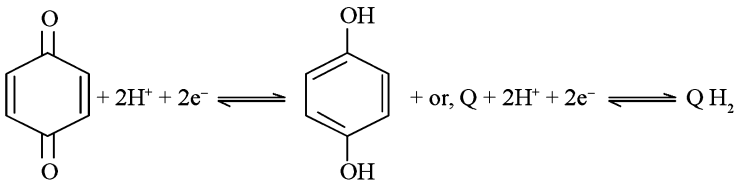
When Both reduced and oxidized states or parts are in ionic form the half cell is called redox half cell.

To represent redox half cell we have to use inert electrode such as platinum.

(i) ***Ferrous–Ferric Electrode:*** An example is a Pt wire dipping in a solution containing ferrous and ferric ions. Such a cell is described as: Pt | Fe^{2+} (C_1), Fe^{3+} (C_2). The comma is used to separate two chemical species in the same solution. The electrode reaction is,

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

(ii) ***Quin–Hydrone Electrode:*** Oxidation reduction electrodes can also be made with organic molecules that can exist in two different oxidation states. A generally used material of this type is related to important biochemical oxidation–reduction reactions, is the system of hydroquinone, which can form the oxidation reduction system, between quinone (Q) and hydroquinone (QH_2).



The presence of a Pt electrode in a solution containing these two species again clearly provides an electrode that can donate or accept electrons. If hydro-quinone is represented by QH_2 and quinone by Q, the electrode is abbreviated as Pt.|QH_2,Q,H^+ (C)

This electrode is called a quin-hydrone electrode, because of the charged complex that is formed between QH_2 and Q.

$$Fe^{2+}(aq) \xrightarrow[\text{anode}]{\text{Oxidation}} Fe^{3+} + e^- \ldots\ldots\ldots \text{representation: } Pt|Fe^{2+}(aq), Fe^{3+}(aq)$$

$$MnO_4^- + 8H^+ + 5e^- \xrightarrow[\text{Cathode}]{\text{Reduction}} Mn^{2+} + 4H_2O \ldots\ldots\ldots \text{representation: } Mn^{2+}, H^+, MnO_4^- \mid Pt$$

If we combine two above half cell we get theceel as follows:

$$Pt|Fe^{2+}(aq), Fe^{3+}(aq) \parallel Mn^{2+}, H^+, MnO_4^- \mid Pt$$

(Stoichiometry coefficient is never present in representation of half cell

Do it yourself

Type III Representation of Galvanic Cell

1. Represent the cell from the following cell reaction.

   $H_2(g) + Cl_2(g) \rightarrow Cl_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq)$

   Solution $Pt|H_2(g)|H^+||Cl^-|Cl_2(g)|Pt$

2. Represent the cell from the following cell reaction.

   $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \uparrow$

   $Zn(s)|Zn^{2+}(aq)||H^+|H_2|Pt$

3. Write down the cell reaction from the following cell representation.

   $Pt \mid Cl_2(g) \mid Cl^-(aq) \parallel Cu^{2+} \mid Cu(s)$

   $Cl_2 + 2e^- \rightarrow Cl^-$

   $Cu + 2e \rightarrow Cu^{2+} + 2e^-$

   $Cu + Cl_2 \rightarrow Cu^{2+} + 2Cl^-$

4. For the galvanic cell:

$Pt(s) \mid Fe^{2+}, Fe^{3+} \parallel Fe^{2+} \mid Fe$

cell reaction is:

(a) $3Fe^{3+} + Fe \rightarrow 2Fe^{3+}$ (b) $3Fe^{2+} \rightarrow Fe + 2Fe^{3+}$

(c) $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$ (d) none of the above

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Fe^{2+} + 2e^- \rightarrow Fe(s)$

$3Fe^{2+} \rightarrow 2Fe^{3+} + Fe(s)$

Relation between chemical energy and Electrical Energy (work done)

We know,

ΔG = change in Gibbs energy (chemical energy) associated with the chemical reactions.

Electrical work done at e.m.f.(electro motive force) 'E' is given by,

$W_{electrical}$ = charge × potential difference

(Joules) = charge × e.m.f

= (nF) × E (n = number of moles of electrons transferred in the reaction

F = Faraday of charge

= 96500 C)

Now from the conservation of energy we get,

$\Delta G + nFE = 0$ (net energy change is Zero)

$\Rightarrow \Delta G = -nFE$

For spontaneous process, ΔG = –ve $\Rightarrow$ E = +ve

The greater the positive value the more spontaneous is the reaction

For non spontaneous change $\Rightarrow \Delta G$ = +ve $\Rightarrow$ E = –ve

The greater the negative value, the more non spontaneous is the reaction

$\Delta G = -nFE$

↓ ↓ ↓

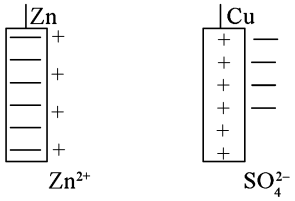
(joules) (coulombs) (volts)

This equation is applicable to individual half cell reaction as well as overall cell reaction.

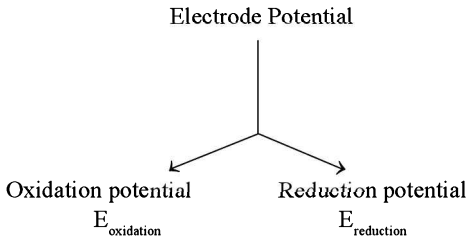
We will frequently use the word 'e.m.f' of a reaction' which means the e.m.f that could have developed when ΔG associated with that reaction is converted to electrical work.

Half cell emf

The half cell emf or electrode potential is develops due to the potential difference between the double layer formed in the half cell.



The electrode potential can be of two types:



$E_{Zn|Zn^{2+}}$ → Here left to right the suffix represents the direction of chemical changes from left to right

example, $E_{Zn|Zn^{2+}}$ is the e.m.f. for the reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

since the reaction is oxidation, it is called oxidation potential.

$E_{Zn|Zn^{2+}}$ → Reduction potential

$E_{Zn|Zn^{2+}}$ → Reduction potential

E↑ ΔG↓ [The greater the positive value of e.m.f. the more negative is the free energy
+ve –ve change and more spontaneous in the reaction]

- Greater value of oxidation potential represents greater tendency to be oxidized (means it is a strong reducing agent).
- The greater the reduction potential, the greater the tendency to be reduced (means it is a strong oxidizing agent).
- Stronger oxidizing agents have high reduction potential.
- Stronger reducing agents have high oxidizing potential.
- **The term 'Electrode potential' is used to represent reduction potential**

Judging the oxidizing or reducing ability from E° values

The more negative the E° (electrode potential ⇒ reduction potential) value, the more the position of equilibrium lies to the left, the more readily the metal loses electrons. The more negative the value, the stronger reducing agent the metal is.

The more positive the E°(electrode potential ⇒ reduction potential) value, the more the position of equilibrium lies to the right-the less readily the metal loses electrons, and the more readily its ions pick them up again. The more positive the value, the stronger oxidizing agent the metal ion is.

Factors on which emf (and consequently ΔG) depends→

(i) nature of reaction
(ii) concentration of ions
and pressure of gases.
The condition in which reaction also effect emf.
(iii) temperature
When condition (ii) and (iii) are fixed up it will depend only on nature of reaction. It will fixed for a given reaction and different for different reaction.

SATP (Standard Ambient Temperature And Pressure)

The values are for the following conditions:

- the temperature of 298.15 K (25 °C);
- the effective concentration of 1 mol/L for each aqueous species or a species in a mercury amalgam;

- the partial pressure of 101.325 kPa (absolute) (1 atm, 1.01325 bar) for each gaseous reagent. This pressure is used because most literature data are still given for this value rather than for the current standard of 100 kPa.
- the activity of unity for each pure solid, pure liquid, or for water (solvent).

$$H_2(1\ atm) \rightarrow 2H^+(1\ M) + 2e^-$$

This reaction is under standard state, then corresponding e.m.f is known as standard e.m.f and it is represented as E^o

E^o is constant for a given reaction but different for different reactions.

For example, when the following reaction takes place under standard state, the corresponding standard e.m.f. is 0.74 V.

$$Zn(s) \rightarrow Zn^{2+}(1M) + 2e^- \ldots\ldots\ldots\ldots E^o_{Zn|Zn^{2+}} = 0.74\ V$$

$$\Delta G \propto n \Rightarrow \frac{\Delta G}{n} = \text{constant} = -FE$$

Since 'E' belongs to the proportionality constant, it has to be independent of 'n'. Hence, e.m.f. 'E' is an intensive property.

Hence, emf is an intensive property and it does not depend on stoichiomeric coefficient

To know how we measure standard electrode, we need to know about **The standard hydrogen electrode first**

The standard hydrogen electrode

The S.H.E. consists of hydrogen gas bubbling over a platinum electrode immersed in a solution of hydrochloric acid (Figure 9.9). At standard conditions, the hydrogen must be at a pressure of 1 atm (101.325kPa) and the acid must be 1 mol dm^{-3} in concentration. (Strictly, the acid should be at unit activity, which is approximately 1.18 mol dm^{-3}, but we can ignore the difference.) The temperature should be 25°C (298 K). The platinum electrode is usually coated with finely divided platinum called platinum black. This acts as a catalyst to allow equilibrium between the gas and the solution to be established quickly.

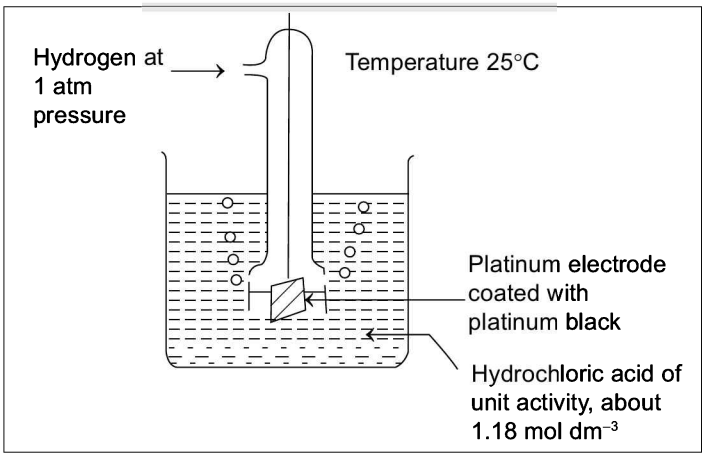


Fig. 9.9 A standard hydrogen electrode (S.H.E.)

The reaction that takes place in the S.H.E. is,

$$2^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

Under standard conditions the electromotive force, e.m.f., of the S.H.E. is defined to be exactly zero volts. A standard e.m.f. is given the symbol E^0, so we have,

$$E^0_{S.H.E.} = 0.000\ V$$

The more systematic way of writing this is to put

$$E^{0}_{S.H.E.} = 0.000 \text{ V}$$

A note on the hydrogen value

Remember that each E° value shows whether the position of the equilibrium lies to the left or right of the hydrogen equilibrium.

That difference in the positions of equilibrium causes the number of electrons which build up on the metal electrode and the platinum of the hydrogen electrode to be different. That produces a potential difference which is measured as a voltage.

Obviously, if you connect one standard hydrogen electrode to another one, there will be no difference whatsoever between the positions of the two equilibria. The number of electrons built up on each electrode will be identical and so there will be a potential difference of zero between them.

Standard electrode potentials

Having established our standard, we can connect metal electrodes to the S.H.E. and measure the voltage between the two. Figure 9.10 shows an arrangement using a zinc electrode.

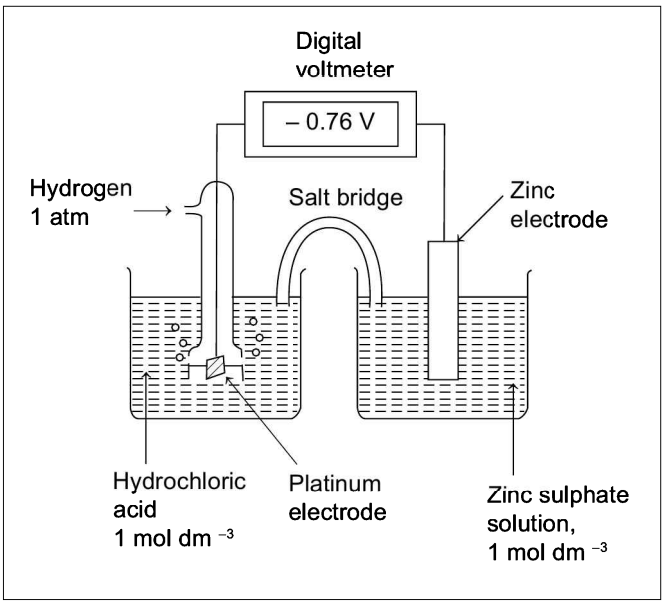


Fig. 9.10 An apparatus to measure the standard electrode potential of zinc

For accurate work, the solution should have an activity of 1, rather than a concentration of 1 mol dm^{-3}. The temperature should be 25° C. It is not essential to use a digital voltmeter, but the meter must have a very high resistance.

At standard conditions, the zinc should be dipping into a 1 mol dm^{-3} solution of the zinc ions. (Strictly the solution should have an activity of 1. Using activities makes an allowance for the way ions influence each other in solution.) The entire arrangement makes up an electrochemical cell, with the S.H.E. making one half-cell, and the zinc in a solution of zinc ions the other half-cell. The two half-cells are connected by a salt bridge. A typical salt bridge is made by dissolving an ionic substance such as potassium chloride in agar. The warm agar is used to fill a U-tube and when it cools it sets to a jelly. The charge on the potassium and chloride ions provides electrical contact between the two half-cells. We shall say more about salt bridges a little later.

Now, we have another convention that you must know. It is we define the e.m.f. of a combination of two half-cells to be the difference between the e.m.f. of the half-cell on the right-hand side minus the e.m.f. of the half-cell on the left-hand side, i.e.,

$$E^{\circ}_{cell} = E^{\circ}_{right} - E^{\circ}_{left}$$

A S.H.E. is always used as the left-hand half-cell. In this case, we have

$$E^\circ_{cell} = E^\circ_{Zn2+/Zn} - E^\circ_{H+/H2}$$

So,

$$E^\circ_{cell} = E^\circ_{Zn2+/Zn}$$

Because, $E^\circ_{H+/H2} = 0$ V by definitio

If you were to perform this experiment you would discover that the voltmeter would only give a reading if its negative terminal (the black coloured one) was connected to the zinc. This means that the zinc is negative compared to the S.H.E. Indeed, you should find that Eln2+/zn = –0.76V. This figure is known as the standard electrode potential of zinc.

The standard electrode potential of many other half-cells can be measured in a similar way. A cell is made up with the metal dipping into a 1 mol dm^{-3} solution of its ions and connected to a S.H.E.

The more negative the value of the standard electrode potential, the greater is the tendency for a metal to give up its electrons, and the stronger is its reducing power. Conversely, the more positive the value of E°, the greater is the oxidising power.

Type III emf is an intensive property but ΔG is an extensive property (Relating standard emf of various half cell reactions.)

Example $Cu^{2+} + e^- \rightarrow Cu^+$ …… $E^o = 0.15$ V

$Cu^+ + e^- \rightarrow Cu(s)$ …… $E^o = 0.5$ V

Calculate $E^\circ_{Cu^{2+}/Cu}$

Solution $Cu^{2+} + e^- \rightarrow Cu^+$ $\quad E^\circ_1 = 0.15$ V

$Cu^+ + e^- \rightarrow Cu(s)$ $\quad E^\circ_2 = 0.5$ V

$Cu^{2+} + 2e^- \rightarrow Cu$ $\quad E^\circ_3 \neq (0.15+0.5)$V

$\neq 0.65$ V**(Wrong)**

Extensive properties are additive but intensive properties are not additive.

$$\Delta G^\circ_1 = -1 \times F \times E^\circ_1$$

$$\Delta G^\circ_2 = 1 \times F \times E^\circ_2$$

$$\Delta G_3 = -2 \times F \times E^\circ_3$$

$$\Delta G^\circ_1 + \Delta G^\circ_2 = \Delta G^\circ_3$$

$$E^\circ_1 = E^\circ_2 = 2E^\circ_3$$

$$E^\circ_3 = 0.325 \text{ V}$$

Prove: $E^\circ_{Fe^{3+}|Fe^{2+}} = 3E^\circ_{Fe^{3+}|Fe} - 2E^\circ_{Fe^{2+}|Fe}$

Example $Fe^{3+} + 3e^- \rightarrow Fe(s)$ …… $3E^\circ_{Fe^{3+}|Fe}$

$Fe(s) \rightarrow Fe^{2+} + 2e$…… $2E^\circ_{Fe|Fe^{2+}} = -2E_{Fe^{2+}}$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ …… $E^\circ_{Fe^{3+}|Fe^{2+}} = 3E^\circ_{Fe^{3+}|Fe} - 2E^\circ_{Fe^{2+}|Fe}$

Standard emf for cell reaction E°_{cell}:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \ldots\ldots E^{\circ}_{Zn|Zn^{2+}} \qquad (n = 2)$$

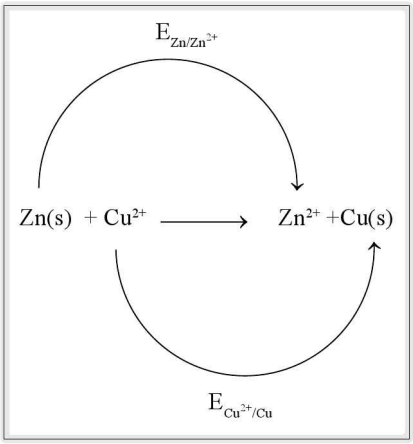
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \ldots\ldots\ldots E^{\circ}_{Cu^{2+}|Cu} \qquad (n = 2)$$

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu \ldots\ldots E^{\circ}_{cell} \qquad (n = 2)$$

(Calculate the total change in oxidation number for oxidizing/reducing agent to get the vale of 'n')

$$\Delta G^{\circ}_{cell} = -nFE^{\circ}$$

The number of moles of e^{-} (n) for the cell reaction is same to that of the half cell reactions.

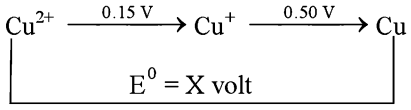


To write down the cell e.m.f. we can simply go with the direction of chemical change i.e., $E_{reactant/product}$ for the half cell reactions and add them to get the cell e.m.f.

$$E^{\circ}_{cell} = E^{\circ}_{Zn|Zn^{2+}} + E^{\circ}_{Cu^{2+}|Cu}$$

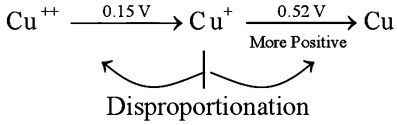
Worked-out Example

22. The reduction potential for Cu in acid solution is,



Calculate X. Does Cu^{+} disproportionate in solution?

If intermediate oxidation state is stronger oxidizing agent then next higher oxidation state, than that eintermediate oxidation state will undergo disproportion.



Solution $Cu^{2+} + e \longrightarrow Cu^{2+}$ $E^0_1 = 0.15V$ ΔG_1^0 ... (1)

$Cu^+ + e \longrightarrow Cu$ $E_2^0 = 0.5V$ ΔG_2^0 ... (2)

$Cu^{2+} + 2e \longrightarrow Cu$ $E_3^0 = ?$ ΔG_3^0 ... (3)

$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0 \Rightarrow 2 \times E_3^0 \times F = -1 \times 0.15 \times F + (1 \times 0.5 \times F)$

$$\Rightarrow E_3^0 = \frac{-0.65F}{-2F} = 0.325 \text{ volt}$$

$\therefore$ X = 0.3225 V

For disproportionation

$Cu^+ \longrightarrow Cu^+ + e$ $E^0_{OP} = -0.15$ V

$Cu^+ + e \longrightarrow Cu$ $E^0_{RP} = 0.50$ V

$2Cu^+ \longrightarrow Cu^{2+} + Cu$ $E^0 = 0.15 + 0.5$

$\therefore$ $E^0 + E^0_{Cu^+/Cu^{2+}} = E^0_{Cu^+/Cu} = -0.15 + 0.5 = 0.35V$

Electrochemical series

1. The standard reduction potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing or decreasing order of their reduction potentials. The arrangement of elements in order of increasing reduction potential values is called ***electrochemical series***. It is also called ***activity series***, of some typical electrodes.
2. **Characteristics of electrochemical series** Metals at the top of the series are good at giving away electrons. They are good reducing agents. The reducing ability of the metal increases as you go up the series.

   Metal ions at the bottom of the series are good at picking up electrons. They are good oxidizing agents. The oxidizing ability of the metal ions increases as you go down the series.

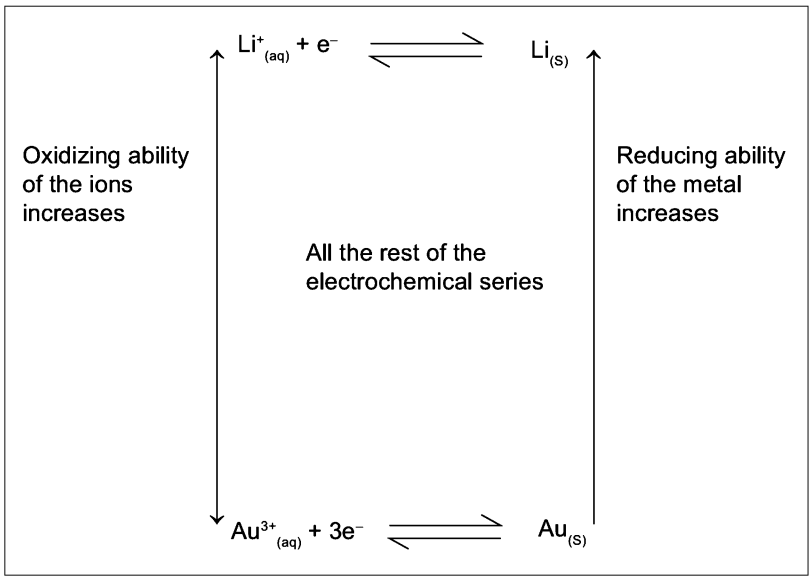


Fig. 9.11

(i) The negative sign of standard reduction potential indicates that an electrode when joined with *SHE* acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is –0.76 *volt*, When zinc electrode is joined with SHE, it acts as anode (*–ve* electrode) i.e., oxidation occurs on this electrode. Similarly, the *+ve* sign of standard reduction potential indicates that the electrode when joined with *SHE* acts as cathode and reduction occurs on this electrode.

(ii) The substances, which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances, which are stronger oxidizing agents than H^+ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative value of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

Standard reduction electrode potentials at 298K

Element	*Electrode Reaction (Reduction)*	Standard Electrode Reduction potential E^0, volt
Li	$Li^+ + e^- = Li$	–3.05
K	$K^+ + e^- = K$	–2.925
Ba	$Ba^{++} + 2e = Ba$	–2.90
Sr	$Sr^{++} + 2e = Sr$	–2.89
Ca	$Ca^{2+} + 2e^- = Ca$	–2.87
Na	$Na^+ + e^- = Na$	–2.714
Mg	$Mg^{2+} + 2e^- = Mg$	–2.37
Al	$Al^{3+} + 3e^- = Al$	–1.66
Mn	$Mn^{++} + 2e = Mn$	–1.18
Zn	$Zn^{2+} + 2e^- = Zn$	–0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	–0.74
Fe	$Fe^{2+} + 2e^- = Fe$	–0.44
Cd	$Cd^{2+} + 2e^- = Cd$	–0.403
Co	$Co^{++} + 2e = Co$	–0.27
Ni	$Ni^{2+} + 2e^- = Ni$	–0.25
Sn	$Sn^{2+} + 2e^- = Sn$	–0.14
Pb	$Pb^{++} + 2e = Pb$	–0.12
H_2	$2H^+ + 2e^- = H_2$	**0.00**
Cu	$Cu^{2+} + 2e^- = Cu$	+0.337
I_2	$I_2 + 2e^- = 2I^-$	+0.535
Hg	$Hg^{2+} + 2e^- = Hg$	+0.885
Ag	$Ag^+ + e^- = Ag$	+0.799
Br_2	$Br_2 + 2e^- = 2Br^-$	+1.08
Pt	$Pt^{++} + 2e = Pt$	+1.20
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- = Au$	+1.50
F_2	$F_2 + 2e^- = 2F^-$	+2.87

Increasing tendency to accept electrons Increasing strength as oxidising agent

Increasing strength as reducing agent Increasing tendency to lose electrons

3. **Application of Electrochemical series**

(i) ***Reactivity of metals***: The activity of the metal depends on its tendency to lose electron or electrons, i.e., tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active. The *chemical reactivity of metals decreases from top to bottom in the series*. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like *Fe*, *Pb*, *Sn*, *Ni*, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like *Cu*, *Ag* and *Au* which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) ***Electropositive character of metals:*** The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups:

(a) *Strongly electropositive metals:* Metals having standard reduction potential near about – 2.0 *volt* or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) *Moderately electropositive metals*: Metals having values of reduction potentials between 0.0 and about–2.0 *volt* are moderately electropositive *Al*, *Zn*, *Fe*, *Ni, Co*, etc., belong to this group.

(c) *Weakly electropositive*: The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. *Cu*, *Hg, Ag*, etc., belong to this group.

(iii) ***Displacement reactions***

(a) *To predict whether a given metal will displace another, from its salt solution*: A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., The metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) *Displacement of one nonmetal from its salt solution by another non-metal*: A non-metal higher in the series (towards bottom side), i.e., having high value of reduction potential will displace another non-metal with lower reduction potential, i.e., occupying position above in the series. The non-metal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the nonmetal having low value of reduction potential. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.

$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$

$$2I^- \rightarrow I_2 + 2e^- \quad \text{.....(Oxidation)}$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \quad \text{.....(Reduction)}$$

[*The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.*]

(c) *Displacement of hydrogen from dilute acids by metals:* The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.

$$Mn \rightarrow Mn^{n+} + ne^- \quad \text{.....(Oxidation)}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{.....(Reduction)}$$

The metal having negative values of reduction potential possess the property of losing electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.

The metals which are below hydrogen in electrochemical series like *Cu, Hg, Au, Pt,* etc., do not evolve hydrogen from dilute acids.

(d) *Displacement of hydrogen from water:* Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series. Alkali and alkaline earth metals liberate hydrogen from cold water but *Mg*, *Zn* and *Fe* liberate hydrogen from hot water or steam.

(iv) ***Reducing power of metals***: Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. Thus reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases, as the standard reduction potential becomes more and more negative. Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron. (decreasing order of reducing nature)

Element:	Na	>	Zn	>	Fe
Reduction potential:	−2.71		−0.76		−0.44

Alkali and alkaline earth metals are strong reducing agents.

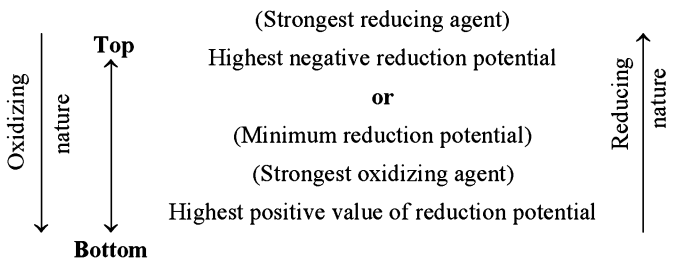
(v) ***Oxidizing nature of non-metals***: Oxidizing nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. Thus, oxidizing nature increases from top to bottom in the electrochemical series. The strength of an oxidizing agent increases as the value of reduction potential becomes more and more positive.

F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2, Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2.

Element:	I_2	Br_2	Cl_2	F_2
Reduction potential:	+0.53	+1.06	+1.36	+2.85

Oxidizing nature increases →

Thus, in an ***electrochemical series,***



(vi) ***Thermal stability of metallic oxides:*** The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction

potentials are not stable towards heat. The metals which come below copper form unstable oxides, i.e., these are decomposed on heating.

$$Ag_2O \xrightarrow{\Delta} 2Ag + \frac{1}{2}O_2$$

$$2HgO \xrightarrow{\Delta} 2Hg + O_2;\ \left.\begin{matrix} BaO \\ Na_2O \\ Al_2O_3 \end{matrix}\right] \xrightarrow{\Delta} \text{No decomposition}$$

(vii) ***Extraction of metals***: A more electropositive metal can displace a less electropositive metal from its salt's solution. This principle is applied for the extraction of *Ag* and *Au* by cyanide process. Silver from the solution containing sodium argento cyanide, $NaAg(CN)_2$, can be obtained by the addition of zinc as it is more electro-positive than Ag.

$$2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$$

Relation between E°_{cell} and K_{eq}

We have seen in the chemical equilibrium that,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

ΔG at equilibrium = 0 and Q= K_{eq}.

Hence it follows,

$$\Delta G^\circ = -RT \ln K_{eq}$$
$$\downarrow$$

Gibb's energy change when reaction occurs under standard state.

$$\Delta G^\circ = -RT \ln K_{eq} = -nFE^\circ$$

$$E^\circ = \left(\frac{RT}{F}\left(\frac{\ln K_{eq}}{n}\right)\right) \quad \text{(I)}$$

$$E^\circ = \left(\frac{2.303RT}{F}\right)\left(\frac{1}{n}\right) \log_{10} K_{eq}$$

$$\downarrow$$
volt

When E° increases K_{eq} increases.

Putting R = 8.314J/k$^-$/mole^{-1} T = 298K and F = 96500 Coulomb

$$E^\circ = \frac{0.0591}{n} \log_{10} K_{eq}$$

Reaction quotient has similar expression to that of equilibrium constant but the system may or may not be at equilibrium.

Case I: In standard state

$$Q = 1$$

$$E = E^\circ$$

Case II: At equilibrium $\Delta G = nFE$

$$E = 0$$

$$E^\circ = \frac{0.0591}{n} \log_{10} K_{eq}$$

Nature of cell reaction	*ΔG°*	*Equilibrium constant*	*E°_{cell}*
Spontaneous	(–)	>1	(+)
At equilibrium	0	1	0
Non-spontaneous	(+)	<1	(–)

Type IV Evaluation of Equilibrium constant

Example $AgCl + e^- \rightarrow Ag + Cl^-$ $\quad E^\circ = 0.08$ V

$E^\circ_{Ag^+|Ag} = 0.8$ V

Calculate K_{sp}

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ ..... $E^\circ = 0.08$ V

$Ag \rightarrow Ag^+ + e^-$ ..... $E^\circ_{Ag|Ag^+} = E_{Ag^+|Ag} = 0.8$ V

$AgCl \rightleftharpoons Ag^+(aq) + Cl^-(aq)$..... K_{eq}

$$E^\circ_3 = \frac{0.06}{n} \log_{10} K_{eq}.$$

$$0.08 - 0.8 = E^\circ_1 + E^\circ_2 = 0.06 \log_{10} K_{sp}$$

$$--\frac{0.72}{0.06} = \log_{10} K_{sp}$$

$$\log_{10} K_{sp} = -12$$

$$K_{sp} = 10^{-12}$$

Example **Formation constant of complex ion**

It is the equilibrium constant when one mole of the complex ion is formed from the assembly of its constituent ions and molecules.

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$ ..... K_f = formation constant

$$\text{Formation constant } K_f = \frac{1}{\text{dissociation constant}(K_D)}$$

Higher value of K_f, more is the stability of corresponding complex ion



Worked-out Examples

23. Calculate K_f

$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2NH_3 \qquad E^\circ = -0.15\ V$$

$$Ag \longrightarrow Ag^+ + e^- \qquad E^\circ = -0.8\ V$$

$$Ag(NH_3)_2^+ \longrightarrow Ag^+ + 2NH_3 \qquad E^\circ = -2.96\ V$$

$$\therefore\ Ag^+ + 2NH_3 \longrightarrow Ag(NH_3)_2^+ \qquad E^\circ = 0.96\ V$$

$$E^\circ = \frac{0.06}{1} \log K_f = 0.96$$

$$\text{Log } K_f = 16$$

$$K_f = 10^{16}$$

24. For a cell reaction involving a two electron change, the standard e.m.f., of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be **[AIEEE-2003]**

(a) 1×10^{-10} (b) 29.5×10^{-2}

(c) 10 (d) 1×10^{10}

Solution (d) $E^\circ_{cell} = \frac{0.059}{n} \log K_c \quad 0.295 = \frac{0.059}{2} \log K_c$

$$0.295 = \frac{0.059}{2} \log K_c \qquad K_c = 1 \times 10^{10}$$

25. For the redox change;

$Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu_{(s)}$, taking place in a cell E°_{cell} is 1.10 volt. E_{cell} for the cell would be: **[AIEEE-2003]**

(a) 1.07 V (b) 0.82 V (c) 2.14 V (d) 180 V

Solution (a) $E = E^\circ_{cell} + \frac{0.059}{2} \log \left[\frac{Cu^{2+}}{Zn^{2+}}\right] = 1.10 + \frac{0.059}{2} \log \frac{0.1}{1} = 1.07\ V$

26. The standard emf of a cell having one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is **[AIEEE-2004]**

(a) 1.0×10^{30} (b) 1.0×10^{5}

(c) 1.0×10^{10} (d) 1.0×10^{1}

Solution (c) $E^\circ_{cell} = \frac{0.059}{1} \log K_c$

$$0.591 = \frac{0.059}{1} \log K_c \qquad \therefore K_c = 1 \times 10^{10}$$

27. A standard hydrogen electrode has zero electrode potential because **[IITJEE-1997]**

(a) hydrogen is easiest to oxidize

(b) this electrode potential is assumed to be zero

(c) hydrogen atom has only one electron

(d) hydrogen is the lighest element

Solution (b) By general convention, it is assumed that the standard electrode potential of hydrogen is zero.

Reduction Potential

28. The standard reduction potentials of $Cu^{2+} \mid Cu$ and $Cu^{2+} \mid Cu^{+}$ are 0.337 V and 0.153 respectively. The standard electrode potential of $Cu^{+} \mid Cu$ half cell is **[IIT-JEE-1997]**

(a) 0.184 V (b) 0.827 V

(c) 0.521V (d) 0.490 V.

29. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 MY^{-} and M Z^{-} at 25°C. If the reduction potential of Z > Y > X, then, **[IIT-JEE-1999]**

(a) Y will oxidize X and not Z

(b) Y will oxidize Z and not X

(c) Y will oxidize both X and Z

(d) Y will reduce both X and Z

Solution (c) We have

Half-cell	*Half-cell reaction*	$\Delta G^\circ = -nFE^\circ$
$Cu^{2+} \mid Cu$	$Cu^{2+} + 2e^{-} = Cu$	$\Delta G_1^\circ = -2FE^\circ_{Cu^{2+}\mid Cu}$
$Cu^{2+} \mid Cu^{+}$	$Cu^{2+} + e^{-} = Cu^{+}$	$\Delta G_2^\circ = -FE^\circ_{Cu^{2+}\mid Cu^{+}}$
$Cu^{+} \mid Cu$	$Cu^{+} + e^{-} = Cu$	$\Delta G_3^\circ = -FE^\circ_{Cu^{+}\mid Cu}$

From the half-cell reactions, it follows that

$$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$$

i.e., $-FE^\circ_{Cu^{2+}\mid Cu} = 2FE^\circ_{Cu^{2+}\mid Cu} - (-FE^\circ_{Cu^{2+}\mid Cu})$

or $E^\circ_{Cu^{+}\mid Cu} = 2E^\circ_{Cu^{2+}\mid Cu^{+}} - E^\circ_{Cu^{2+}\mid Cu^{+}}$

$= 2(0.337\ V) - 0.153\ V = 0.521\ V$

Solution (a) The given order of reduction potentials is Z > Y > X. A spontaneous reaction will have the following characteristics

Z reduced and Y oxidized Z reduced and X oxidized Y reduced and X oxidized

Hence, Y will oxidize X and not Z.

30. The standard reduction potential values of three metallic cations, X, Y and Z are 0.52, – 3.03 and –1.18 V respectively. The order of reducing power of the corresponding metals is **[IIT-JEE-1998]**

(a) Y > Z > X (b) X > Y > Z

(c) Z > Y > X (d) Z > X > Y

Solution (a) More negative or lower is the reduction potential, more is the reducing property. Thus the reducing power of the corresponding metal will follow the reverse order, i.e., Y > Z > X.

31. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below: **[IIT-JEE-2002]**

$Mn^{+}(aq.) + 8H^{+}(aq.) + 5e^{-} \rightarrow Mn^{2+}(aq.) + 4H_2O(l)$ $E^\circ = 1.51$ V

$Cr_2O_7^{2-}(aq.) + 14H^{+}(aq.) + 6e^{-} \rightarrow 2Cr^{3+}(aq.) + 7H_2O(l)$ $E^\circ = 1.38$ V

$Fe^{3+}(aq.) + e^{-} \rightarrow Fe^{2+}(aq.)$ $E^\circ = 0.77$ V

$Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq.)$ $E^\circ = 1.40$ V

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$.

(a) MnO_4^- can be used in aqueous HCl

(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(c) MnO_4^- can be used in aqueous H_2SO_4

(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

Solution (a) MnO_4^- will oxidize Cl^- ion according to the equation

$$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2 \uparrow$$

The cell corresponding to this reaction is as follows:

$$Pt, Cl_2(1\ atm) \mid Cl^- \parallel MnO_4^-, Mn^{2+}, H^+ \mid Pt$$

$$E^\circ_{cell} = 1.51 - 1.40 = 0.11\ V$$

E°_{etll} being +ve, ΔG° will be –ve and hence the above reaction is feasible. MnO_4^- will not only oxidize Fe^{2+} ion but also Cl^- ion simultaneously.

32. The more..... the standard reduction potential, the..... is its ability to displace hydrogen from acids.

Solution Negative, greater; Among the various metals, since sodium has the minimum reduction potential, it must be strongest reducing agent. In general, more the reduction potential lesser is its reducing action.

33. If Φ denotes standard reduction potential, which is true: **[AIEEE-2002]**

(a) $E^\circ_{cell} = \Phi_R - \Phi_L$ (b) $E^\circ_{cell} = \Phi_L + \Phi_R$

(c) $E^\circ_{cell} = \Phi_L - \Phi_R$ (d) $E^\circ_{cell} = -(\Phi_L + \Phi_R)$

Solution (a) $E^\circ_{cell} = E^\circ_{OP_L} + E^\circ_{RP_R} = -\Phi_L + \Phi_R$

34. Emf of a cell in terms of reduction potential of its left and right electrodes is:

[AIEEE-2002]

(a) $E = E_{left} - E_{right}$ (b) $E = E_{left} + E_{right}$

(c) $E = E_{right} - E_{left}$ (d) $E = -[E_{right} + E_{left}]$

Solution (c)

35. Standard reduction electrode potentials of three metals A, B and C are +0.5 V, –3.0 V and –1.2 V respectively. The reducing power of these metals are: **[AIEEE-2003]**

(a) B > C > A (b) A > B > C

(c) C > B > A (d) A > C > B

Solution (a) More is E°_{RP} more is oxidizing power or lesser is reducing power.

36. Consider the following E° values. $E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77$ V, $E^\circ_{Sn^{2+}/Sn} = -0.14$ V, The E°_{cell} for the reaction; $Sn_{(s)} + 2Fe^{3+}_{(aq.)} \longrightarrow 2Fe^{2+}_{(aq.)} + Sn^{2+}_{(aq.)}$ is: **[AIEEE-2004]**

(a) 0.63 V (b) 1.40 V

(c) 0.91 V (d) 1.68 V

Solution (c) $E^\circ_{cell} = E^\circ_{OPSn/Sn^{2+}} + E^\circ_{RP\ Fe^{3+}/Fe^{2+}} = 0.14 + 0.77 = 0.91$ V

37. The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co respectively. For which one of these metals, the change in oxidation state from +2 to +3 is the easiest? **[AIEEE-2003]**

(a) Co (b) Mn

(c) Fe (d) Cr

Solution (d) More is E°_{RP} more is the tendency to get reduced or lesser is tendency to get oxidized. $E^{\circ}_{RP\,Cr^{3+}/Cr^{2+}}$ is lowest or $E^{\circ}_{OP\,Cr^{2+}/Cr^{3+}}$ is maximum among all.

38. Given: $E^{\circ}_{Fe^{3+}/Fe} = -0.036V$, $E^{\circ}_{Fe^{3+}/Fe} = -0.439V$. The value of standard electrode potential for the change, $Fe^{2+}_{(aq)} + e^{-} \rightarrow Fe^{2+}(aq)$ will be: **[AIEEE-2009]**

(a) –0.072 V (b) 0.385 V
(c) 0.770 V (d) –0.270

Solution (c) $\because Fe^{3+} + 3e^{-} \rightarrow Fe;\ E^{\circ} = -0.036V$

$\therefore \quad \Delta G^{\circ}_{1} = -nFE^{\circ} = -3F(0.036)$

$= +0.108\ F$

Also $Fe^{2+} + 2e^{-} \rightarrow Fe;\ E^{\circ} = -0.439\ V$

$\therefore \quad \Delta G^{\circ}_{2} = -nFE^{\circ}$

$= -2\ F(-0.439)$

$= 0.878\ F$

To find E° for $Fe^{3+}_{(aq)} + e^{-} \rightarrow Fe^{2+}(aq)$

$\Delta G^{\circ} = -nFE^{\circ}$

$= -1FE^{\circ}$

$\because \quad G^{\circ} = G^{\circ}_{1} - G^{\circ}_{2}$

$\therefore \quad G^{\circ} = 0.\ 108F - 0.878F$

$\therefore \quad -Fe^{\circ} = +0.108F - 0.878F$

$\therefore \quad E^{\circ} = 0.878 - 0.108$

$= 0.77V$

39. For the reduction of NO_3^- ioin in an aqueous solution E is +0.96 V. Values of E° for some metal ions are given below:

$V^{2+}(aq) + 2e^{-} \rightarrow V \qquad E^{\circ} = -1.19V$

$Fe^{3+}(aq) + 3e^{-} \rightarrow Fe \qquad E^{\circ} = -0.04V$

$Au^{3+}(aq) + 3e^{-} \rightarrow Au \qquad E^{\circ} = +1.40V$

$Hg^{2+}(aq) + 2e^{-} \rightarrow Hg \qquad E^{\circ} = +0.86V$

The pair(s) of metals that is(are) oxidized by NO_3^- in aqueious solution is (are) **[IIT-2009]**

(a) V and Hg (b) Hg and Fe
(c) Fe and Au (d) Fe and V

Solution (a, b, d) NO_3^- ion will oxidise all those metal ions whose $E^{\circ}_{reduction}$ is less than 0.96V

40. For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$, $E^{\circ}M^+/M = 0.44V$ and $E^{\circ}(X/X^-) = 0.33$ V. From this data one can deduce that **[IIT-JEE-2000]**

(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction
(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction
(c) $E_{cell} = 0.77V$
(d) $E_{cell} = -0.77V$

Solution (b) For $M^+ + X^- \rightarrow M + X$, $E^{\circ}_{cell} = 0.44 - 0.33 = 0.11V$ is positive, hence the reaction is spontaneous.

Relation between actual EMF and standard EMF

The Nernst equation

Electrode potential depends upon the concentration of the species in solution, so also emf of a galvanic cell is controlled by the concentration of the ions. Nernst equation gives a relation between emf of a galvanic cell and the concentration of ions in solution. The equation is deduced as follows:

Let us consider a reversible reaction,

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

$$\text{Equilibrium constant } K = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}}$$

We know from thermodynamics that decrease of free energy (ΔG) measures the tendency of a chemical reaction to reach the equilibrium state.

If, G_1 = total free energy of the reactants and

G_2 = total free energy of the products, the

$\Delta G = G_2 - G_1$, If $G_1 > G_2$, then ΔG = negative

A negative ΔG of a reaction implies its spontaneity. ΔG is a measure of the ability of a system to do useful work. Since we can draw electricity from a galvanic cell, it implies that a spontaneous reaction is going on inside the cell and hence ΔG of such reaction must be negative. Electrical work is the result of the decrease of free energy of the cell reaction.

We know that, the electrical work obtained from any spontaneous reaction supplying nF coulomb of electricity at a potential E is given by,

Net electrical work = nFE

Again net electrical work = $-\Delta G$ (decrease of free energy)

$$\therefore \quad \Delta G = -nFE$$

Applying standard state,

$$\Delta G^{\circ} = -nFE^{\circ}$$

Again from thermodynamics, ΔG is related to K by the following equation:

$$\Delta G = \Delta G^{\circ} + RT \ln K$$

Substituting the value of ΔG,

$$-nFE = -nFE^{\circ} + RT \ln K$$

$$E = E^{\circ} - \frac{RT}{nF} \ln K$$

$$\text{(or)} \qquad E = E^{\circ} - \frac{RT}{nF} \ln \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \qquad \ldots \text{(i)}$$

Putting R = 8.314J/k^{-}/mole^{-1} T = 298K and F = 96500 Coulomb.

$$\text{We get, } E = E^{\circ} - \frac{0.059}{n} \log \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \qquad \ldots \text{(ii)}$$

This is the fundamental form of Nernst equation. Nernst equation is applicable to half cell emf as well as the overall cell emf.

Remember, emf increases when concentration of reactants are increased and it decreased when concentration of products is increased.

(i) If we represent an oxidation reaction as follows:

Reductant $\rightleftharpoons$ oxidant + ne

Here product is OX and reactant is Red.

$$\therefore \quad E = E° - \frac{0.059}{n} \log \frac{[OX]}{[Red]} \qquad \ldots (iii)$$

Equation (iii) is one from of Nernst equation. When [OX] = [Red], then E = E°. E° is called standard oxidation potential.

(ii) If we represent a reduction reaction in the following way,

oxidant + ne^- $\rightleftharpoons$ reductant

then by applying Nernst equation,

$$E = E° - \frac{0.059}{n} \log \frac{[Red]}{[OX]}$$

$$\text{(or) } E = E° + \frac{0.059}{n} \log \frac{[OX]}{[Red]} \qquad \text{---------- (iv)}$$

Equation (iv) is another form of Nernst equation.

Here also, when [OX] = [Red], E = E°. In this case, E° is called standard reduction potential.

(iii) Equation (iii) and (iv) are both infact, two forms of Nernst equation, but must be remembered that $E_{OX} = -E_{red}$, like $E^\circ_{OX} = -E^\circ_{red}$.

Type V Relation Between Actual EMF and E°

Example Calculate the oxidation potential developed when Zn rod is immersed in 0.1M solution of $ZnSO_4$.
Given: Electrode potential of Zn = –0.74 V

Solution Electrode potential of Zn represents the reduction potential $\Rightarrow E^\circ_{Zn^{2+}|Zn}$

$E_{Zn|Zn^{2+}} = 0.74$ V $\qquad [Zn^{2+}] = 0.1$ M

$E_{Zn^{2+}|Zn} = -0.74$ V

$Zn(s) \longrightarrow Zn^{2+}(0.1M) + 2e^- \ldots\ldots\ldots Q(Zn^{2+}) = 0.1$

$$E_{Zn|Zn^{2+}} = E^\circ_{Zn|Zn^{2+}} - \left(\frac{0.06}{2}\right) \log_{10}(0.1)$$

[For simple calculation we have taken 0.059≈0.06 might be costly sometimes)]

= (0.74 + 0.03) V

= 0.77 V

Example What pressure of has to be maintained over pure water so that electrode potential of H_2 electrode becomes zero? Also prove that e.m.f. does not depend on the stoichiometric coefficient

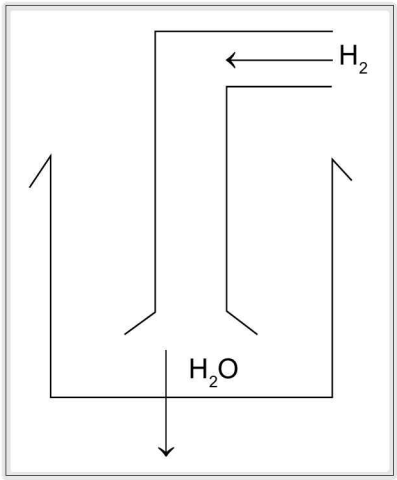


Fig. 9.12

Solution $[H^+] = 10^{-7}$ M

$$H_2(g) \rightarrow 2H^+ + 2e^- \quad \ldots. 1 \qquad Q_1 = \frac{[H^+]^2}{P_{H_2}} \quad n=2$$

$$\frac{1}{2}H_2 \rightarrow H^+ + e^- \quad \ldots..2 \qquad Q_2 = \frac{[H^+]}{(P_{H_2})^{1/2}} \quad n=1$$

$$E_{H_2|H^+} = E^\circ_{H_2|H^+} - \frac{0.06}{2}\log_{10} Q_1$$

$$= E^\circ_{H_2|H^+} - 0.06 \log_{10} Q_2$$

Thus, emf does not depend on stoichiometry coefficient.
To make the actual e.m.f. (E) zero,we need to assume,

$Q = 1$

$P_{H_2} = [H^+]^2 = (10^{-7})^2$ atm $= 10^{-14}$ atm

Evaluation of Actual Cell E.M.F.

Type VI Nernst Equation and its applications

Example $Zn(s) \mid Zn^{2+}(0.1\ M) \| Cu^{2+}(0.01\ M) \mid Cu(s)$

$Z^\circ_{Zn|Zn^{2+}} = 0.74V$

$Z^\circ_{Cu^{2+}|Cu} = 0.36$ V

Calculate E_{cell}.

Solution **Process 1:** Application of Nernst equation to individual half-cell reaction

Anode:

$Zn(s) \rightarrow Zn^{2+}(0.1\ M) + 2e^-$

$Q = [Zn^{2+}] = 0.1$

$n = 2$

$$E_{Zn|Zn^{2+}} = E^{\circ}_{Zn|Zn^{2+}} - \frac{0.06}{2} \log_{10} 10^{-1}$$

$$= (0.74 + 0.03)\ V = 0.77\ V$$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu(s)$

$$Q = \frac{1}{[Cu^{2+}]} \quad n = 2$$

$$= \frac{1}{(0.01)} = 10^2$$

$$E_{Cu^{2+}|Cu} = E^{\circ}_{Cu^{2+}|Cu} - \frac{0.06}{2} \log_{10} Q$$

$$E_{Cu^{2+}|Cu} = (0.36 - 0.06)V = 0.3\ V$$

$$E_{cell} = E_{Zn|Zn^{2+}} + E_{Cu^{2+}|Cu} = 0.77 + 0.3$$

$$E_{cell} = 1.07\ V$$

Even if the number of electrons in oxidation and reduction are not same the above method can provide the e.m.f. of the cell.

Process 2: Application of Nernst equation for the overall cell reaction.

In this, number of e^- in the half-cell reactions must be the same.

$$Zn(s) \longrightarrow Zn^{2+} + 2e^-$$

$$Cu^{2+}(0.01M) + 2e^- \longrightarrow Cu(s)$$

$$Zn(s) + Cu^{2+}(0.01\ M) \longrightarrow Cu(s) + Zn^{2+}(0.1M)$$

$$Q_{cell} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.1}{0.01} = 10.$$

$$E^{\circ}_{cell} = E^{\circ}_{Zn|Zn^{2+}} + E^{\circ}_{Cu^{2+}|Cu} \quad (0.74 + 0.36)\ V = 1.1\ V$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.06}{2} \log_{10} Q_{cell} = 1.1 - 3.03$$

$$E_{cell} = 1.07\ V$$

This is preferred when we are able to easily balance the number of e^-.



Worked-out Examples

41. Given that $E^{\circ}_{Mn^{2+}/MnO_2}$ = 1.28V and $E^{\circ}_{Mn^{2+}/Mn^{3+}}$ = 1.51 V. What is the E° for Mn^{2+}/Mn^{4+} couple?

Solution We know that $\Delta G = -nFE$

The half cell reactions are,

$$Mn^{2+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + 2e \quad \ldots (i)$$

$$Mn^{2+} \rightleftharpoons Mn^{3+} + e \quad \ldots (ii)$$

On subtracting,

$$Mn^{3+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + e \quad \ldots (iii)$$

Now, we are to find $E^{\circ}_{Mn^{3+}/Mn^{4+}}$

For the couple Mn^{2+}/Mn^{4+} for equation (i)

$\Delta G = -nFE$ (or)

$\Delta G^{\circ} = -2\,(-1.28)F$

$= 2.56F$

For equation (ii) (i.e.,) for Mn^{2+}/Mn^{3+} couple,

$\Delta G^{\circ} = -1(-1.51)F = 1.51F$

On substracting $\Delta G^{\circ} = 2.56\,F - 1.51\,F = +1.05\,F$

Now in the half reaction $Mn^{3+} - e^- \rightleftharpoons Mn^{4+}$, n = 1 (n is the number of electrons transferred)

$\therefore \quad \Delta G^{\circ} = -nFE$

$= -1 \times F \times E^{\circ}$ (or)

$1.05\,F = -1 \times F \times E^{\circ}$

(or) $E^{\circ} = -1.05$ Volt

Thus we see that, $E^{\circ}_{Mn^{2+}/Mn^{4+}}$ is not (–1.28 – 1.51)

$= -2.79$ V

42. The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337V and 0.799 V respectively. Construct a galvanic cell using these electrodes so that its E^0_{cell} is +ve. For what $[Ag^+]$ will the emf of cell at 25°C be zero if $[Cu^{2+}]$ is 0.1 M?

Solution For E^0 to be +ve, the cell diagram should be.

$Cu \mid CuSO_4\,(aq) \parallel AgNO_3(aq) \mid Ag$

Cell reaction $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag \quad \left[E^0 = E^0_{RP(RHS)} - E^0_{RP(LHS)}\right]$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

$\because \quad E_{cell} = 0$ and $[Cu^{2+}] = 0.01$ M

$$\therefore \quad 0 = \left[E^0 = E^0_{R_pLHS} - E^0_{R_pRHS}\right] - \log\frac{0.059}{2}\log\frac{0.01}{[Ag^+]^2}$$

$$\Rightarrow \quad 0 = (0.799 - 0.337) - \frac{0.0591}{2}\log\frac{0.01}{[Ag^+]^2}$$

$\therefore [Ag^+] = 1.477 \times 10^{-9}$ mol/lit.

More applications of EMF-Measurement from Nernst Equation

1. ***Determination of Equilibrium constant:***

From Nernst equation $E_{cell} = E^0_{cell} - \frac{2.303RT}{nF} \log Q$ (Q = Reaction Quotient)

At equilibrium $E_{cell} = 0$, $Q = K_{eq}$ (equilibrium constant)

$$\therefore \quad E^0_{cell} = \frac{2.303RT}{nF} \log K_{eq}$$

$$\Rightarrow \quad E^0_{cell} = \frac{0.0591}{n} \log K_{eq}$$

$$\therefore \quad \log K_{eq} = \frac{E^0_{cell} \times n}{0.0591}$$

2. ***Determination of solubility product:***

Solubility product of sparingly soluble salts can be evaluated from EMF measurement. Suppose we want to determine K_{sp} of AgX(s). Its saturated solution is placed in Ag electrode. Reference half cell is Ag electrode in Ag^+ion.

$Ag \mid Ag^+$, saturated $AgX \parallel Ag^+(C) \mid Ag$

Anode: $Ag \longrightarrow Ag^+(c)$ (in saturated AgX) + e $\quad E^0_{OX} = -0.80V$

Cathode: Ag^+ (in given solution C) + e $\longrightarrow$ Ag $\quad E^0_{cell} = +0.80V$

Cell reaction $\quad Ag^+(c) \longrightarrow Ag^+$ (unknown) $\quad E^0_{cell} = 0.00V$

$$\therefore \quad E_{cell} = E^0_{cell} - \frac{0.0591}{1} \log \frac{[Ag^+]}{C}$$

Hence $\Rightarrow E_{cell} = \frac{0.0591}{1} \log \frac{C}{[Ag^+]}$ ...(1)

At equilibrium $E_{cell} = 0$

From equation (Ag^+) can be calculated

$$K_{sp_{(AgCl)}} = [Ag^+]\,[Cl^-] = [Ag^+]^2$$

3. ***Ionization constant of weak acid or weak base:***

$\therefore$ We can determine $[H^+]$ using suitable reference electrode.

$Pt(H_2) \mid H^+, HA(C_1) \parallel Cu^{2+}(C_2) \mid Cu$

Its E_{cell} is measured

$$E^0_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[H^+]^2}{[Ag^+]}$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{\left(\sqrt{K_a C_1}\right)^2}{C_2}$$

$[H^+] = \sqrt{K_a C}$, (Oswald dilution law)

K_a can be calculated

4. ***Determination of pH of a solution:***
We can calculate the pH of a unknown solution by using suitable reference half cell.

$Pt(H_2)$ (1 atm) | H^+ (pH = ?) || Cl^- (1M) | Hg_2Cl_2, Hg (calomel electrode)

Cell reaction:

At anode $H_2(g) \longrightarrow 2H^+_{(aq)} + 2e$ $\quad E^0 = 0$

At cathode $Hg_2Cl_{2(S)} + 2e \longrightarrow 2Hg_{(l)} + 2Cl^-$ $\quad E^0_{red} = 0.2676$

$$H_2(g) + Hg_2Cl_2(s) \longrightarrow 2H^+_{(aq)} + 2Hg(l) + 2Cl^-_{(aq)} \quad E^0_{cell} = 0.2675V$$

$$Q = [H^+]^2\,[Cl^{-1}]^2 = [H^+]^2\,[Cl^{-1}]^2 = 1\ M$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log[H^+]^2$$

$$\Rightarrow E_{cell} = E^0_{cell} + 0.0591\ pH$$

$$\therefore \quad pH = \frac{E_{cell} - E^0_{cell}}{0.0591}$$

Cell Thermodynamics

It deals with the evaluation of change in thermodynamic parameters associated with the cell reactions. We can evaluate ΔG, ΔH, ΔS from the determination of e.m.f. of the cell.

We know,

$$\Delta G_{cel} = -nFE_{cell}$$

$dG = VdP - S\,dT$ …… (From the 2nd law of thermodynamics)

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \Rightarrow \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

$\left(\frac{\partial \Delta G}{\partial T}\right)_P$ represents the change in the magnitude of free energy change of a reaction with temperature

For example, we have the following reaction at two different temperatures with the different magnitude of free energy changes.

$A \rightarrow B$ …… $\Delta G = xKJ\ mol^{-1}$ at 25°C

$A \rightarrow B$ …… $\Delta G = yKJ\ mol^{-1}$ at 35°C

$$\frac{\partial}{\partial T}(-nFE) = -\Delta S$$

$$nF\left(\frac{\partial E}{\partial T}\right)_P = \Delta S$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

$\left(\frac{\partial E}{\partial T}\right)_P = \beta$ = temperature coefficient of emf

$\Delta G = -nF\, E_{cell}$

$\Delta S = nF\beta$

$\Delta G = \Delta H - T\Delta S$... from this equation ΔH can be evaluated

If $\partial T = 1^\circ$

$\beta = \partial E$

$\Rightarrow$ **Temperature coefficient of emf** (β) is the change in the emf value associated with 1° increase in the temperature.If β is positive the entropy change of the reaction must be positive.

Type VIII Cell Thermodynamics

Example 1

Anode $\rightarrow$

$\frac{1}{2}H_2(g) \longrightarrow H^+ + e^-$

$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$

$E^\circ_{Cell} = \left(\frac{0.23 + 0.21}{2}\right) = 0.22V$

$\Delta^\circ_G = -nFE$

$= -(0.22 \times 96500)\ J$

$\Delta S^\circ = +nF\beta$

$= (96500\ C)\ (10^{-3}\ VK^{-1})$

$\Delta S = -96.5\ JK^{-1}$

$\Delta G\uparrow$, spontaneity decreases, It p is –ve, then reaction is les spontaneous.

$T\Delta S^\circ + \Delta G^\circ = \Delta H^\circ$

$\Delta G\uparrow$, spontaneity decreases. If p is –ve, then reaction is less spontaneous.

(iii) $E^\circ_{cell} = 0.22V$ $\qquad E^\circ_2 = 0.22V$

$AgCl + e^- \longrightarrow Ag(s) + Cl^-$ ..... E°

$Ag(s) \longrightarrow Ag + e^-$ ..... E°

$AgCl \rightleftharpoons Ag^+ + Cl^-$

Determination of Thermodynamic data:

$$\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_P \text{ (Gibbs-Helmhotlz Equation)}$$

$$\Rightarrow -nFE_{cell} = \Delta H - nFT\left[\frac{dE_{cell}}{dT}\right]_P \quad (\Delta G = -nFE)$$

$$\Delta H = -nFE_{cell} + nFT\left[\frac{dE_{cell}}{dT}\right] \Rightarrow \Delta H = -nF\left[E_{cell} - T\left(\frac{dE_{cell}}{dT}\right)\right]$$

$$\left(\frac{dE_{cell}}{dT}\right)_P = \frac{\Delta H}{nFT} + \frac{E_{cell}}{T}$$ (Temperature coefficient of the emf of the cell

Also $\Delta G = \Delta H - T\Delta S$

$$\therefore \quad \Delta S = -\left(\frac{d(\Delta G)}{dT}\right)_P = -\left[\frac{d(-nFE_{cell})}{dT}\right]_P$$

$$\therefore \quad \Delta S = nF\left(\frac{dE_{cell}}{dT}\right)_P$$



Worked-out Examples

43. The emf of cells Zn | $ZnSO_4$ || $CuSO_4$ } Cu at 25°C is 0.03 V per degree. Calculate the heat of reaction for the change taking place inside the cell.

Solution According to Gibbs Helmhotz equation, heat of reaction (ΔH) can be given as

$$\Delta H = nF\ T\left[\left(\frac{dE}{dT}\right)_p - E\right]$$

$T = 273 + 25 = 298$ K, $n = 2$, $F = 96500$ C, $E = +0.03$V

$$\left[\frac{dE}{dT}\right]_P = 1.4 \times 10^{-4}\text{V per degree}$$

$$\Delta H = 2 \times 96500\ (298 \times (-1.4 \times 10^{-4}) - 0.03)$$

$= -13842$ Joule $= -13.842$ kJ **Nernest Equation**

44. The dependence of electrode potential for the electrode M^{n+}/M with concentration under STP conditions is given by the expression: $E = E° + \frac{0.0591}{n}\log_{1o}[M^{n+}]$. **(True or False)** **[IIT-JEE-1993]**

Solution **False:** When the temperature is 273, the value of the factor will come out as 0.0541 instead of 0.0591. The value 0.0591 comes out at 298 K and not at 273 K.

45. The emf of the cell **[IIT-JEE-2004]**

Zn | Zn^{2+} (0.01 M) | | Fe^{2+} (0.001 M) | Fe

at 298 K is 0.2905 then the value of equilibrium constant for the cell reaction is

(a) $\frac{0.32}{e^{0.0295}}$ (b) $\frac{0.32}{10^{0.0295}}$

(c) $\frac{0.26}{10^{0.0295}}$ (d) $\frac{0.32}{10^{0.0591}}$

Solution (b) Cell reaction: $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

$$E = E^0 - \frac{0.0591}{2}\log\frac{10^{-2}}{10^{-3}}$$

$$E^0 = 0.2905 + \frac{0.0591}{2} = 0.32$$

or $$0.32 = \frac{0.0591}{2}\log K_{eq}$$

or $$K_{eq} = 10^{\frac{0.32}{0.0295}}$$

46. In a cell that utilizes the reaction;

$Zn_{(s)} + 2H^+_{(aq.)} \longrightarrow Zn^{2+}_{(aq.)} + H_{2(g)}$, addition of H_2SO_4 to cathode compartment will:

[AIEEE-2004]

(a) increase the E and shift equilibrium to the left
(b) lower the E and shift equilibrium to the right
(c) increase the E and shift equilibrium to the right
(d) lower the E and shift equilibrium to the left

Solution (c) $E_{cell} = E^\circ_{cell} + \frac{0.059}{1}\log\frac{[H^+]^2}{p_{H_2} \times [Zn^{2+}]}$

Addition of H_2SO_4 will increase $[H^+]$ and thus E_{cell} will be more and equilibrium will shift to right.

47. At 25°C,

$Ag + I^- \longrightarrow AgI + e$; $\quad E^\circ = 0.152$ V

$Ag \longrightarrow Ag^+ + e$; $\quad E^\circ = -0.80$ V

The $\log K_{SP}$ of AgI is : $\left(\frac{2.303RT}{F} = 0.059V\right)$ **[AIEEE-2006]**

(a) –8.12 (b) +8.612
(c) –37.83 (d) –16.13

Solution (d) $E^\circ_{I^-/AgI/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.059}{1}\log K_{SP_{AgI}}$

$-0.152 = +0.8 + \frac{0.059}{1}\log K_{SP_{AgI}} \quad \therefore \log K_{SP_{AgI}} = -16.13$

48. The cell, $Zn|Zn^{2+}(1M) \parallel Cu^{2+}(1M)\ Cu$ ($E^\circ_{cell} = 1.10V$), was allowed to be completely discharge at 298 K. The relative concentration of Zn^{2+} to Cu^{2+}, $\left[\frac{Zn^{2+}}{Cu^{2+}}\right]$ is **[AIEEE-2007]**

(a) antilog (24.08) (b) 37.3
(c) $10^{37.3}$ (d) 9.65×10^4

Solution (c) $E_{cell} = 0$; when cell is completely discharged.

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2} \log \left(\frac{[Zn^{2+}]}{[Cu^{2+}]} \right)$$

$$\text{or } 0 = 1.1 - \frac{0.059}{2} \log \left(\frac{[Zn^{2+}]}{[Cu^{2+}]} \right)$$

$$\log \left(\frac{[Zn^{2+}]}{[Cu^{2+}]} \right) = \frac{2 \times 1.1}{0.059} = 37.3 \ \therefore \ \left(\frac{[Zn^{2+}]}{[Cu^{2+}]} \right) = 10^{37.3}$$

49. Given $E^{\circ}_{Cr^{3+}/Cr} = -0.72\text{V}$, $E^{\circ}_{Fe^{2+}/Fe} = -0.42$ V. The potential for the cell $Cr|Cr^{3+}(0.1\text{ M})||Fe^{2+}(0.01\text{M})|Fe$ is **[AIEEE-2008]**

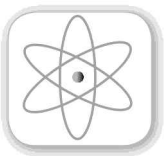
(a) 0.26 V (b) 0.336 V
(c) –0.339 (d) 0.26V

Solution (d) From the given representation of the cell, E_{cell} can be found as follows.

$$E_{cell} = E^{\circ}_{Fe^{2+}/Fe} - E^{\circ}_{Cr^{3+}/Cr} - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{3+}]^3} \quad \text{[Nernst-Equ.]}$$

$$= -0.42 - (-0.72) - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3} = 0.26 \text{ V}$$

REVERSIBLE AND IRREVERSIBLE CELLS



In dealing with the energy relations of cells, thermodynamic principles find extensive applications. However, the use of these principles is subject to one important restriction, namely, that the systems to which they are applied be reversible in the thermodynamic sense. This requires that:

1. the driving and opposing forces be infinitesimally di ferent from each other, and
2. it should be possible to reverse any change taking place by applying a force infinitesimally greater than the acting one.

A cell satisfying the above two requirements constitutes a reversible cell. The potential difference of the cell can be substituted into the relevant thermodynamic relations and hence the values of thermodynamic properties such as free energy change, entropy change and enthalpy change of the cell reaction can be determined. When the above conditions are not satisfied, the cell is said to be irreversible, and thermodynamic relations do not apply.

The difference between reversible and irreversible cells may be illustrated with the following two examples.

An Example of Reversible Cell

Consider a cell composed of Zn and Ag-AgCl electrodes dipping into an aqueous solution of zinc chloride. As seen earlier, the following reactions take place on connecting the electrodes externally.

$$\text{Anode} \quad \frac{1}{2}Zn(s) \rightarrow \frac{1}{2}Zn^{2+}(aq) + e^-$$

$$\text{Cathode} \quad AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$

With the net reaction

$$\frac{1}{2}Zn(s) + AgCl(s) \rightarrow Ag(s) + \frac{1}{2}Zn^{2+}(aq) + Cl^-(aq)$$

The above process continues as long as the external opposing potential is infinitesimally smaller than that of the cell. However, if the opposing potential becomes slightly larger than that of the cell, the direction of current flow is reversed, and so is the cell reaction. Now zinc ions are converted to zinc at one electrode, silver chloride is formed from silver and chloride ions at the other, and the overall cell reaction

Chemical Cells

The cells in which emf is produced as a result of chemical reaction are called chemical cells. These are of two types:

(i) Chemical cells without transport (without transference)

(ii) Chemical cells with transport (without transference)

Chemical cells without transference

In these cells, the liquid junction potential is absent, because both the electrodes are dipped into the same solution. In such cells, one electrode is reversible to the cations and the other electrode is reversible to the anion of the common electrolyte. For example:

(a) Pt, $H_2(g)$ | HCl(aq) | $Cl_2(g)$, Pt

(b) Pt, $H_2(g)$ | HCl(aq), AgC(s) | Ag

Let us consider the following chemical cell without transport:

$$Pt, H_2(g) \mid HCl(aq), AgCl(s) \mid Ag$$

Anode (Oxidation) Cathode (Reduction)

$$\text{At anode:} \quad \frac{1}{2}H_2(g) \rightleftharpoons H^+_{(aq)} + e^- \qquad (n = 1)$$

$$\text{At anode} \quad AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \qquad (n = 1)$$

The corresponding electrode potentials are

$$E_{(anode)} = E^0_{(\frac{1}{2}H_2/H^+)} - \frac{2.303\,RT}{F}\log\left(\frac{C_{H^+}}{p_{H_2}^{1/2}}\right) \quad \ldots 1$$

But $E^0_{(\frac{1}{2}H_2/H^+)} = 0$

Hence $E_{anode} = -\frac{2.303RT}{F}\log\left(\frac{C_{H^+}}{P_{H_2}^{1/2}}\right)$

Similarly, $E_{(cathode)} = E^0_{(AgCl/Ag)} - \frac{2.303RT}{F}\log(C_{Cl^-})$

$$\therefore \quad E_{(cathode)} = E^0_{(AgCl/Ag)} - \frac{2.303\,RT}{F}\log Cl^- \quad \ldots .2$$

The cell reaction is the sum of both electrode reactions.

$$\frac{1}{2}H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + Cl^- + H^+$$

and the cell emf is the algebraic sum of electrode potentials of anode and cathode; hence

$$E_{cell} = E_{anode} + E_{cathode}$$

$$= -\frac{2.303RT}{F}\log\left(\frac{C_{H^+}}{P_{H_2}^{1/2}}\right) + E^0_{(AgCl/Ag)} - \frac{2.303RT}{F}\log C_{Cl^-}$$

$$= E^0_{(AgCl/Ag)} - \frac{2.303RT}{F}\left[\log\left(\frac{C_{H^+}}{P_{H_2}^{1/2}}\right) + \log C_{Cl^-}\right]$$

$$\text{or } E_{cell} = E^0_{AgCl/Ag} - \frac{2.303RT}{F}\log\left(\frac{C_{H^+} \times C_{Cl^-}}{P_{H_2}^{1/2}}\right)$$

But, $C_{H^+} \times C_{Cl^-} = C_{HCl}$

$$\therefore E_{cell} = E^0_{(AgCl/Ag)} - \frac{2.303RT}{F}\log\frac{C_{HCl}}{P_{H_2}^{1/2}} \quad \ldots.3$$

Equation (3) says that emf of such a cell depends on:

(i) Activity of HCl in solution
(ii) Pressure of hydrogen gas.

Chemical cell with transport

In these cells, emf is produced due to a chemical reaction taking place within the cell, but there exists a liquid junction between the solutions of different electrolytes. At the contact or junction of both solutions a potential difference is developed called liquid junction potential or diffusion potential. Hence emf of such a cell will be given by

$$E_{cell} = E_1 + E_2 + E_j$$

Where E_1 = Electrode potential of anode
E_2 = Electrode potential of cathode
E_j = Liquid junction potential

The examples of such cells are:

(i) $Zn \mid Zn^{2+}(aq) \mid\mid Cd^{2+}(aq) \mid Cd$
(ii) $Zn \mid Zn^{2+}(aq) \mid\mid Ag^+(aq) \mid Ag$

Concentration Cells

The cells in which electrical energy is produced due to physical transfer of material from one concentration to another, are called concentration cells. Or the cells in which emf is produced due to decrease in free energy, accompanying the physical transfer of material from one part of the cell to another part are called concentration cells. The difference in concentration may be in the electrode material or the electrolyte. On this basis, concentration cells are of two types:

(i) Electrode concentration cells
(ii) Electrolyte concentration cells

Electrode concentration cells

The concentration cells in which electrode of the same material, having different concentrations, are dipped in the solution of same electrolyte, are called electrode concentration cells. These may be of two types:

Electrode Amalgam Concentration Cells.

In these cells, the concentration of electrode materials can be varied taking their amalgams i.e., solution of metal electrode in mercury. For example.

$$Zn(Hg)\ (Cl_{Zn}=Cl_1)\ |\ ZnSO_4\ \text{Solution}\ (Cl_{Zn^{2+}})\ |\ Zn(Hg)\ Cl_{Zn}=Cl_2)$$

Electrode (Half-cell) reactions are:

(i) Left electrode (oxidation): $Zn(Cl_1) \rightleftharpoons Zn^{2+} + 2e^-$ ... (1) (n = 2)

$$\therefore\ E_{1(Zn/Zn^{2+})} = E^0_{(Zn/Zn^{2+})} - \frac{2.303RT}{2F}\log\left(\frac{Cl_{Zn^{2+}}}{Cl_1}\right)$$

(ii) Right electrode (Reduction): $Zn^{2+} + 2e^- \rightleftharpoons Zn(Cl_2)$ .... (2) (n = 2)

$$E_{2(Zn^{2+}/Zn)} = E^0_{(Zn^{2+}/Zn)} - \frac{2.303RT}{2F}\log\left(\frac{Cl_2}{Cl_{Zn^{2+}}}\right)$$

$\therefore$ Overall cell reaction: Adding equations (1) and (2),

$$Zn(Cl_1) \rightleftharpoons Zn(Cl_2)$$

$\therefore$ emf of cell (E) = $E_1 + E_2$

$$E_{cell} = -\frac{2.303RT}{2F}\left[\log\left(\frac{Cl_{Zn^{2+}}}{Cl_1}\right)+\log\left(\frac{Cl_2}{Cl_{Zn^{2+}}}\right)\right] \quad \text{... (3)}$$

or $E_{cell} = -\frac{2.303\ RT}{2F}\log\ (a_2/a_1)$

Conclusions:

1. Equation (3) indicates that emf of this cell is due to physical transfer of Zn from amalgam where its activity is Cl_1 to amalgam where its activity is Cl_2.
2. This equation shows that the emf of this cell depends only on the ratio of zinc activities in the two amalgams and not at all on the activity of zinc ions in the electrolyte.
3. E^0 does not appear in the final equation for emf of the cell

Gas Concentration Cells

In these cells, the electrodes are made up of gas material maintained at different partial pressures and being dipped in the solution of gas ions. For example,

$$Pt,\ H_2(p_1)\ |\ \text{Solution of}\ H^+\ \text{ions}\ (Cl_{H^+})\ |\ H_2(p_2),\ Pt$$

The electrode reactions are:

(i) Left electrode (Oxidation): $\frac{1}{2}H_2(p_1) \rightleftharpoons H^+ + e^-$ ... (1) (n = 1)

$$\therefore\ E_{1(\frac{1}{2}H_2/H^+)} = E^0_{(\frac{1}{2}H_2/H^+)} - \frac{2.303RT}{F}\log\left(\frac{Cl_{H^+}}{p_1^{1/2}}\right)$$

(ii) Right electrode (reduction): $H^+ + e \rightleftharpoons \frac{1}{2}H_2(p_2)$ ... (2) (n = 1)

$$\therefore\ E_{2(H^+/\frac{1}{2}H_2)} = E^0_{(H^+/\frac{1}{2}H_2)} - \frac{2.303RT}{F}\log\ (p_2^{1/2}/Cl_{H^+})$$

Overall cell reaction: Adding equations (1) and (2)

$$\frac{1}{2}H_2(p_1) \rightleftharpoons \frac{1}{2}H_2(p_2) \quad \ldots(3)$$

and, emf of cell, $E = E_1 + E_2$

$$E = E^0_{(\frac{1}{2}H_2/H^+)} + E^0_{(H^+/\frac{1}{2}H_2)} - \frac{2.303RT}{F}\left[\log\left(\frac{Cl_{H^+}}{p_1^{1/2}}\right) + \log\left(\frac{p_2^{1/2}}{Cl_{H^+}}\right)\right]$$

Since $E^0_{(\frac{1}{2}H_2/H^+)} + E^0_{(H^+/\frac{1}{2}H_2)} = 0$

Hence $E = -\frac{2.303RT}{F}\log (p_2/p_1)^{1/2}$

or $E = -\frac{2.303RT}{2F}\log (p_2/p_1) \quad \ldots.(4)$

Conclusions:

(i) From equation (4) it follows that emf of the cell depends only on the two pressures and is independent of activity of H^+ ions of the solution in which the two electrodes are immersed.

(ii) For the cell reaction to be spontaneous, ΔG should be negative. Since,

$$\Delta G = -nFE$$

Hence E should be positive. Thus in equation (4), p_1 should be greater than p_2. That is, gas must expand from pressure p_1 to pressure p_2.

Electrolyte Concentration Cells

The cells in which the two electrodes are of same material and dipped in two solutions of the sameelecrolyte, though of different concentrations, are called electrolyte concentration cells. The two solutions may be in actual contact or not. Depending on this we have two types of electrolyte concentration cells.

Concentration cells without Transport (without Transference): The concentration cell, in which the two electrolyte solutions are not in direct contact and the transfer of ions from one electrolytic solution to the other does not take place directly, is called concentration cell without transport. The emf arises from difference in concentrations of the electrolytic solutions.

General design of such cells: A concentration cell without transport can be assembled if two simple cells with electrodes reversible with respect to the ions constituting the electrolyte are oppositely combined.

Let us consider a simple chemical cell whose electrodes are reversible with respect to H^+ and Cl^- ions:

$$H_2(g, 1\text{ atm}) \mid HCl\ (Cl_1), AgCl(s) \mid Ag$$

The cell reaction of this chemical cell is

At anode: $\frac{1}{2}H_2 \rightleftharpoons H^+ + e^-$ (n = 1)

At cathode: $AgCl + e^- \rightleftharpoons Ag + Cl^-$ (n = 1)

Overall reaction: $\underset{(1\text{ atm})}{\frac{1}{2}H_2} + AgCl(s) \rightleftharpoons Ag(s) + \underset{(Cl_1)}{HCl}$

$\therefore$ emf of cell: $E_1 = E^0 - \frac{2.303RT}{F}\log\left(\frac{Cl_{HCl} \times Cl_{Ag(s)}}{Cl^{1/2}_{H_2} \times Cl_{AgCl}}\right)$

Since activity of solid is arbitrarily taken as unity and activity of gas is equal to its pressure, we get

$$E_1 = E^0 - \frac{2.303RT}{F} \log Cl_1 \quad \ldots(1)$$

Let us now consider the same cell but with different activity of HCl, i.e., Cl_2:

$$H_2(g, 1 \text{ atm}) \mid \underset{(Cl_2)}{HCl}, AgCl(s) \mid Ag$$

The cell reaction can similarly written as

$$\frac{1}{2}H_2 (1 \text{ atm}) + AgCl(s) \rightleftharpoons Ag(s) + HCl(Cl_2)$$

and similarly, the emf of cell is

$$E_2 = E^0 - \frac{2.303RT}{F} \log Cl_2 \quad \ldots(2)$$

If these two simple chemical cells are connected so as to oppose each other (i.e., oppositely combined) we get what is called, concentration cell without transport, represented as follows:

$$H_2(g, 1 \text{ atm}) \mid \underset{(Cl_1)}{HCl}, AgCl(s) \mid Ag - Ag \mid AgCl(s), \underset{(Cl_2)}{HCl} \mid H_2 (g, 1 \text{ atm})$$

Since both the simple cells are combined oppositely, the overall cell reaction of this concentration cell without transport will be the difference of above cell reactions. That is

$$\frac{1}{2}H_2(g, 1 \text{ atm}) + Ag(s) \rightleftharpoons Ag(s) + HCl(Cl_1)$$

$$\frac{1}{2}H_2(g, 1 \text{ atm}) + Ag(s) \rightleftharpoons Ag(s) + HCl(Cl_2)$$

Subtracting $\quad 0 + 0 \rightleftharpoons HCl(Cl_1) - HCl(Cl_2)$

or $\quad HCl(Cl_2) \rightleftharpoons HCl(Cl_1)$

Similarly the emf of the cell is obtained by substracting E_2 from E_1

$$E_1 = E^0 - \frac{2.303\ RT}{F} \log Cl_1$$

$$E_2 = E^0 - \frac{2.303RT}{F} \log\ Cl_2$$

Subtracting $\quad E_1 - E_2 = \frac{2.303RT}{F} [\log Cl_2 - \log Cl_1]$

Or $\quad E = \frac{2.303RT}{F} \log\left(\frac{Cl_2}{Cl_1}\right) \quad ..(3)$

Where $Cl_2 > Cl_1$

Conclusions:

(i) From equation (3), it follows that emf of cell without transport depends on the difference in concentration of solution in both sides.

(ii) For emf of the cell to be positive, Cl_2 should be greater than Cl_1.

(iii) Other examples of such cells are:

(a) $Na\,(Hg) \mid NaCl, AgCl(s) \mid Ag\text{–}Ag \mid AgCl(s), NaCl \mid Na(Hg)$

(b) $Zn(Hg) \mid \underset{(Cl_2)}{ZnSO_4}, PbSO_4(S) \mid Pb(Hg) - Pb(Hg) \mid PbSO_4(s), \underset{(Cl_2)}{ZnSO_4} \mid Zn(Hg)$

Concentration Cells with Transport or Concentration Cells with Liquid Junction

The cells, in which two solutions containing the same electrolyte but at different concentrations are in direct contact and the identical electrodes reversible to either ion of the electrolyte are placed in these solutions are called concentration cells with transport. In these cells, the liquid junction potential at the interface of two solutions is taken into account.

The typical concentration cell with transport is

$$\underset{(Cl_1)}{Pt, H_2(1\text{ atm}) \mid HCl} \qquad \underset{(Cl_2)}{HCl \mid H_2\,(1\text{ atm}), Pt}$$

The electrode reactions for each faraday of electricity drawn from the cell are:

Left electrode (oxidation): $\frac{1}{2}H_2 \rightleftharpoons H^+(Cl_1) + e^-$ ... (1)

Right electrode (reduction): $H^+(Cl_2) + e^- \rightleftharpoons \frac{1}{2}H_2$ ....(2)

$\therefore$ Overall reaction in cell: Adding equations (1) and (2)

$H^+(Cl_2) \quad H^+(Cl_1)$

Hence, when the current flows, the H^+ ions generated at the left electrode are consumed at the right electrode. Since the solutions are in direct contact with each other, the ions (H^+ and Cl^-) are free to move from one solution to the other with the flow of current in the cell. This current in the cell is composed, of course, not of free electrons but of negative chloride ions (Cl^-) moving from right to left and positive H^+ ions moving across the junction fromleft to right.

$$H_2 \quad HCl(Cl_1) \quad \underset{\rightarrow H^+}{\underset{Cl^- \leftarrow}{HCl(Cl_2)}} \quad H_2$$

$$\left(\frac{1}{2}H_2 \rightarrow \underset{(Cl_1)}{H^+}\right) \rightarrow \left(\underset{(Cl_2)}{H^+} \rightarrow \frac{1}{2}H_2\right)$$

(Transference at liquid junction)

$Cl_2 > Cl_1$

Let t_a = Transport number of Cl^-

t_c = Transport number of H^+

Then, for every faraday passing through the cell, t_c faraday is carried by t_c g ion of H^+ from left to right, i.e., from solution of activity Cl_1 to Cl_2. Thus we can write

$$T_c.H^+(Cl_1) = t_c.H^+(Cl_2) \qquad \text{...(4)}$$

Also t_a faraday of electricity will be carried by t_a g ion of Cl^- from right to left, i.e., from solution of activity Cl_2 to Cl_1. Thus e can write

$$t_a.Cl^-(Cl_2) = t_a.Cl^-(Cl_1) \qquad \text{...(5)}$$

Therefore, in order to obtain the net transfer of material, we must add equation (3), (4) and (5). We thus get for the overall process of the cell.

$$H^+(Cl_2) + t_c.\,H^+(Cl_1) + t_a.Cl^-(Cl_2) = H^+(Cl_1) + t_c.H^+(Cl_2) + t_a.Cl^-(Cl_1)$$

But $\quad t_a + t_c = 1 \qquad \therefore \; t_c = 1 - t_a$

$$\therefore \quad H^+(a_2) + (1-t_a) + H^+(Cl_1) + t_a.Cl^-(Cl_2) = H^+(Cl_1) + (1-t_a).H^+(Cl_2) + t_a.Cl^-(Cl_1)$$

$$\text{or} \quad t_a.H^+(Cl_2) + t_a.Cl^-(Cl_2) = t_a.H^+(Cl_1) + t_a.Cl^-(Cl_1)$$

$$\text{or} \quad t_a.[H^+(Cl_2) + Cl^-(Cl_2)] = t_a[H^+(Cl_1) + Cl^-(Cl_1)]$$

$$\text{or} \quad t_a.HCl(Cl_2) = t_a.HCl(Cl_1) \qquad \ldots(6)$$

Equation (6) shows that t_a equivalents of HCl are transferred from solution of concentration Cl_2 to the solution of concentration Cl_1 for the passage of every faraday of electricity.

[**Note:** This may be contrasted with the same process in a concentration cell without transport, where for one Faraday, electricity drawn from the cell, the transfer of full equivalent of electrolyte is accomplished.]

The emf of complete cell will be given by equation (6)

$$E = -\frac{2.303RT}{F} \log (Cl_1)^{t_a} / (Cl_2)^{t_a} = -\frac{2.303RT}{F} \log \left(\frac{Cl_1}{Cl_2}\right)^{t_a}$$

$$\text{or} \quad E = -\frac{2.303RT.t_a}{F \log} \log(Cl_1 / Cl_2)$$

$$\text{or} \quad E = \frac{2.303RT.t_a}{F} \log(Cl_1 / Cl_2)$$

(ii) However, when the electrodes are reversible to anion, as in the cell

$$Ag \mid AgCl(s), HCl(Cl_1) \qquad HCl(Cl_2), AgCl(s) \mid Ag$$

Where electrodes are reversible to Cl^- (anion), then the net transfer will be given by

$$t_c.\ HCl(Cl_1) = t_c.HCl(Cl_2)$$

$$\therefore \quad E_{cell} = \frac{2.303RT.t_c}{F} \log (Cl_1/Cl_2)$$

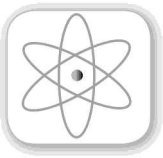
where $Cl_1 > Cl_2$, then the cell reaction will be spontaneous. The above equation in terms of m and γ will be

$$E_{cell} = \frac{2 \times 2.303RT.t_c}{F} \log (m_1\gamma_1/m_2\gamma_2) \qquad \ldots.(8)$$

(iii) The emf of the cell given by equation (7) or (8) includes the liquid junction potential (E_j).

$$E_{cell} = E_1 + E_2 + E_j$$

LIQUID JUNCTION POTENTIAL OR DIFFUSION POTENTIAL



What is Liquid Junction Potential?

When two electrolytic solutions of different concentrations are brought in contact with one another, a potential difference develops at the junction of two solutions. This potential difference is called liquid junction potential.

The liquid junction potential arises mainly due to unequal rates of diffusion of ions across the junction (interface). In other words, it is due to difference in migration velocities of ions. Consider the following cell:

	I		II			
$Pt, H_2(g)$		HCl		HCl	$H_2(g), Pt$	$(Cl_1 > Cl_2)$
	(Cl_1)		(Cl_2)			

There will be diffusion of electrolyte from solution of higher concentration to that of lower concentration. Because different ions have different velocities, they tend to diffuse across the boundary (junction) at different speeds. Both H^+ and Cl^- ions diffuse from concentrated solution to dilute solution. The ionic velocity of H^+ ions is greater than that of Cl^-. So H^+ ions will diffuse more rapidly from Cl_1 to Cl_2. The dilute solution in II compartment will thus become positively charged with respect to solution in I. As a result of this, concentrated solution (I) is left with an excess of Cl^- ions and thus acquires negative charge. Hence an electrical double layer of +ve and –ve charges is formed at the junction of two solutions and a potential difference is developed at the junction. It is called liquid junction potential. Thus, we can say that:

(i) The liquid junction potential is due to difference in velocity of ions.
(ii) The magnitude of liquid junction potential depends upon the relative speed of ions.
(iii) If two ions are moving with the same speed, there will be no liquid junction potential.
(iv) The liquid junction potential cannot be measured directly but it can be calculated.

Salt bridge and its significance

(i) Salt bridge is *U*-shaped glass tube filled with a gelly like substance, agar-agar (plant gel) mixed with an electrolyte like *KCl, KNO_3, NH_4NO_3* etc.
(ii) The electrolytes of the two half-cells should be inert and should not react chemically with each other.
(iii) The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, viz., KCl, KNO_3, NH_4NO_3 etc.
(iv) The following are the functions of the salt bridge,
  (a) It connects the solutions of two half-cells and completes the cell circuit.
  (b) It prevent transference or diffusion of the solutions from one half cell to the other.
  (c) It keeps the solution of two half-cells electrically neutral.
  (d) It prevents liquid–liquid junction potential i.e., the potential difference which arises between two solutions when they contact with each other.

Commercial Cell or Batteries

One of the main use of galvanic cells is the generation of portable electrical energy. These cells are also popularly known as ***batteries.*** The term battery is generally used for two or more Galvanic cells connected in series. Thus, a ***battery*** *is an arrangement of electrochemical cells used as an energy source*. The basis of an electrochemical cell is an oxidation–reduction reaction.

Main types

Cells are classified into three broad categories

1. Primary cells
2. Secondary cells
3. Fuel cell

Primary electrochemical cells

Primary cells irreversibly (within limits of practicality) transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the electrochemical cell by an electrical means. In these cells, the electrode reactions cannot be reversed by an external electric

energy source. In these cells, reactions occur only once and after use they become dead. Therefore, they are ***not chargeable***. Some common example are, dry cell, mercury cell, Daniell cell and alkaline dry cell

Primary electrochemical cells can produce current immediately on assembly. Disposable cells are intended to be used once and discarded. Disposable primary cells cannot be reliably recharged, since the chemical reactions are not easily reversible and active materials may not return to their original forms.

(i) **Voltaic cell**

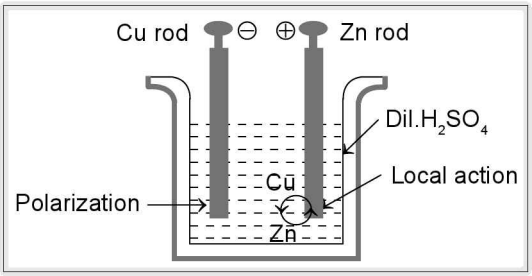


Fig. 9.13

Cathode : Cu rod **Anode** : Zn rod
Electrolyte : dil. H_2SO_4 **Emf** : 1.08 V
At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$
At Anode : $Zn \rightarrow Zn^{2+} + 2e^-$
Over all reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(ii) **Daniel cell**

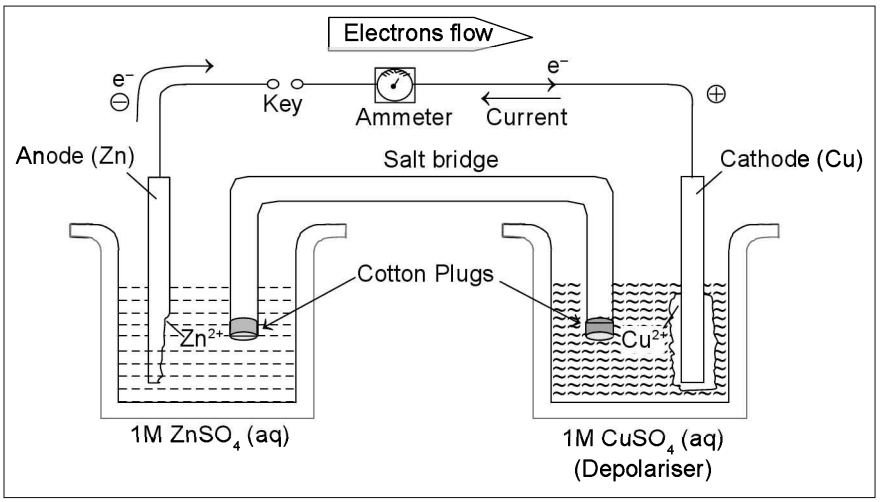


Fig. 9.14

Cathode : Cu rod **Anode** : Zn rod
Electrolyte : dil. H_2SO_4 **Emf** : 1.1 V
At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$
At Anode : $Zn \rightarrow Zn^{2+} + 2e^-$
Over all reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(iii) **Carbon-zinc dry cell**

One of the most common primary batteries is the carbon—zinc dry cell. (We usually call it a battery, but there is only one cell in it.) It has a zinc case surrounding a paste made of water, zinc(II) chloride and ammonium chloride (Figure 9.15). This paste is in contact with a mixture of manganese(iv) oxide

and graphite powder in which rests a graphite rod. The changes that take place in the cell are complicated, but the chief reaction in $Zn(s) + 2MnO_2(s) + H_2O(1) \rightarrow Zn^{2+}(aq) + Mn_2O^{+}(s) + 2OH^{-}(aq)$ The cell has an e.m.f. of about 1.5 V.

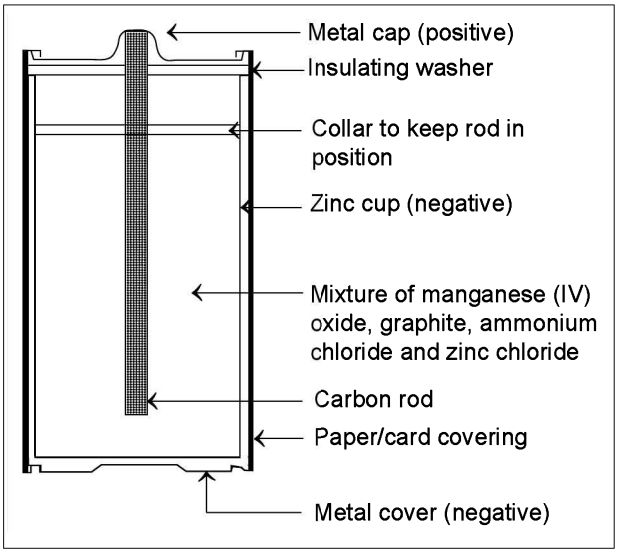


Fig. 9.15 The construction of a typical battery (strictly, a Leclanché primary cell)

Advantage
It is economical, safe and available in many sizes.

Disadvantage
The reaction between Zn anode and acidic NH_4^+ ion corrode the Zn vessel, even if it is not working, i.e., why Zn anode covered with another inert metal. Such cells are then called leak proof cells.

(iv) **Mercury cell**
It consists of zinc and mercury amalgam which acts as anode and a paste of HgO and carbon rods which act as cathode. The electrolyte is a paste of KOH and ZnO.

Mercury batteries use either pure mercuric oxide or a mixutre of mercuric oxide with manganese dioxide as the cathode. Mercuric oxide is a non-conductor so some graphite is mixed with it; the graphite also helps prevent collection of mercury into large droplets. The anode is made of zinc and separated from the cathode with a layer of paper or other porous material soaked with electrolyte. During discharge, zinc oxidizes to zinc oxide and mercuric oxide get reduced to elementary mercury. A little extra mercuric oxide is put into the cell to prevent evolution of hydrogen gas at the end of life. Mercury batteries are very similar to silver-oxide batteries.

Sodium hydroxide or potassium hydroxide are used as an electrolyte. Sodium hydroxide cells have nearly constant voltage at low discharge currents, making them ideal for hearing aids, calculators, and electronic watches. Potassium hydroxide cells, in turn, provided constant voltage at higher currents, making them suitable for applications requiring current surges, e.g., photographic cameras with flash, and watches with a backlight. Potassium hydroxide cells also have better performance at lower temperatures. Mercury cells have very long shelf life, up to 10 years.

A different form of mercury battery uses mercuric oxide and cadmium. This has a much lower terminal voltage around 0.9 volts and so has lower energy density, but it has an extended temperature range, in special designs up to 180 °C.

Electrical Characteristics

Mercury batteries using mercury(II) oxide cathode have a very flat discharge curve, holding constant 1.35 V (open circuit) voltage until about last 5% of their lifetime, when their voltage drops rapidly. The

voltage remains within 1% for several years at light load, and over a wide temperature range, making mercury batteries useful as a reference voltage in electronic instruments and in photographic light meters. Mercury batteries with cathodes made of a mix of mercuric oxide and manganese dioxide have output voltage of 1.4 V and more sloped discharge curve.

Advantage
It is small in size having relatively large voltage.

Disadvantage
Discarded mercury cells causes pollution, so should not be disposed as such.

(v) **Silver oxide-zinc cell**
One type of small button-shaped cell that is used in calculators and digital watches consists of a combination of silver(I) oxide, Ag_2O, mixed with potassium or sodium hydroxide, and zinc. The cell has an e.m.f. of around 1.6V. Provided the cell is used to supply small currents, e.g., a few milliamps, it can have a working life of over a year. Lithium is also used in button cells, but often for special purposes, e.g. in powering a pacemaker implanted into the chest of a person with heart disease. A combination of nickel and cadmium is another favourite for button cells. Batteries come in many sizes reflecting their wide range of uses.

Secondary cell

Secondary cells can be recharged; that is, they can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition. Secondary electrochemical cells must be charged before use; they are usually assembled with active materials in the discharged state. Rechargeable electrochemical cells or *secondary electrochemical cells* can be recharged by applying electrical current, which reverses the chemical reactions that occur during its use. These are also celled ***storage cells.*** Devices to supply the appropriate current are called chargers or rechargers.

Lead—acid battery

Lead-acid batteries are found in almost all cars and lorries. They are made from a combination of secondary cells, i.e., cells that can be recharged. A typical battery has two types of metal plate; one type has lead as its active ingredient, the other has lead(iv) oxide, PbO_2. The plates are separated by an inert material and immersed in a solution of sulphuric acid of density 1.25 g cm^{-3}. The PbO_2 plates are the positive electrodes, and the lead the negative electrodes. The reactions that go on in the cells are complicated, but it is thought that there are two main ones. At the negative plates:

$$Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$$

At the positive plates:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$$

The reactions both go to the right when current is being drawn from the battery. That is, lead sulphate, $PbSO_4$, is made at both the negative and positive plates. However, this happens by two different processes, and for each mole of $PbSO_4$ made two moles of electrons travel through the external circuit. These are the electrons that, for example, make the lights, indicators and a car radio work.

When a car or lorry moves, an electric current is generated by the alternator. This current is passed into the battery in the direction that forces the two reactions to go to the left. That is, the $PbSO_4$ is decomposed. In theory, at least, the charging and discharging can go on indefinitel . However, in practice, this is not so. The sulphuric acid decomposes, and has to be replaced; and in time the plates themselves change their structure. Eventually the battery becomes much less efficient and has to be changed. One of the worst things that can happen to a car battery is for it to spend most of its time in a discharged state. This causes so much $PbSO_4$ to build up that it is almost impossible to remove. A typical car battery provides a voltage of 12V. This is not a large voltage, but the battery can provide a large current, e.g., over 10 A, without being destroyed.

Advantage

1. It provide a large burst of current to the engine.
2. It is reliable, having long life and effective at low concentration.
3. There is no need for the lead-storage cell to have separate anode and cathode compartment because the oxidizing and reducing agents are both solids.

Disadvantage

1. $PbSO_4$ formed during discharging stick to the electrodes. So there is some mechanical strain which reduces its capacity.
2. During replacing of water, which is lost during discharging, some water can be electrolyzed to H_2 and O_2 and if sparked, the gases can explode.



Worked-out Example

50. A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 mL^{-1} at 25°C) to one of 27% by weight. The original volume of electrolyte is one litre. How many Faraday have left the anode of battery? Note the water is produced by the cell reaction as H_2SO_4 is used up Overall reaction is:

Solution Before electrolysis:

Volume of solution = 1 litre = 1000 mL

$\therefore$ Wt. of solution = $1000 \times 1.261 = 1261$ g ($\because$ w = V × d)

$\therefore$ Wt. of $H_2SO_4 = \dfrac{34.6 \times 1261}{100} = 436.306$ g

$\therefore$ Wt. of water = $1261 - 436.306 = 824.694$ g

After electrolysis:

Now during reaction wt. of H_2O formed = X g

$\therefore$ Mole of H_2O formed = $\dfrac{X}{18}$

$\therefore$ Mole of H_2SO_4 used = $\dfrac{X}{18}$

($\because$ mole ratio of $H_2SO_4 : H_2O :: 1:1$)

$\therefore$ Wt. of H_2SO_4 used = $\dfrac{98X}{18} = 5.44X$ g

$\therefore$ Wt. of H_2SO_4 left = $(436.306 - 5.44X)$ g

New weight of solution = wt. of old solution + wt. of H_2O formed – wt. of H_2SO_4 lost

$= 1261 + X - 5.44X$

$\therefore$ % by wt. of new solution = $\dfrac{436.306 - 5.44X}{(1261 + X - 5.44X)} = \dfrac{27}{100}$

$\therefore$ X = 22.59 g

$\therefore$ $\dfrac{22.59}{18}$ mole of H_2O are formed

$\because$ Mole of H_2O = Eq. of H_2O ($\because$ $2H_2O$ consume 2 electrons)

Now 1 mole of H_2O formed by the passage of 1 Faraday

$\therefore$ $\dfrac{22.59}{18}$ mole of H_2O formed by the passage = $\dfrac{22.59}{18}$ Faraday

= 1.255 Faraday

Nickel-cadmium (nicad battery)

This call consist of Cadmium anode, which gets oxidized in basic NaOH or KOH electrolyte and NiO_2 which act as cathode. The reactions taking place at electrodes are:

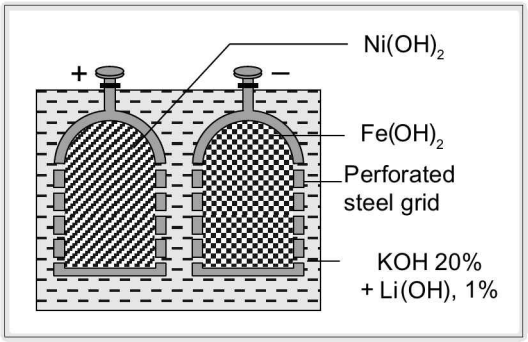


Fig. 9.16

Anode: $Cd(s) + 2OH^-(aq) \rightleftharpoons CdO(s) + H_2O(l) + 2e^-$

Cathode: $2Ni(OH)_3 + 2e^- \rightleftharpoons 2Ni(OH)_2(s) + 2OH^-(aq)$

Overall cell reaction is:

$$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(O)_2(s) + H_2O(l) \quad E_{cell} = 1.4\ V$$

Uses

It is used in cordless razors, photoflash units and power tools

A simple version can be set up in a laboratory as shown in figure 9.16. Practical fuel cells have a different design (Figure 9.16b). At the negative electrode, electrons are released through the reaction

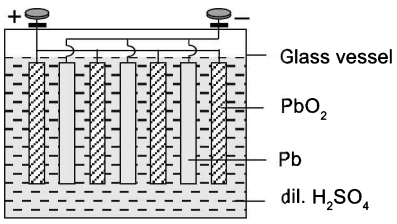
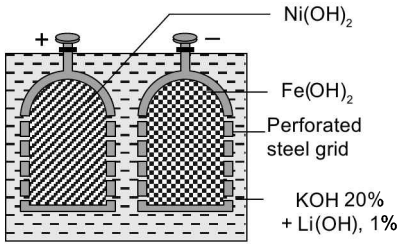
$$2H_2(g)+4OH^-(aq) \rightarrow 4H_2O(l)+4e^-$$

The electrons released travel to the positive terminal where oxygen is used up:

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$. Overall, the change is $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Not only does the cell produce a reliable supply of electricity, it also produces water. Both features have given hydrogen-oxygen fuel cells a use in space exploration. Other fuel cell systems have been investigated using different electrolytes and reactants. One of the aims of the research has been to find a system that could be used to power cars and other vehicles. There has been some success, with some experimental cars travelling at over 80 km/h. However, the economics of fuel cells mean that they cannot as yet compete with petrol as a fuel.

Comparison of LSC and Nickle Cadmium Cell

In charged	*Lead storage cell*	*Nickel cadmium cell (Nicad battery)*
		

In charged	Lead storage cell	Nickel cadmium cell (Nicad battery)
Positive electrode	Perforated lead plates coated with PbO_2	Perforated steel plate coated with $Ni(OH)_4$
Negative electrode	Perforated lead plates coated with pure lead	Perforated steel plate coated with Fe
Electrolyte	dil. H_2SO_4	20% solution of KOH + 1% $LiOH$
During charging	**Chemical reaction** ***At anode***: $PbSO_4 + 2H^+ + 2e^- \rightarrow Pb + H_2SO_4$ ***At cathode***: $PbSO_4 + SO_4^{--} + 2H_2O - 2e^- \rightarrow PbO_2 + 2H_2SO_4$ Specific gravity of H_2SO_4 increases and when specific gravity becomes 1.25 the cell is fully charged. **Emf of cell**: When cell is fully charged then E = 2.2 *volt*	**Chemical reaction** ***At anode***: $Ni(OH)_2 + 2OH^+ - 2e^- \rightarrow Ni(OH)_4$ ***At cathode***: $Fe(OH)_2 + 2K^+ + 2e^- \rightarrow Fe + 2KOH$ **Emf of cell:** When cell is fully charged then E = 1.36 *volt*
During discharging	**Chemical reaction** **At *anode***: $Pb + SO_4^{--} - 2e^- \rightarrow PbSO_4$ ***At* cathode**: $PbO_2 + 2H^+ + 2e^- + H_2SO_4 \rightarrow PbSO_4 + 2H_2O$ Specific gravity of H_2SO_4 decreases and when specific gravity falls below 1.18 the cell requires recharging. ***Emf of cell***: When emf of cell falls below 1.9 *volt* the cell requires recharging.	**Chemical reaction** ***At anode***: $Fe + 2OH^- - 2e^- \rightarrow Fe(OH)_2$ ***At* cathode**: $Ni(OH)_4 + 2K^+ + 2e^- \rightarrow Ni(OH)_2 + 2KOH$ ***Emf of cell***: When emf of cell falls below 1.1 V it requires charging.
Efficiency	80%	60%

Fuel Cells

A fuel cell is a primary cell of a special type. The chemicals that produce electricity are constantly replaced as soon as they are used. These are Voltaic cells in which the reactants are continuously supplied to the electrodes. These are designed to convert the energy from the combustion of fuels such as H_2, CO, CH_4, etc., directly into electrical energy. The common example is ***hydrogen-oxygen fuel cell*** as described below,

In this cell, hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated aqueous sodium hydroxide or potassium hydroxide. Hydrogen (the fuel) is fed into the anode compartment where it is oxidized. The oxygen is fed into cathode compartment where it is reduced. The diffusion rates of the gases into the cell are carefully regulated to get maximum efficienc . The net reaction is the same as burning of hydrogen and oxygen to form water. The reactions are

***At anode*:** $2[H_2(g) + 2OH^-](aq) \longrightarrow 2H_2O(l) + 2e^-$

***At cathode*:** $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

***Overall reaction*:** $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Each electrode is made of porous compressed carbon containing a small amount of catalyst (Pt, Ag or CoO) . This cell runs continuously as long as the reactants are fed. Fuel cells convert the energy of the fuel directly into electricity EMF of fuel cell is 1.23 V. This cell has been used for electric power in the ***Apollo space programme.*** The important advantages of fuel cells are

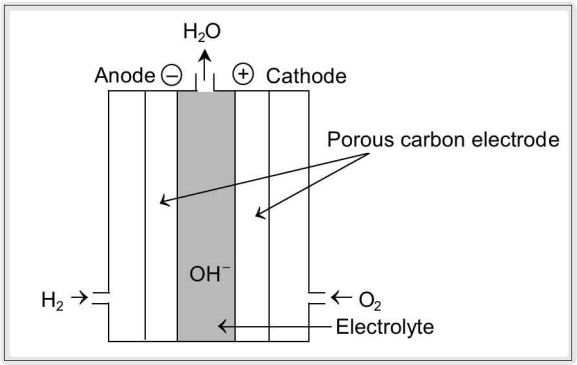


Fig. 9.17

1. **High efficiency:** The fuel cells convert the energy of a fuel directly into electricity and therefore, they are more efficient than the conventional methods of generating electricity on a large scale by burning hydrogen, carbon fuels. Though we expect 100 % efficiency in fuel cells, so far ***60–70% efficiency*** has been attained. The conventional methods of production of electrical energy involve combustion of a fuel to liberate heat which is then used to produce electricity. The efficiency of these methods is only about 40%.
2. **Continuous source of energy:** There is no electrode material to be replaced as in ordinary battery. The fuel can be fed continuously to produce power. For this reason, $H_2 - O_2$ fuel cells have been used in space crafts.
3. **Pollution free working:** There are no objectionable byproducts and, therefore, they do not cause pollution problems. Since fuel cells are efficient and free from pollution, attempts are being made to get better commercially practical fuel cells.

CORROSION



It is the oxidative deterioration of a metal due to its reaction with environment.

or

It is the process by which metals have the tendency to go back to there combined state i.e., reverse of extraction of metals.

Example, Rusting of Iron.

Rusting of Iron

Condition

Rusting of iron requires both oxygen and water, it does not occur in oxygen free water or in dry air.

Mechanism of Rusting

The rusting of iron

You may have performed some simple experiments to show that iron rusts only when there is water and oxygen present. Rust is a complicated material that contains various types of hydrated iron (III) oxide, $Fe_2O_3.xH_2O$. (The number of moles of water, x, varies.) Iron begins to rust at places on its surface where there is an impurity, or where the iron lattice has imperfections. At these points some iron atoms produce iron (II) ions in solution.

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

which shows that the iron suffers an oxidation. You may remember that an electrode where oxidation occurs is called the anode. As the iron(II) ions move away from the anode region they meet hydroxide ions and produce iron(II) hydroxide:

$$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2(s)$$

It is the dissolved oxygen that oxidizes the iron(II) hydroxide to the complicated substance we call rust:

$$Fe(OH)_2(s) + \text{dissolved oxygen} \rightarrow \text{rust, } Fe_2O_3xH_2O$$

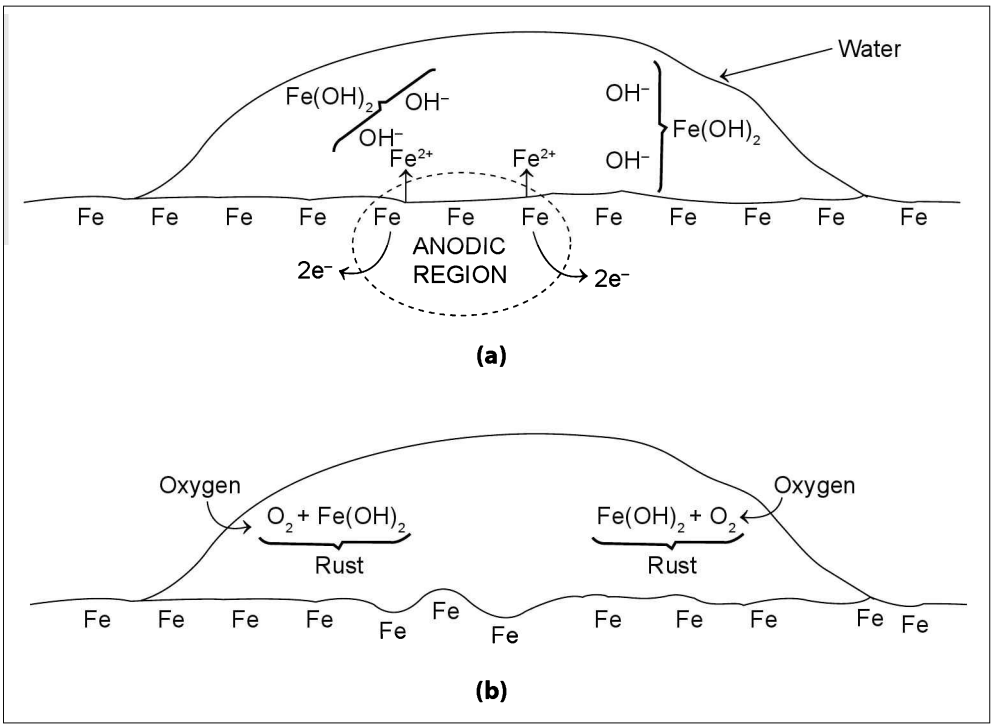
In water, there are hydrogen ions, especially if the water is at all polluted by gases such as sulphur dioxide. At a neighbouring point on the surface of the iron, the hydrogen ions take up the electrons liberated from the anode area:

$$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$$

This is a process of reduction, so we can call the place where it occurs the cathode. The hydrogen produced at the cathode also reacts with dissolved oxygen to make water.

It illustrates the fact that iron rusts at the anodic area. The surface of the iron and a droplet of surface water constitute a tiny galvanic cell in which different regions of the surface act as anode and cathode while the aqueous phase serves as the electrolyte.

If a drop of water covers an iron surface, the anodic region will be found near the centre of the drop, and the cathode at the edges. One reason for this is that there will be more oxygen dissolved from the air near the edges of the drop. Therefore, initially more rust will be made at the edges than at the centre. The layer of rust at the edges tends to prevent further corrosion taking place there. However, nearer the centre of the drop, where there is less oxygen, the iron(II) ions have time to float away from the surface, and rust particles are not made directly at the surface. This means the surface does not become coated with rust, so further corrosion can take place. This is why even a small break in the paintwork of a car can, in time, produce an enormous amount of corrosion under the paint some distance from the original blemish: the greatest amount of corrosion occurs some distance from the region where the most oxygen is available.



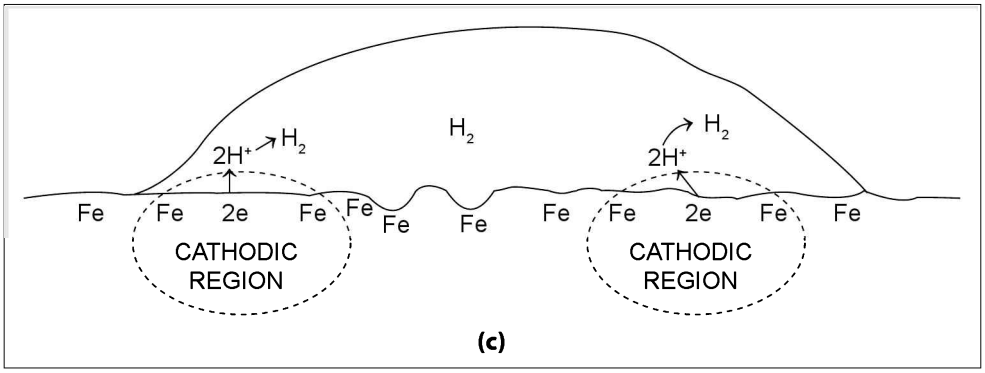


Fig. 9.18 Three stages in the rusting of iron. (a) Fe^{2+} ions go into the water and make $Fe(OH)_2$ with OH^- ions present in the water. Each Fe^{2+} ion leaves $2e^-$ in the metal lattice. (b) At the surface of the drop there is moer oxygen dissolved. Here rust is made. Where Fe atoms have made Fe^{2+}, holes appear in the lattice. (c) The electrons released combine with H^+ ions in water to give H_2 gas

Factors which enhance corrosion are:

(i) Presence of impurities in the metal (pure metals do not corrode)
(ii) Presence of moisture (example, in rainy season)
(iii) Presence of electrolytes (example, saline water)

Corrosion can be prevented by the following methods:

(i) Barrier protection by oil/grease layer, paints or electroplating
(ii) Sacrificial protection by coating the metal with more electropositive metal (example Zn called galvanization). When the metal is oxidized, zinc is oxidized instead of iron (as indicated by potentials). Also zinc can reduce Fe^{2+} to Fe.

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad E^o = 0.45\ V$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^o = -0.76\ V$$

(iii) Electrical protection by connecting the iron pipe to a more electropositive metal with a wire.

Explanation

How does a layer of zinc prevent iron rusting?

If iron is dipped into molten zinc (at about 450° C) it gains a layer of zinc over its surface. Iron with its layer of zinc is said to be galvanised. There are two reasons why the zinc prevents the iron rusting away. The first, most obvious, reason is that it prevents water or oxygen reaching the iron. The second, more interesting, reason is that even if the zinc becomes partially worn away, it still prevents rusting. Figure 9.19 will give you an idea of why this happens.

A somewhat similar situation arises to the zinc and copper. In that case, the copper was not worn away; rather, it provided a path for the reaction of zinc with hydrogen ions to give off hydrogen successfully. So it is with zinc and iron. Zinc has a more negative electrode potential than iron. (The values are $E^{\ominus}_{Zn^{2+}/Zn} = -0.76V, E^{\ominus}_{Fe^{2+}/Fe} = -0.44$ V.) therefore, zinc will react according to the equation and zinc is the anode. Zinc ions are converted into zinc hydroxide by hydroxide ions in the water.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

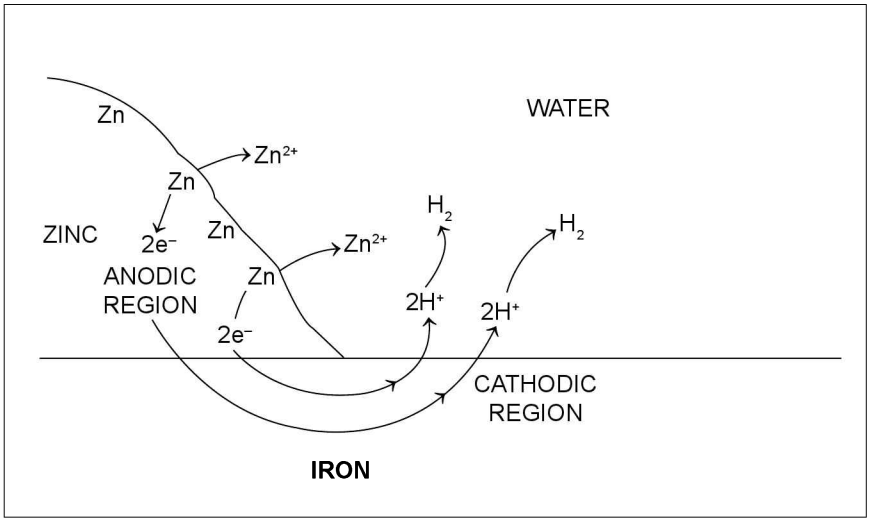


Fig. 9.19 A layer of zinc prevents iron from rusting. Instead of Fe^{2+} ions going into solution, Zn^{2+} ions are lost from the zinc. The electrons released into the lattice join with hydrogen ions in the water to make hydrogen. The hydrogen is produced at the iron surface

The electrons travel directly between the zinc and the iron, which in this case is the cathode. Where the iron is exposed to the surrounding water, hydrogen ions pick up the electrons:

The point is that the iron remains unaffected; it is protected from corrosion.

Why does tin protect iron from corrosion?

The enormous variety of 'tin cans' that are used for preserving foodstuffs, beer and so on shows that tin is very handy for protecting iron or steel. It is possible to plate steel with a very thin layer of tin much more easily than it is to plate with zinc. Also, tin is less reactive than zinc, so it is less likely to dissolve in liquids stored in the cans.

However, tin is not so effective as zinc in preventing corrosion. The electrode potentials are $E^{\ominus}_{Fe^{2+}/Fe} = -0.44$ V, $E^{\ominus}_{Sn^{2+}/Sn} = -0.14$ V. The iron is the more negative, so it behaves like the zinc in the previous example. The iron becomes the anode, at which the reaction takes place.

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

This tells us that the iron will dissolve. That is, it will corrode and the iron(II) ions go on to make rust. You can see that tin only protects iron provided the tin is not holed. Zinc continues to protect iron even if it is holed.

Conductance of Solutions

if an electric current is to pass between two points, there must be a movement of charged particles between the points. In a metal, the particles are the free electrons. If a voltage is applied across the ends of a metal wire, the free electrons will begin to move along the wire, and we could measure the current. However, if a current is to pass through a liquid:

There must be ions that are free to move.

Water itself is only very slightly dissociated into hydrogen and hydroxide ions, so pure water does not conduct very well. However, if we dissolve sodium chloride in water, the large number of free sodium and

chloride ions allows the solution to conduct very easily. Sodium chloride itself will conduct if it is molten. In this case, the crystal structure is broken down, freeing the ions to move about.

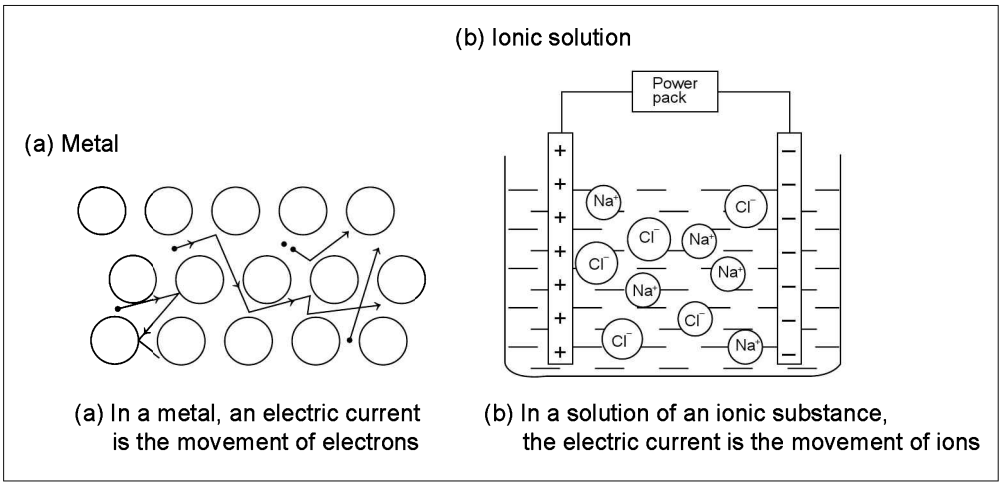


Fig. 9.20 Much exaggerated views of a metal and a solution of an ionic substance conducting an electric current,

You can see diagrams representing the movement of ions through a liquid. We have shown the positive ions moving towards the negative electrode, and the negative ions moving towards the positive electrode. However, our diagrams are much exaggerated; ions do not whizz from one side of the liquid to the other. Instead, there is a gradual drift of the ions in the two directions. A large current flows if there are a large number of ions present, all moving slowly, rather than a few ions moving at great speeds.

The resistance R offered by an electrolytic solution is found to change as follows.

$$R \propto l$$

[where l = distance between the parallel electrodes in the conductivity cell]

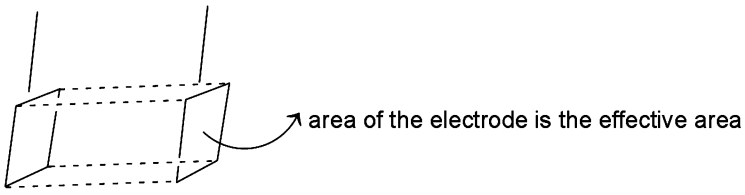
and $$R \propto \frac{l}{A}$$

[where A = **Effective** cross-sectional area of the electrode]

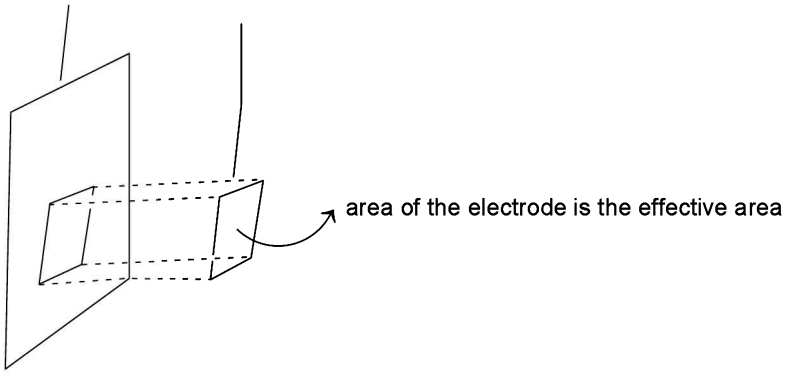
What is effective cross-sectional area?

The effective crosssectional area can be calculated as follows.

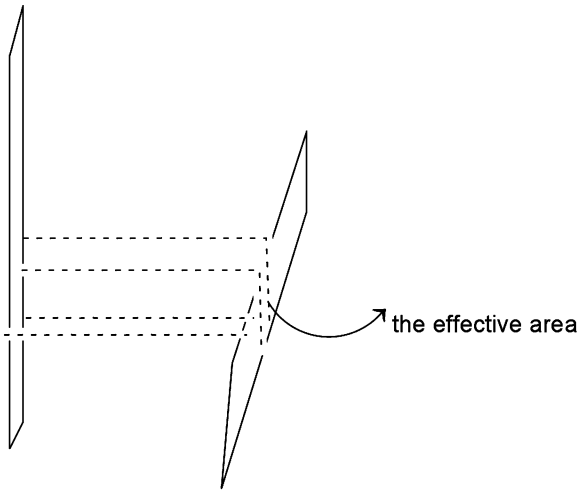
Case 1: When both the electrodes are of exactly equal dimension, we can take the area of either of the electrodes.



Case 2: When both the electrodes are of different dimensions, we can take the area of the smaller electrode.



Case 3: When the electrodes are of different dimension and different shapes the common area is taken



Which give $R \propto \frac{l}{A}$ (1)

Removing the proportionality sign, we have

$$R = \rho\left(\frac{l}{A}\right) \tag{2}$$

Where ρ is constant of proportionality and is called the resistivity. It is the resistance offered by a conductor of unit length and unit area of cross-section. The value of ρ depends on, and is characteristic of, the nature of the conductor.

The expression for the corresponding conductance G is

$$G = \frac{1}{R} = \frac{1}{\rho}\left(\frac{A}{l} = \kappa\left(\frac{A}{l}\right)\right) \tag{3}$$

where κ $(=1/\rho)$ is the conductivity of the conductor. This quantity may be considered to be the conductance of a cubic material of edge length unity.

In SI units, κ is expressed as $\Omega^{-1}\ m^{-1}$. It may also be expressed as $\Omega^{-1}\ cm^{-1}$. The unit Ω^{-1} is also conventionally written as mho, which is ohm spelled backward. In SI units, Ω^{-1} is known as siemens (S).

Conductivity is an additive property. For example, in an aqueous solution containing several electrolytes, the total conductance is

$$G_{total} = \sum_{1} G_1 + G_{water} \tag{4}$$

Where the summation is to be carried over all the electrolytes present in the solution and G_{water} is the conductance of water which is utilized for making the solution. G_{water} is often negligible in comparison to $\sum G_i$ as repeatedly distilled water (known as conductivity water) of very low conductance is employed for making the solution.

Equivalent and molar conducivities

Since the charges of solute ions are critical in determining the conductance of a solution, the comparison of conductance data in CGS units is made between values for solutions corresponding to a total of unit charge on each ion of the solute. It is because of this that the equivalent conductivity of the solution is employed for comparison purposes.

Suppose 1 equivalent mass of an electrolyte is dissolved in the volume V of the solution. Let this whole solution be placed in a conductivity cell. Multiplying and dividing the right hand side of Eq. (3) by the distance *l* between the two electrodes of the cell, we get

$$G = \kappa \frac{A \times l}{l^2} = \frac{\kappa V}{l^2} \quad \text{or } Gl^2 = \kappa V \tag{5}$$

The term Gl^2 is known as equivalent conductivity, abbreviated as Λ_{eq},

Thus, we have

$$\Lambda_{eq} = Gl^2 = \kappa V \tag{6}$$

The equivalent conductivity of an electrolyte may be defined as the conductance of a volume of solution containing one equivalent mass of a dissolved substance when placed between two parallel electrodes which are at a unit distance apart, and large enough to contain between them the whole solution.

The equivalent conductivity thus gives the conducting power of the ions produced by 1 equivalent mass (i.e., mass corresponding to a total of unit charge on each ion) of an electrolyte at any particular concentration.

The units of Λ_{eq} in CGS units are:

$$\Lambda_{eq} = (\Omega^{-1}\ cm^{-1})\ (cm^3) = \Omega^{-1}\ cm^2 \equiv S\ cm^2$$

If c is the concentration of the solution in equivalent per unit volume, then 1 equivalent mass of the substance will be contained in the volume (1 eq/c). Hence, Eq. (6) may be written as

$$\Lambda_{eq} = \kappa(1\ eq/c) \quad \text{or simply as } \Lambda_{eq} = \kappa/c \tag{7}$$

In SI units, c is expressed s the amount per unit volume instead of equivalent per unti volume, and thus one uses the term molar conductivity as defined belo .

The molar conductivity, Λ_m, of an electrolyte may be defined as the conductance of a volume of solution containing one mole of a dissolved substance when placed between two parallel electrodes which are at a unit distance apart, and large enough to contain between them the whole solution. Thus, it gives the conducting power of the ions produced by 1 mole of an electrolyte at any particular concentration. This can be calculated using the expressions analogous to Eqs. (6 and 7):

$$\Lambda_m = \kappa\ V \tag{8}$$

$$\Lambda_m = \kappa(1\ mol/c) \text{ or simply as } \Lambda_m = \frac{\kappa}{c} \tag{9}$$

where V is the volume of the solution containing one mole of the substance and c is the resultant molar concentration. The units of Λ_m will be

$$\Lambda_m = (\Omega^{-1}\ m^{-1})\ (m^3) = \Omega^{-1}\ m^2 \equiv S\ m^2$$

Since 1 mole of the substance is involved, the units are written as $\Omega^{-1}\ m^2\ mol^{-1}$. This unit also follows from Eq. (9).

Relation between Λ_e and Λ_m

$$\Lambda_m = {}_n\Lambda_e$$

Where n = n-factor of the electrolyte = total charge carried by either ion = $\frac{M}{E}$



Worked-out Example

51. When a certain conductance cell was filled with 0.02 M KCl solution (conductivity 0.002768 S cm^{-1}), it had a resistance of 82.4 ohm at 298 K. When filled with 0.005 N K_2SO_4, it had a resistance of 324 ohm. Calculate

(a) Cell constant
(b) Conductance of 0.005 N K_2SO_4 solution.
(c) Conductivity of 0.005 N K_2SO_4 solution.
(d) Equivalent conductivity of 0.005 N K_2SO_4 solution.
(e) Molecular conductivity of 0.005 N K_2SO_4 solution.

Solution **From KCl data:** $\kappa = \frac{1}{R} \times \frac{1}{a}$

$$\therefore \quad \frac{1}{a} = \kappa \times R = 0.002768 \times 82.4$$
$$= 0.2281 \text{ cm}^{-1}$$

From K_2SO_4 data: R = 324 ohm

$$C = \frac{1}{R} = \frac{1}{324} = 3.086 \times 10^{-3} \text{ S}$$

$$\text{Also } \kappa = C \times \frac{1}{a} = 3.086 \times 10^{-3} \times 0.2281$$
$$= 7.04 \times 10^{-4} \text{ S cm}^{-1}$$

$$\text{Now } \lambda = \kappa \times \frac{1000}{N}$$
$$= 7.04 \times 10^{-4} \times \frac{1000}{0.005}$$
$$= 140.80 \text{ S cm}^2 \text{ eq.}^{-1}$$

$$\text{Also } \Lambda = \kappa \times \frac{1000}{M}$$
$$= 7.04 \times 10^{-4} \times \frac{1000 \times 2}{0.005}$$

(N = 2M, because K_2SO_4 is bivalent)

$$= 281.6 \text{ S cm}^2 \text{ mol}^{-1}$$

Variation of Conductance with Dilution

Upon dilution i.e., lowering concentration, specific conductance decrease while equivalent and molar conductances increase. At infinite or almost zero concentration, equivalent conductance and molar conductance attain their respective limiting values called equivalent conductance at infinite dilution (Λ_∞) or

zero concentration ($\wedge_0$) and molar conductance at infinite dilution $\left(\wedge_m^\infty\right)$ or zero concentration $\left(\wedge_m^0\right)$, respectively. The increase of $\wedge$ or $\wedge_m$ with dilution of a weak electrolyte is attributable to increase of degree of dissociation with dilution resulting into more number of ions in solution. Note that ions are carriers of electricity. The increase of $\wedge$ and $\wedge_m$ of a strong electrolyte which remains completely ionised at all dilutions, is attributed to increase in the ionic mobilities of ions due decrease in inter-ionic attraction. As dilution approaches unity, the member of ions becomes maximum and hence $\wedge$ as well as $\wedge_m$ approach their respective maximum value. In the case of strong electrolyte, however, the maximum value of $\wedge$ or $\wedge_m$ is attained due to the maximum ionic mobilities of the ions since at infi nite dilution the dissociation of strong electrolyte is complete and inter-ionic attraction cases to exist completely.

The decrease in K may also be explained in the following way. Upon dilution the number of ions, in the case of weak electrolyte, increase but volume of solution also increases. The increase of volume is in greater proportion than the increase of number of ions resulting into decrease in number of ions per c.c. solution. The specific conductivity being the conductivity of 1 c.c. solution, should obviously decrease.

The variation of molar conductance of a strong electrolyte with concentration is theoretically give by Debye-Hückel-Onsager equation

$$\wedge_m = \wedge_m^0 - \left(A + B \wedge_m^0\right)\sqrt{C}$$

Where A and B are the Debye-Hückel constants depending upon nature of the solvent and temperature and C is the molar concentration of solution. For aqueous medium at 25°C:

$$\wedge_m = \wedge_m^0 - \left(60.2 - 0.299 \wedge_m^0\right)\sqrt{C}$$

According to this equation a plot of $\wedge_m$ vs $\sqrt{C}$ should be a straight line having the slope equal to 60.2 + 0.229 $\wedge_m^0$ and intercept equal to $\wedge_m^0$. This has been checked in the case of a number of uni-univalent electrolytes and found to be true for $C \leq 0.02$ M.

At higher concentration, the observed deviation from linearity is attributable to large inter-ionic attraction.

Determination of conductance (k, $\wedge$ and $\wedge_m$)

As already mentioned above

$$K = \text{conductance} \times \frac{\ell}{a}$$

For a given conductivity cell in a given experiment: $\frac{\ell}{a}$ = constant called cell constant (x). Thus,

$$K = \text{conductance} \times x = \frac{1}{\text{resistance}} \times x$$

The resistance of a solution is determined by Wheatstone bridge method using a meter bridge the conductivity dipped in the test solution. The current used is AC.

The specific conductance of 0.1M KCl solution is known. The resistance of 0.1M KCl solution is first determined experimentally from the cell, it is washed with conductivity water and then filled with test solution. The resistance of the test solution is measured and since cell constant is already known so specific conductance of the test solution can be calculated.

From specific conductance, we determine $\wedge$ and $\wedge_m$ using the equation (3) and equation (4) respectively.

Determination of $\wedge_m^0$ or $\wedge^0$

A plot of $\wedge_m$ vs $\sqrt{C}$ as found experimentally is as shown below graphically.

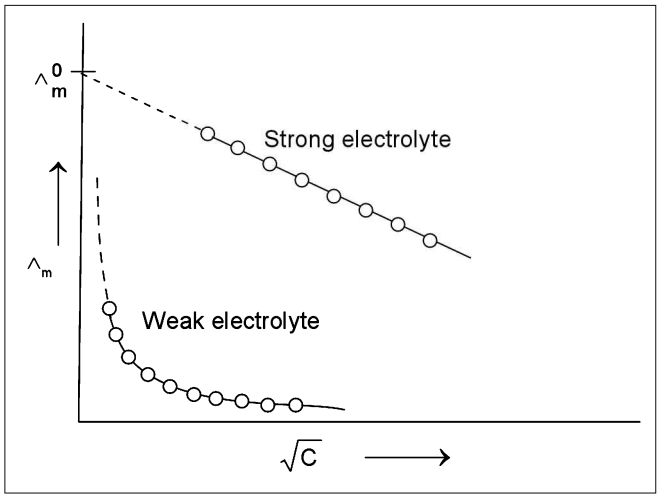


Fig. 9.21

The $\wedge_m$ vs $\sqrt{C}$ plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus, $\wedge_m$ values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

$\wedge_m$ values are then plotted against $\sqrt{C}$ when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects $\wedge_m$ axis is $\wedge_m^0$ of the strong electrolyte.

However, the plot in the case of weak electrolyte being non linear shooting up suddenly at some low concentration and assuming the shape of a straight line to $\wedge_m$ axis. Hence extrapolation in the case is not possible. Thus, $\wedge_0$ of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlransch's law to be discussed later.

Kohlrausch's Law of Independent Migration of Ions

For a strong electrolyte, the value of Λ_m in a very dilute solution, say in 0.001 or 0.000 1 mol dm^{-3} solution, is very close to the limiting value of the conductivity Λ_m^∞ at infinite dilution (or at zero concentration obtained by extrapolation). On the other hand, the corresponding value for a weak electrolyte is very far away from the limiting value at zero concentration. For example, at 25°C for 0.001 mol dm^{-3} sodium chloride solution Λ_m is 123.7 ohm^{-1} cm^2 mol^{-1} s against Λ_m^∞ of 126.5 ohm^{-1} cm^2 mol^{-1}. At the same concentration and temperature, the value for acetic acid is 49.2 ohm^{-1} cm^2 mol^{-1} as compared to 390.7 ohm^{-1} cm^2 mol^{-1} for the value of Λ_m^∞.

Kohlrausch was the first to pin out that when Λ_m for a uni-univalent strong electrolyte is plotted against $\sqrt{c}$, the curve approaches linearity in dilute solutions, i.e.,

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$$

where b is constant. The valueof Λ_m^∞ can, thus, be obtained by extrapolating the above curve to value of $\sqrt{c} = 0$

The extrapolation method cannot be employed for weak electrolytes as Λ_m versus $\sqrt{c}$ curve does not approach linearity in solutions as dilute as 0.0001 mol dm^{-3}. In fact, the variation of Λ_m with dilution is very rapid.

However, the value of Λ_m^∞ for weak electrolytes can be determined by the application of Kohlraush's law of independent migration of ions. This law states that at infinite dilution, where dissociation for all electrolytes is complete (including the weak electrolytes since $\alpha \rightarrow 1$ as $c \rightarrow 0$; Ostwald dilution law) and where all interionic effects disappear (because of larger distance between ions), each ion migrates independently of its co-ion and contributes to the total molar conductivity of an electrolyte a definite share which depends only on its own nature and not at all on the ion with which it is associated.

Evidence for the validity of the above law can be seen from the data of Λ^∞ given in table 9.1.

Table 9.1 Evidence for Kohlrausch's Law

Electrolyte	$\Lambda^\infty/\Omega^{-1}$ *cm²* *mol⁻¹ at 25°C*	*Difference* $\Delta\Lambda^\infty/\Omega^{-1}$ *cm²* *mol⁻¹*	*Electrolyte*	$\Lambda^\infty/\Omega^{-1}$ *cm²* *mol⁻¹ at 25°C*	*Difference* $\Delta^\infty/\Omega^{-1}$ *cm²* *mol⁻¹*
KCl	149.9	34.9	HCl	426.2	4.9
LiCl	115.0		HNO_3	421.3	
KNO_3	145.0	34.9	KCl	149.9	4.9
$LiNO_3$	110.1		KNO_3	145.0	
KOH	271.5	34.8	LiCl	115.0	4.9
LiOH	236.7		$LiNO_3$	110.1	

According to Kohlrausch's law, we should have that is, the difference between they Λ^∞s of electrolytes containing a common ion should be equal to the difference in molar conductivities of ions not in common.

$$\Lambda^\infty(AB) - \Lambda^\infty(CB) = \lambda^\infty(A^+) + \lambda^\infty(B^-) - \lambda^\infty(C^+) - \lambda^\infty(B^-)$$
$$= \lambda^\infty(A^+) - \lambda^\infty(C^+)$$

or $$\Lambda^\infty(AB) - \Lambda^\infty(AC) = \lambda^\infty(A^+) + \lambda^\infty(B^-) - \lambda^\infty(A^+) - \lambda^\infty(C^-)$$
$$= \lambda^\infty(B^-) - \lambda^\infty(C^-)$$

The difference of Λ^∞ of different pairs of uni-univalent electrolytes having either cation or anion common and having the same two anions or cations uncommon should yield a constant value. In line with this requirement, we see that irrespective of the nature of the co-ion, the difference between the conductivities of K^+ and Li^+ is constant (=34.9 Ω^{-1} cm² mol^{-1}) and the same is true for the difference in conductivities between Cl^- and NO_3^- ions (=4.9 Ω^{-1} cm² mol^{-1}).

Based on Kohlrausch's law, it is possible to calculate the molar conductivity of a weak electrolyte at infinite dilution by simply adding and sub-tracting Λ^∞ values of appropriate electrolytes. Taking, for example, acetic acid, we have

$$\Lambda^\infty(HAc) = \Lambda^\infty(NaAc) + \Lambda^\infty(HCl) - \Lambda^\infty(NaCl)$$
$$= \lambda^\infty(Na^+) + \lambda^\infty(Ac^-) + \lambda^\infty(H^+) + \lambda^\infty(Cl^-) - \lambda^\infty(Na^+) - \lambda^\infty(Cl^-)$$
$$= \lambda^\infty(H^+) + \lambda^\infty(Ac^-) = \Lambda^\infty(HAc)$$

For an electrolyte other than uni-univalent, the molar conductivity can be evaluated by using the expression

$$\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu^-\lambda_-^\infty$$

where ν_+ and ν_- are the respective stoichiometric numbers of cation and anion of the electrolyte.

Values of limiting ionic molar conductivities

Since the fraction of the total current carried by any ion is given by its transference number, the latter must also represent the fraction of the total conductivity due to the ion. Consequently, Λ_+^∞ and Λ_-^∞ are also related to Λ^∞ by the relations

$$\lambda_+^\infty = t_+^\infty \Lambda^\infty$$

$$\lambda_-^\infty = t_-^\infty \Lambda^\infty$$

t_+^∞ and t_-^∞ being the transference numbers at infinite dilution as obtained by extrapolation. These equations permit the calculation of the limiting ionic conductivities from transference numbers and Λ^∞ values of strong electrolytes. For example, Λ^∞ for hydrochloric acid at 25 °C is 426.14 Ω^{-1} $cm^2 mol^{-1}$, while t_+^∞ of the hydrogen ion is 0.820 9. Therefore,

$$\lambda^\infty(H^+) = 0.8209 \times 426.14\ \Omega^{-1}cm^2mol^{-1}$$
$$= 349.82\ \Omega^{-1}cm^2mol^{-1}$$
$$\lambda^\infty(Cl^-) = 0.1791 \times 426.14\ \Omega^{-1}cm^2mol^{-1}$$
$$= 76.32\ \Omega^{-1}cm^2mol^{-1}$$

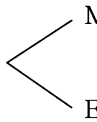
The molar ionic conductivities of other ions have similarly been evaluated. The ionic conductivities of ions of weak acids or bases were deduced from the Λ^∞s of their salts, which are strong electrolytes.

Remember the following points regarding Kohlraush law for indepenent migration of ions.

1. Valid only at infinite dilution
2. 100% ionization of electrolyte will take place regardless of its nature (weak or stray) CO_3 at infinite dilution weak electrolyte will also dissociate completely and behave as strong electrolyte.
3. At infinite dilution, the ions are so far apart from each other that the interionic attraction is zero and coch ion can migrate independently.

At infinite dilution each ion can contribute a definite fraction (Ionic conductance) towards the overall equivalence conductance of the electrolyte

Ionic conductance is fixed for a given ion and it does not depend on combination of ions

Ionic Conductance (λ°_{ion})  Molar ionic conductance $\lambda^\circ_m(Al^{3+})$; Equivalence ionic conductance $\lambda^\circ_c(Al^{3+})$

$\lambda^\circ_m = \lambda^\circ_e \times$ 'n- factor'

' n-factor' of any ion is its valency of that ion i.e., it is the numerical value of the charge on that ion.

For example, it is '2' for SO_4^{2-}, '3' for Al^{3+} etc., and the relation stands as follows:

$$\lambda^\circ_m(Al^{3+}) = \lambda^\circ_e(Al^{3+}) \times 3$$

Relation between the molar or equivalent conductance of an electrolyte with the molar or equivalent ionic conductance

E.g., $Al_2(SO_4)_3$

$$\lambda^\circ_m[Al_2(SO_4)_3] = 2\lambda^\circ_m(Al^{3+}) + 3\lambda^\circ_m(SO_4^{2-})$$

$$\lambda^\circ_e[Al_2(SO_4)_3] = \frac{\lambda^\circ_m[Al_2(SO_4)_3]}{\text{'n factor'}} = \frac{\lambda^\circ_m[Al_2(SO_4)_3]}{6}$$

$$\lambda^\circ_e[Al_2(SO_4)_5] = \frac{1}{3}\lambda^\circ_m(Al^{3+}) + \frac{1}{2}\lambda^\circ_m(SO_4^{2-})$$

Relation between equivalence ionic conductance and molar ionic conductance

To find relation between equivalence ionic conductance and equivalence ionic conductance (R.H.S.

$$\lambda^{\circ}_{e}[Al_2(SO_4)_3] = \frac{1}{3}[\lambda^{\circ}_{e}(Al^{3+}) \times 3] + \frac{1}{2}[\lambda^{\circ}_{e}(SO_7^{2-}) \times 2]$$

$$X^{\circ}_{e}(Al_2(SO_4)_3] = \lambda^{\circ}_{e}(Al^{3+}) + \lambda^{\circ}_{e}(SO_4)^{2-}$$

For single salt equivalence ionic conductances can be directly added to get the value of equivalent conductance of the salt,However, the relation can be different for a double salt.Let us consider the following example.



Worked-out Examples

52. How will you calculate the molar conductivity and equivalent conductivity at infinite dilution of potash alum?

Solution The formula of potash alum is $K_2SO_4.Al_2(SO_4)_3.24H_2O$. Thus, at infinite dilution 1 mol of potash alum will produce 2 mol of K^+, 2 mol of Al^{3+} and 4 mol of SO_4^{2-}.

Hence, Λ^{∞}_{m} (potash alum)$=2\lambda^{\infty}_{m}(K^+) + 2\lambda^{\infty}_{m}(Al^{3+}) + 4\lambda^{\infty}_{m}(SO_4^{2-})$

Since total positive (or negative) charge carried by 1 mol of potash alum in 8, one equivalent of the salt will be equal to (1/8) of one mole.

Hence, Λ^{∞}_{m} (potash alum $= \frac{1}{8}\Lambda^{\infty}_{m}$ (potash alum)

$$= \frac{1}{4}\lambda^{\infty}_{m}(K^+) + \frac{1}{4}\lambda^{\infty}_{m}(Al^{3+}) + \frac{1}{2}\lambda^{\infty}_{m}(SO_4^{2-})$$

Since $\lambda_m(SO_4^{2-}) = 2\lambda_{eq}(\frac{1}{2}SO_4^{2-})$ and $\lambda_m(Al^{3+}) = 3\lambda_{eq}(\frac{1}{3}Al^{3+})$,

We will have

$$\Lambda^{\infty}_{eq}(\text{potash alum}) = \frac{1}{4}\lambda^{\infty}_{eq}(K^+) + \frac{3}{4}\lambda^{\infty}_{eq}(\frac{1}{3}Al^{3+}) + \lambda^{\infty}_{eq}(\frac{1}{2}SO_4^{2-})$$

The degree of dissociation (α) of weak electrolyte at a concentration 'c' molar is given as follows

$$\alpha = \frac{\text{No. of moleculars ionised}}{\text{total number of molecules dissolved}} = \frac{\wedge_m}{\wedge^0_m}$$

Where λ_m is the

53. Calculate molar conductivity for NH_4OH given that molar conductivity for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 S cm^3 mol^{-1} respectively.

Solution $\Lambda^{\circ}_{Ba(OH)_2} = \lambda^{\circ}_{Ba^{2+}} + 2\lambda^{\circ}_{OH^-} = 523.28$ .....(1)

$\Lambda^{\circ}_{BaCl_2} = \lambda^{\circ}_{Ba^{2+}} + 2\lambda^{\circ}_{Cl^-} = 280.00$ ....(2)

$\Lambda^{\circ}_{NH_4Cl} = \lambda^{\circ}_{NH_4^+} + \lambda^{\circ}_{Cl^-} = 129.80$ ...(3)

Multiply Eq. (3) by two and subtract from Eq. (2)

$\lambda^{\circ}_{Ba^{2+}} - 2\lambda^{\circ}_{NH_4^+} = 280 - 2 \times 129.8$ ....(4)

$\therefore \quad \lambda^{\circ}_{Ba^{2+}} - 2\lambda^{\circ}_{NH_4^+} = 20.40$ ....(5)

Now subtract Eq. (5) from Eq.(1)

$$2\lambda^{\circ}_{NH_4^+} + 2\,2\lambda^{\circ}_{OH^-} = 502.88$$

$$\therefore\ \lambda^{\circ}_{NH_4^+} + \lambda^{\circ}_{OH^-} = \Lambda^{\circ}_{NH_4OH} = \frac{502.88}{2}$$

$$= 251.44 \text{ S cm}^2 \text{ mol}^{-1}$$

54. The molecular conductivity of acetic acid at infinite dilution is 390.7 and for 0.1 M acetic acid solution is 5.2 S $cm^2 mol^{-1}$.

Calculate:

(1) degree of dissociation of acetic acid.

(2) $[H^+]$ in solution.

Solution The degree of dissociation 'α' is given by

$$\because\ \alpha = \frac{\lambda_v}{\lambda^{\circ}} = \frac{5.2}{390.7}$$

$\alpha = 0.0133$ or 1.33%

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Before dissociation	1	0	0
After dissociation	(1–α)	α	α

$\therefore\ [H^+] = C\alpha = 0.1 \times 0.0133 = 0.00133$ M

55. Conductance (Siemens, S) is directly proportional to the area of the vessel and the concentration of solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is: **[AIEEE-2002]**

(a) S m mol^{-1} (b) S m^2 mol^{-1}

(c) S^{-2} m^1 mol (d) S^2 $m^2 mol^{-2}$

Solution (b) c ∝ a and c ∝ molarity $\propto \frac{1}{l}$

$$c \propto \frac{a}{l} \times \text{molarity} = K \times \frac{a}{l} \times \text{molarity}$$

$$\therefore \text{ Unit of } K = S\ \frac{m}{m^2} \times \frac{(m^3)}{mol.} = S\ m^2\ mol^{-1}$$

56. The limiting molar conductivities Λ° for NaCl, KBr and KCl and 126, 152 and 150 S cm^2 mol^{-1} respectively. The Λ° for NaBr S cm^2 mol^{-1} is: **[AIEEE-2004]**

(a) 302 (b) 176 (c) 278 (d) 128

Solution (d)

57. The highest electrical conductivity of the following aqueous solutions is of: **[AIEEE-2005]**

(a) 0.1 M acetic acid (b) 0.1 M chloroacetic acid

(c) 0.1 M fluoroacetic acid (d) 0.1 M difluoroacetic acid

Solution (d) Difluoroacetic acid is strong acid due to –IE of fluorine atoms.

58. The molar conductance of acetic acid at infinite dilution Λ° for CH_3COONa, NaCl and HCl are 91.0, 126.5 and 426.2 S cm^2 mol^{-1} respectively: **[AIEEE-2005]**

(a) 517.2 (b) 552.7

(c) 390.7 (d) 217.5

Solution (c)

59. The molar conductivity Λ°_{NaOAc} and Λ°_{HCl} at infinite dilution in water at 25°C are 91.0, 426.2 S cm^2 mol^{-1} respectively. To calculate Λ°_{HAc}, the additional value required is: **[AIEEE-2006]**

(a) $\Lambda^{\circ}_{H_2O}$ (b) Λ°_{KCl}

(c) Λ°_{NaOH} (d) Λ°_{NaCl}

Solution (d)

60. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 ohm. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell filled with 0.02 M of the same solution if the electrolyte is 520 ohm. The molar conductivity of 0.02 M solution of electrolyte would be: **[AIEEE-2006]**

(a) 124×10^{-4} S m^2 mol^{-1}

(b) 1240×10^{-4} S m^2 mol^{-1}

(c) 1.24×10^{-4} S m^2 mol^{-1}

(d) 12.4×10^{-4} S m^2 mol^{-1}

Solution (a) at C = 0.1 M;

$$\frac{l}{a} = \kappa R = 1.29 \times 100$$

at C = 0.02 M;

$$\kappa = \frac{1}{a \times R} = \frac{1.29 \times 100}{520} = 0.248 \text{ ohm}^{-1} \text{ m}^{-1}$$

Also

$$\Lambda = \frac{\kappa}{M(\text{in mole/l})} = \frac{\kappa}{M \times 10^3 (\text{in mole/m}^3)} = \frac{0.248}{0.02 \times 10^3} = 124 \times 10^{-4} \text{ Sm}^2 \text{mol}^{-1}$$

Mobility

The velocity (w) of an ion in the solution depends on the following factors:

1. Nature of the ion
2. Nature of the solvent
3. Distance between the parallel electrodes (l)
4. Potential difference applied across the electrodes (V)

If we fix up the first two factor by specifying the nature of the ion and nature of the solvent, it will depend on distance between the parallel electrodes(l) and potential difference applied across the electrodes(V) only.

Therefore, the velocity of a given ion in the aqueous solution has been found to change with 'V' and 'l' as follows:

$$w \propto \text{'V'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$w \propto \frac{1}{l} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Combining the above equation we get.

$$w \propto \frac{V}{l} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Now we can bring a proportionality constant, say 'u' and we get the following relation:

$$w = u\frac{V}{l} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Like every proportionality constant, this 'u' does not depend on the variables i.e., distance between the parallel electrodes(l) and potential difference applied across the electrodes(V). It depends on nature of the ion and nature of the solvent. If we specify the nature of the ion and nature of the solvent, it will have a fixed value.This 'u' is called the mobility and it is constant for a given ion in the aqueous solution.

What is this $\frac{V}{l}$?

The ratio $\frac{V}{l}$ represents the potential defference applied per unit length between the parallel electrodes. This is known as **Potential gradient.** It has the unit of Volt cm^{-1} or Volt m^{-1}.

We can see from equation (4) that velocity is proportional to Potential gradient but mobility being a proportionality constant is independent of the potential gradient.

What can be the definition of mobility

We know, $w = u\frac{V}{l}$ **.....(4)**

When potential gradient $\frac{V}{l}$ is unity we get, $w = u$.

Hence, we can say

'Absolute mobility is the velocity of the ion in the solution under unit potential

$$\text{equivalent ionic conductance} = \frac{\text{Absolute Ionic mobility}}{96{,}500}$$

What is the unit of mobility?

We know, $w = u\frac{V}{l}$ or, $u = \frac{wl}{V} = \frac{(cms^{-1})(cm)}{Volt} =$ **$cm^2Volt^{-1}s^{-1}$** (Unit of mobility)

How does mobility change with solvent?

In ionic or polar protic solvent, the mobility decreases with increasing charge density of the ion.This is due to greater extent of hydration of the ion with increasing charge density. More hydrated ion cannot move that freely, hence, they are less mobile.

The mobilties of the following ion in water are given as:

$$Li^+_{aq} > Na^+_{aq} > K^+_{aq} > Rb^+_{aq}$$

Exactly opposite order is found in nonpolar aprotic solvent (such as CCl_4)

$$Li^+ < Na^+ < K^+ < Rb^+$$

Worked-out Examples

61. At 18°C, the velocity of migration of Ag^+ ion is 0.00057 cm sec^{-1} and that of NO_3^- is 0.00063 cm sec^{-1} and that of NO_3^- is 0.00063 cm sec^{-1} at infinite dilution. What is the equivalent conductivity of $AgnO_3$ at infinite dilution?

Solution We have, $\lambda^\circ_{cation} = u^\circ_{cation} \times$ Faraday

$= 0.00057 \times 96500$

$\lambda^\circ_{Ag^+} = 55.005$ S cm^2 $eq.^{-1}$

Also $\lambda^\circ_{anion} = u^\circ_{anion} \times$ Faraday

$= 0.00063 \times 96500$

or $\lambda^{\circ}_{NO_3^-} = 60.795 \text{ S cm}^2 \text{ eq.}^{-1}$

Now from Kohlrausch law,

$$\lambda^{\circ}_{AgNO_3} = \lambda^{\circ}_{Ag^+} + \lambda^{\circ}_{NO_3^-}$$
$$= 55.005 + 60.795$$
$$= 115.8 \text{ S cm}^2 \text{ eq.}^{-1}$$

62. A dilute solution of KCl was placed between two Pt electrode 10.0 cm apart, across which a potential difference of 6.0 volt was applied. How for would K^+ ions move in 2 hour at 25°C? Ionic conductivity of K^+ at infinite dilution is 73.52 S cm^2 eq^{-1}. at 25°C.

Solution $\lambda^{\circ}_{K^+} = 73.52$

Ionic mobility, $u^{\circ}_{K^+} = \dfrac{\lambda^{\circ}_{K^+}}{F} = \dfrac{73.25}{96500}$

$$= 7.619 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$$

Potential gradient applied $= \dfrac{6.0}{10} = 0.6 \text{ volt cm}^{-1}$

$\therefore$ Speed of K^+ = ionic mobility × potential gradient

$$= 7.619 \times 10^{-4} \times 0.6 \text{ cm sec}^{-1}$$
$$= 45.714 \times 10^{-5} \text{ cm sec}^{-1}$$

$\therefore$ Distance traveled by K^+ in 2 hour

$$= 45.714 \times 2 \times 60 \times 60 \times 10^{-5}$$
$$= 3.292 \text{ cm}$$

63. The ionic mobility of alkali metal ion in aqueous solution is maximum for: **[AIEEE-2006]**

(a) K^+ (b) Rb^+

(c) Li^+ (d) Na^+

Solution (b) The hydrated ion size is:

$$Li^+_{aq} > Na^+_{aq} > K^+_{aq} > Rb^+_{aq}$$

Larger is size of ion, lesser is its conductance.

Abnormal mobilities or ionic conductances of hydrogen and hydroxyl ions

Hydrogen and hydroxyl ions were found to have unusually high mobilities, and hence ionic conductances in hydroxylic solvents, particularly in water, are comparatively large, At one time, the high mobility of hydrogen ion (H^+) was attributed to its small size. But with the discovery of the fact that in water of hydrogen ion always remains hydrated, i.e., as H_3O^+ it was found that the effective radius of hydrogen ion is not so small that it could account for the high mobility of the ion. On the other hand if the mechanism of conduction of electricity by thee ions was same as that by other ions, the mobility would have not assumed such a high value. In most of the non-aqueous solvents, H_3O^+ and OH^- have normal values of mobilities**. It is to be remembered that the abnormal values are manifested only in water and lower alcohols.** It is quite likely, therefore, that the solvent somehow helps in the conduction of electricity. It is now believed that these high mobilities of the two ions may be due to Grotthuss type of mechanism. This process involves the transfer of a proton (H^+) from H_3O^+ to the adjacent H_2O molecule and from the resulting H_3O^+ to the next H_2O molecule, and it is in this way that proton would move through much larger distance in shorter time. The actual distance traveled is about 0.86×10^{-10} m, while the effective distance through which the proton moves is 3.1×10^{-10} m. Entire mechanism may be seen in the diagram (Fig. 9.22) given ahead.

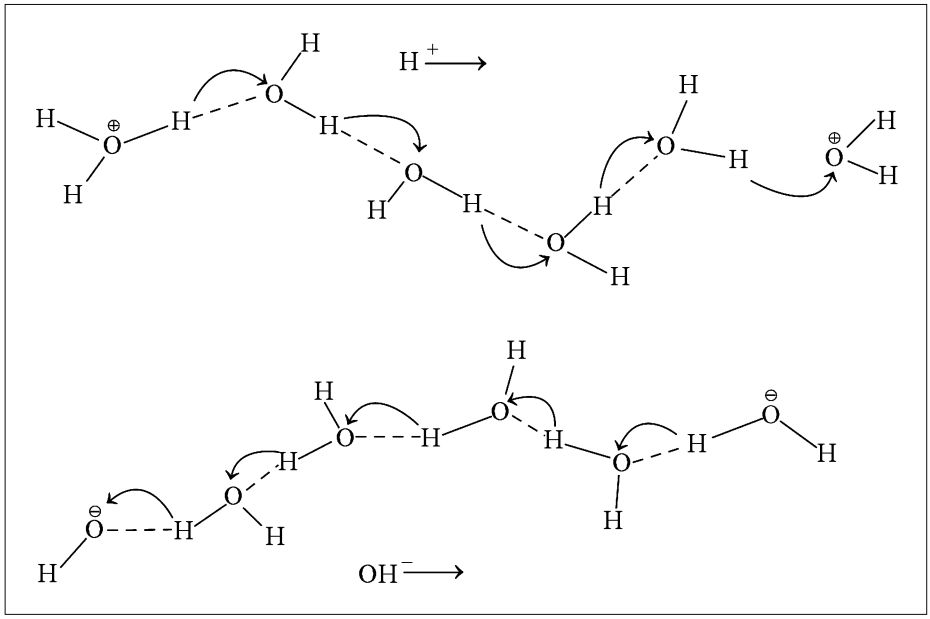
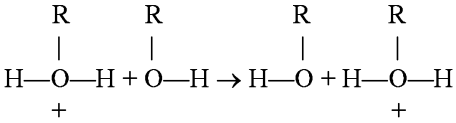


Fig. 9.22 Grotthus mechanism in aqueous solutions—transport of H^+ and OH^- under the applied field.

With alcohols, the proton transfer, likewise, occurs as follows:



The abnormality in the case of OH^- ion isnot as greater as in the case of H_3O^+ ion. Nevertheless the mobility of ions in water is nearly three times the average mobility of other ions. The movement of hydroxyl ion in water is also believed to occur via a proton transfer as shown in Fig. 9.22.

Transport number or Transference number

1. **Definition:** "*The fraction of the total current carried by an ion is known as transport number, transference number or Hittorf number may be denoted by sets symbols like* t_+ *and* t_- *or* t_c *and* t_a *or* n_c *and* n_a*"*. From this definition

$$t_a = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}}$$

$$t_c = \frac{\text{Current carried by a cation}}{\text{Total current passed through the solution}}$$

evidently, $t_a + t_c = 1$.

2. **Determination of transport number:** Transport number can be determined by *Hittorf's method, moving boundary method, emf method and from ionic mobility.*
3. **Factors affecting transport number**
   A rise in temperature tends to bring the transport number of cation and anion more closer to 0.5
4. **Transport number and Ionic mobility:** Ionic mobility or Ionic conductance is the conductivity of a solution containing 1 *g* ion, at infinite dilution, when two sufficiently large electrodes are placed 1 cm apart.
   Ionic mobilities (λ_a or λ_c) $\propto$ speeds of ions (u_a or u_c)
   Unit of ionic mobility is Ohm^{-1} cm^2 *or* $V^{-1}S^{-1}cm^2$
   Ionic mobility and transport number are related as,

$$\lambda_a \text{ or } \lambda_c = t_a \text{ or } t_c \times \lambda_\infty .$$

Worked-out Example

64. The equivalent conductivity of KCl at infinite dilution is 130 S cm^2 eq^{-1}. The transport no. of Cl^- ion in KCl at the same temperature is 0.505. What is the limiting ionic mobility and ionic conductance of K^+ ion?

Solution Transport no. $t_{Cl^-} = 0.505$

$\because \quad t_{K^+} + t_{Cl^-} = 1$

$\therefore \quad t_{K^+} = 1 - 0.505 = 0.495$

Also we have

Ionic conductance $\quad \lambda^\circ_{K^+} = \lambda^\circ_{KCl} \times t^\circ_{K^+} = 130 \times 0.495 = 64.35$

Also $\quad \lambda^\circ_{K^+} = u^\circ_{K^+} \times F$

$\therefore$ Limiting ionic mobility $(u^\circ_{K^+}) = \dfrac{64.35}{96500} = 6.67 \times 10^{-4}$ cm^2 sec^{-1} $volt^{-1}$

Conductometric titration

Exceptionally high conductivities of H_3O^+ and OH^- form the basis of such titrations. When an alkali is added to a strong acid solution, highly conducting hydrogen ions are replaced by slow moving alkali metal ions, and non-conducting water molecules are formed.

$$H + A^- + MOH \rightarrow M^+ A^- + H_2O$$

As a result, there is a fall in the conductance until the neutralization point is reached. Further addition of OH^- (from base) results in an increase in the conductivity. Thus, at the neutral point, the conductance of the system will be minimum. The end point can be estimated graphically by plotting the conductance values (y-axis) as a function of the amount of titrant added (x-axis). The shape of such titration curves depends upon the nature of the acid and the base being titrated.

Some typical titrations are described below.

Strong acid vs strong base

Let us follow the variation of conductance of a solution of a strong acid on gradual addition of a solution of a strong base. Suppose that we had taken 10 cm^3 of an N/10 HC1 solution in a conductivity cell and that 1*N* NaOH solution is added to it dropwise.

At the start, the solution contains only H^+ and Cl^- ions, and naturally it would have appreciable conductance due to the presence of hydrogen ion. As the drops of alkali are added, H^+ ions are removed from the solution, forming undissociated water molecules, according to the following equation;

$$(H^+ + C1^-) + (Na^+ + OH^-) \rightarrow (Na^+ + Cl^-) + H_2O$$

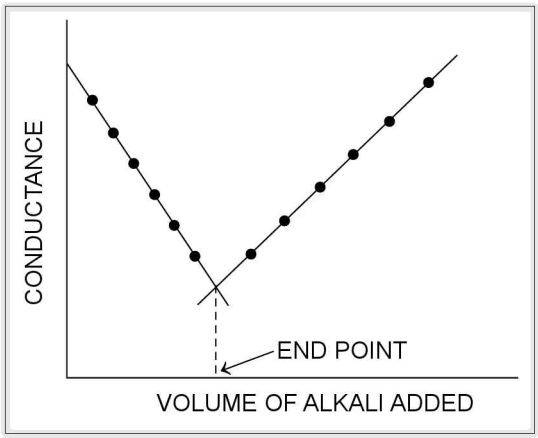


Fig. 9.23 Conductometric titration of a strong acid with a strong base

In effect, H^+ ions in solution are replaced by Na^+ ions, and thus there would be a decrease in the conductance of the solution. But, after the neutralization point is reached,, further addition of NaOH means an addition of Na^+ and OH^- ions. This results in an increase in the conductance. Thus, the conductance of the system which is titrated with NaOH solution at first decreases, reaches a minimum point, and then increases. Actually, we get two intersecting straight lines, one between start and the neutralization point and the other for the excess addition of NaOH. The intersection point gives the end point of the titration.

As regards the slopes of the curves, these may be approximately determined as follows. Before the neutralization point, the decrease of conductance is proportional to

$\lambda_{H^+} - \lambda_{Na^+} \approx 350 - 50 \approx 300$; whereas the increase of conductance after the neutralization point, is proportional to $\lambda_{Na^+} + \lambda_{OH^-} \approx (50 + 198) \approx 248$. So it is found that the rate of decrease of conductance is greater than the rate of increase.

Strong base vs strong acid

If a strong base is neutralized with a strong acid, the nature of the titration curves will remain the same, but the slopes will be different, because in this case the reaction is

$$(Na^+ + OH^-) + (H^+ - Cl^-) \rightarrow Na^+ + Cl^- + H_2O$$

and OH^- ions are replaced by Cl^- ions resulting in a decrease of conductance, proportional to $\lambda_{OH^-} - \lambda_{Cl^-} \approx (198 - 76) \approx 122$;

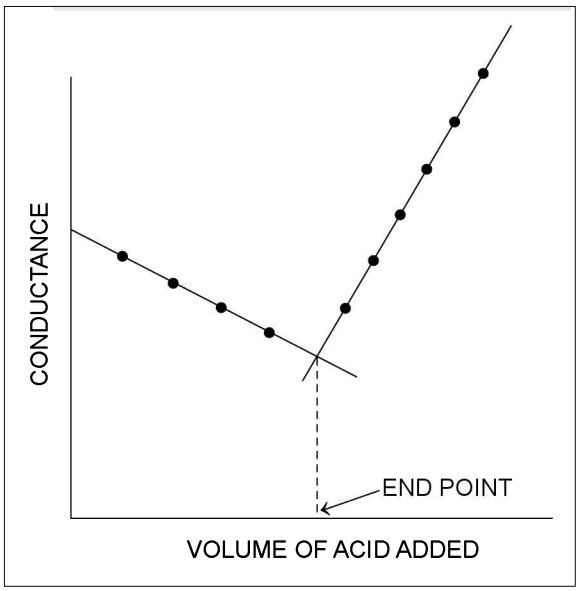


Fig. 9.24 Conductometric titration of a strong base with a strong acid.

whereas the increase after the neutralization point, is proportional to $\lambda_{H^+} + \lambda_{Cl^-} \approx (350+76) \approx 426$. Obviously the rate of increase of conductance after the neutralization point is much greater than the rate of decrease before it.

Strong acid vs weak base

In the titration of a strong acid, if the titrant is a weak base, i e., practically undissociated in solution, *e.g.*. ammonium hydroxide, then the conductance after the neutralization point will not show any practical change, although the initial decrease remains appreciable. The same arguments apply to the titration of a strong base with a weak acid, e.g., acetic acid. In such cases however, the curve exhibits an appreciable curvature near the equivalence point. This is due to the hydrolysis of the salt of weak base and strong acid.

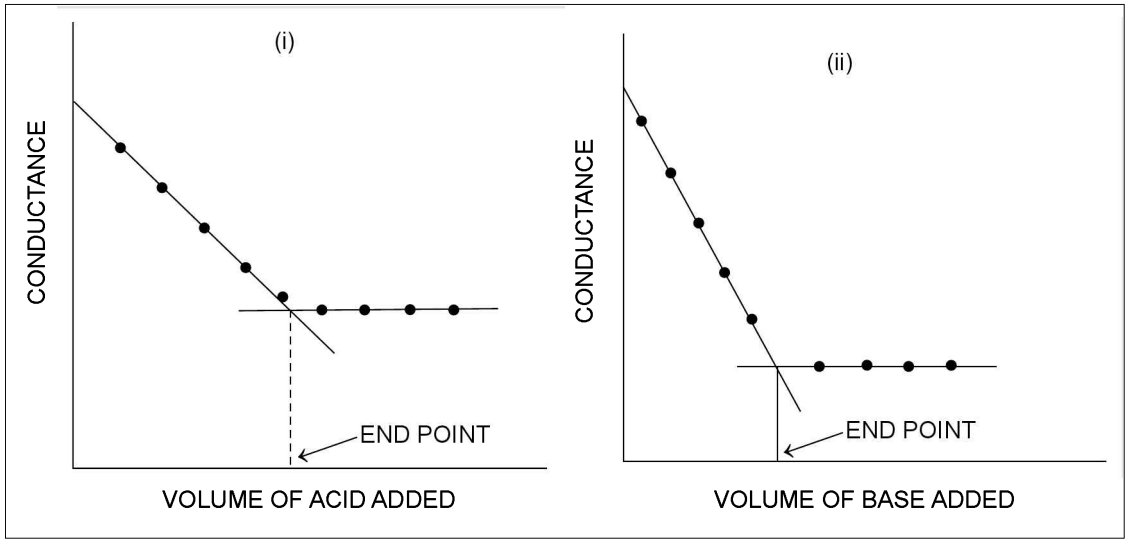


Fig. 9.25 Conductometric titration (i) strong base with a weak acid and (ii) strong acid with a weak base.

Weak acid vs strong base

When a weak acid, e.g., acetic acid, is titrated with a base, the conductance of the solution first decreases and them increases in the first stage. This is due to the tact that the H^+ ions produced by the dissociation of the acid are removed by the added OH^- ions as usual, but since there is an equilibrium between the undissociated acid molecules and the H+ and CH_3COO^- ions, the latter will be produced by further dissociation of the acid and this will continue up to the neutralization point. The conductance, thus, increases due to the formation of CH_3COO- and Na^+ ions in the solution. To have a precise idea of the rate of increase of the conductance, a knowledge of the dissociation constant of the acid is recessaiy. A slight fall in the very initial stages, is due to the predominance of the common ion effect, viz., the suppression of dissociation of

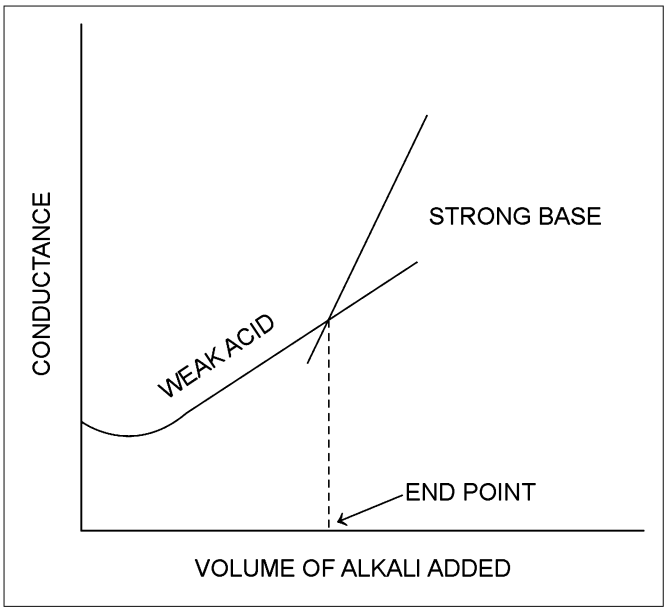


Fig. 9.26 Conductometric titration of a weak acid with a strong base.

the weak acid. After the equivalence point, the conductance of the solution increases (cf. post neutralization region in the case of strong acid vs strong base titration).

The curve for the titration of a weak base with strong acid follows the same rule.

Mixture of strong and weak acids

A mixture of a strong acid and a weak acid can be titrated conductometrically by a base. At first the strong acid is neutralized and a decrease in the conductance is observed. After the whole of the strong acid is neutralized, the weak acid begins to get neutralized, and the conductance goes on increasing until the whole of the acid is neutralized. After the neutralization, the conductance shows a further increase or remains constant, depending upon if the base is strong or weak. Thus, two intersections are found in the titration curve,

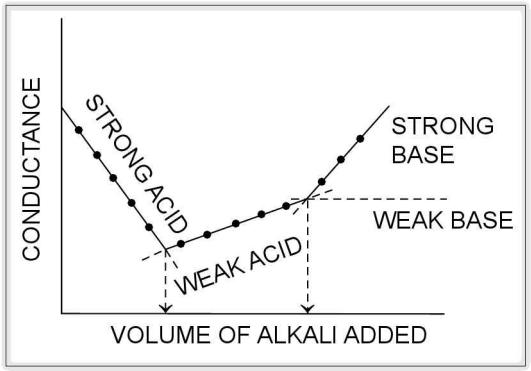


Fig. 9.27 Conductometric titration for a mixture of strong and weak acids.

the first one giving the neutralization of the strong acid, and the second one giving the neutralization of the total acid. So, the amoutit of weak acid may be found from the difference of the two.

Since, a polyprotic acid during titration behaves like a mixture of two or more acidic species, their titration against a strong base would be similar to that for a mixture of acids of different strengths. Thus, in the titration of oxalic acid against NaOH, such plots would be characterized by two breaks.

ONE CORRECT OPTION TYPE QUESTIONS

1. If $E^{\circ}_{Fe^{+2}/Fe}$ is X_1, $E^{\circ}_{Fe^{3+}/Fe^{2}}$ is X_2, then $E^{\circ}_{Fe^{+3}/Fe^{+2}}$ will be

(a) $3X_2 - 2X_1$ (b) $X_2 - X_1$
(c) $X_2 + X_1$ (d) $2X_1 + 3X_2$.

2. A hydrogen electrode placed in a buffer solution of NaCN and HCN in the ratio of X : Y and Y : X has an oxidation electrode potential values E_1 and E_2 volts respectively at 25 °C. The pK_a value of HCN is

(a) $\frac{(E_1 + E_2)}{0.118}$ (b) $-\frac{(E_1 + E_2)}{0.118}$
(c) $\frac{(E_1 - E_2)}{0.118}$ (d) $\frac{(E_2 - E_1)}{0.118}$

3. Let a fully charged battery contains 1.50 L of 5.00 M H_2SO_4. What will be the concentration of H_2SO_4 in the battery after 2.50 amperes of current is drawn from battery for 6.0 hours?

(a) 0.1865 M (b) 4.8135 M
(c) 0.3730 M (d) 9.6270 M.

4. What will be the reduction potential of copper at pR = 14 if K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19} and $E^{\circ}_{Cu^{+2}/Cu} = 0.34$ V?

(a) + 0.34 V (b) –0.22 V
(c) – 0.33 V (d) –0.34 V.

5. The specific conductivity of a saturated solution of silver chloride is 2.30×10^{-6} S cm^{-1} at 25° C. What will be the solubility of silver chloride at 25° C if molar conductivities at infinite dilution for Ag^+ and Cl^- ions are 61.9 and 76.3 S cm^2 mol^{-1} respectively?

(a) 1.66×10^{-5} M (b) 2.382×10^{-3} M
(c) 2.33×10^{-5} M (d) none of these

6. A 100 watt, 110 volt lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for 10 hours?
(Given atomic mass of Cd =112.4)

(a) 19 g (b) > 91 g
(c) 17 g (d) > 26 g.

7. The standard reduction potential of the reaction, $H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$ at 298 K is

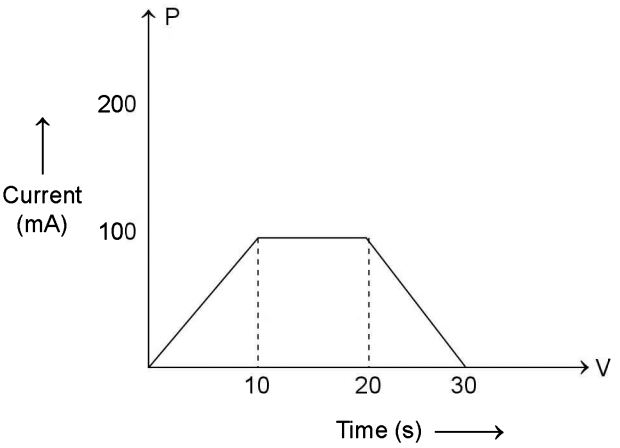
(a) $E^{\circ} = \frac{RT}{R} \ln K_w$

(b) $E^{\circ} = \frac{RT}{F} \ln [P_{H_2}]^{1/2} [OH]^-$

(c) $E^{\circ} = \frac{RT}{F} \ln \frac{[P_{H_2}]^{1/2}}{[H^+]}$

(d) $E^{\circ} = \frac{RT}{F} \ln K_w$

8. In a copper voltameter, mass deposited in 30 sec. in 'm' g. If the time current graph is as shown in figure, calculate the electrochemical equivalent of Cu.



(a) z = m

(b) $z = \frac{m}{2}$

(c) $z = \frac{m}{5}$

(d) z cannot be calculated from the given data

9. By how much would the oxidising power of the MnO_4^-/Mn^{2+} couple change if the H^+ ions concentration is decreased 100 times?

(a) increases by 189 mV
(b) decreases by 189 mV
(c) will increase by 19 mV
(d) will decrease by 19 mV

10. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at cathode and anode are respectively

(a) H_2, O_2 (b) O_2, H_2
(c) O_2, Na (d) O_2, SO_2.

11. A solution containing one mole per litre of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$; $Mg(NO_3)_2$ is being electrolysed using inert electrodes. The values of standard electrode potentials (reduction potentials in

volts are $Ag/Ag^+ = 0.80$ V, $2Hg/Hg_2^{++} = 0.79$ V, $Cu/Cu^{++} = +0.24$ V, $Mg/Mg^{++} - 2.37$ V. With increasing voltage, the sequence of deposition of metals on the cathode will be

(a) Ag, Hg, Cu (b) Cu, Hg, Ag
(c) Ag, Hg, Cu, Mg (d) Mg, Cu, Hg, Ag.

12. If $E^\circ_{MnO_4^-/Mn^{2+}} = 15.1$ and $E^\circ_{MnO_2/Mn^{2+}} = 1.23$ V, then $E^\circ_{MnO_4^-/Mn_2}$ is

(a) + 0.28 V (b) – 0.28 V
(c) + 0.74 V (d) + 1.69 V.

13. For the electrochemical cell $M \mid M^+ \parallel X^- \mid X$ $E^0_{M^+/M} = 0.44$V, $E^0_{X/X^-} = 0.33$V from this data one can deduce that

(a) $M + X \longrightarrow M^+ + X^-$ is spontaneous reaction
(b) $M^+ + X^- \longrightarrow M + X$ is spontaneous reaction
(c) $E_{cell} = 0.77$V
(d) $E_{cell} = -0.77$V

14. A lead storage battery containing 5.0 L of (1N) H_2SO_4 solution is operated for 9.65×10^5 s with a steady current of 100 mA. Assuming volume of the solution remaining constant, normality of H_2SO_4 will

(a) remain unchanged
(b) increases by 0.20
(c) increase by unity
(d) decrease by 0.40

15. Specific conductance of 0.01 N – KCl solution is x ohm^{-1} cm^{-1} having conductance y ohm^{-1}. Specific conductance of 0.01 N – NaCl having conductance z ohm^{-1} is

(a) xy/z (b) xz/y
(c) z/xy (d) None

16. On passing C amperes of current through an electrolyte solution for t seconds, m gram of metal deposits on the cathode. The equivalent weight of the metal is

(a) $\frac{Ct}{m} \times 96500$ (b) $\frac{Cm}{t} \times 96500$
(c) $96500 \times \frac{m}{c} \times t$ (d) $c \times t \times \frac{96500}{m}$

17. One coulomb is equal to

(a) 96500 Faraday
(b) charge on 6.24×10^{18} electrons
(c) charge on 1 electron
(d) none of the above

18. If three Faradays (F) of electricity is passed through the solutions of $AgNO_3$, $CuSO_4$ and $AuCl_3$, the molar ratio of the cations deposited at the cathode is

(a) 1 : 1 : 1 (b) 1 : 2 : 3
(c) 3 : 2 : 1 (d) 6 : 3 : 2

19. In the electrolysis of $CuCl_2$ solution using Cu electrodes, the weight of Cu anode increased by 2 gram at cathode. At the anode

(a) 0.2 mole of Cu^{2+} will go into solution.
(b) 560 ml O_2 liberate
(c) No loss in weight
(d) 2 gram of copper goes into solution as Cu^{2+}

20. During electrolysis of $CuSO_4$ using Pt-electrodes, the pH of solution

(a) increases
(b) decreases
(c) remains unchanged
(d) cannot be predicted

21. One coulomb of charge passes through solution of $AgNO_3$ and $CuSO_4$ connected in series and the conc. of two solution being in the ratio 1:2. The ratio of weight of Ag and Cu deposited on Pt electrode is

(a) 107.9 : 63.54
(b) 54 : 31.77
(c) 107.9 : 31.77
(d) 54 : 63.54

22. A current of I amere was passed for t second through three cells P, Q and R connected in series. These contain respectively silver nitrate, mercuric nitrate and mercurous nirate. At the cathode of the cell P, 0.216 g of Ag was deposited. The weights of mercury deposited in the cathode of Q and R respectively are:

(a) 0.4012 and 0.8024 g
(b) 0.4012 and 0.2006 g
(c) 0.2006 and 0.4012 g
(d) 0.1003 and 0.2006 g

23. Find the standard cell potential involving the cell reaction

$$In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^+, \text{ at } 298\ K$$

Given:

$$E^\circ_{Cu^{2+}/Cu^+} = x_1 V;\ E^\circ_{In^{3+}/In^+} = x_2 V;\ E^\circ_{In^{2+}/In^+} = x_3 V$$

(a) $x_1 + x_3 - x_2$ (b) $(x_1 + x_3 - 2x_2)/3$
(c) $x_1 + x_3 - 2x_2$ (d) $x_1 + x_3 + 2x_2$

24. Given: $2Br^- \rightarrow Br_2 + 2e^-$ $E^\circ = -1.09$ V; $I_2 + 2e^- \rightarrow 2I^-$ $E^\circ = 0.54$ V

$Fe^{2+} + 2e \rightarrow Fe \quad E^\circ = -0.44$

Which of the following reactions will not be spontaneous?

(a) $Fe + Br_2 \rightarrow FeBr_2$
(c) $Fe + I_2 \rightarrow FeI_2$
(c) $I_2 + 2Br^- \rightarrow 2I^- + Br_2$
(d) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

25. $Pt(H_2)|\ H^+\ (1M)||\ H^+\ (1M)\ |\ Pt(H_2)$,

$P_1 \qquad\qquad P_2$

P_1 and P_2 are pressure, cell reaction will be spontaneous if:

(a) $P_1 = P_2$ (b) $P_1 > P_2$
(c) $P_2 > P_1$ (d) $P_1 = 1$ atm

26. The ionization constant of a weak electrolyte is 25×10^{-6} and the equivalent conductance of its 0.01 M solution is 19.6 s cm^2 eq^{-1}. The equivalent conductance at infinite dilution of the electrolyte in s cm^2 eq^{-1} is

(a) 250 (b) 196
(c) 392 (d) 384

27. Specific conductance of 0.01 N – KCl solution is x ohm^{-1} cm^{-1} having conductance y ohm^{-1}. Specific conductance of 0.01 N – NaCl having conductance z ohm^{-1} is

(a) xy/z (b) xz/y
(c) z/xy (d) None

28. Molar conductances of $BaCl_2$, H_2SO_4 and HCl are x_1, x_2 and x_3S cm^2 $equiv^{-1}$ at infinite dilution. If specific conductance of saturated $BaSO_4$ solution is of y S cm^{-1}, then k_{sp} of $BaSO_4$ is:

(a) $\dfrac{10^3 y}{2(x_1 + x_2 - 2x_3)}$ (b) $\dfrac{10^6 y^2}{(x_1 + x_2 - 2x_3)^2}$

(c) $\dfrac{10^6 y^2}{4(x_1 + x_2 - 2x_3)^2}$ (d) $\dfrac{x_1 + x_2 - 2x_3}{10^6 y^2}$

29. The cost of electricity required to deposit 1 g of Mg is Rs 5.00. How much would it cost to deposit 10.0 g of Al? (Al = 27, Mg = 24)

(a) Rs 10.0 (b) Rs 27.0
(c) Rs 44.44 (d) Rs 66.67

30. Given: $2Br^- \rightarrow Br_2 + 2e^-$ $E^\circ = -1.09$ V;
$I_2 + 2e^- \rightarrow 2I^-$ $E^\circ = 0.54$ V
$Fe^{2+} + 2e \rightarrow Fe$ $E^\circ = -0.44$

Which of the following reactions will not be spontaneous?

(a) $Fe + Br_2 \rightarrow FeBr_2$
(c) $Fe + I_2 \rightarrow FeI_2$
(c) $I_2 + 2Br^- \rightarrow 2I^- + Br_2$
(d) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

31. $Pt(H_2)|\ H^+\ (1M)||\ H^+\ (1M)\ |\ Pt(H_2)$,

$P_1 \qquad\qquad P_2$

P_1 and P_2 are pressure, cell reaction will be spontaneous if:

(a) $P_1 = P_2$ (b) $P_1 > P_2$
(c) $P_2 > P_1$ (d) $P_1 = 1$ atm

32. In alkaline solutions, the electrode potential of quinhydrone electrode will be given as

(a) $E = E^\circ - 0.059$ pH
(b) $E = E^\circ + 0.059$ pH
(c) $E = E^\circ - \dfrac{0.059}{2}$ pH
(d) $E = E^\circ + \dfrac{0.059}{2} \log K_1K_2$

where K_1 and K_2 are the dissociation constants of hydroquinone.

33. How long will it take for a current of 3 amperes to decompose 36 g of water? (Eq. wt. of hydrogen is 1 and that of oxygen is 8)

(a) 36 hours approx. (b) 18 hours approx.
(c) 9 hours approx. (d) 4.5 hours approx.

34. What is the electrode potential of Fe^{3+}/Fe electrode in which concentration of Fe^{3+} ions is 0.1 M? Given $E^\circ_{Fe^{3+}/Fe} = +0.771$ V

(a) +0.79 V (b) +0.75 V
(c) 1.50 V (d) +1.0 V

35. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:

$MnO_4^-(aq.) + 8H^+(aq.) + 5e^- \rightarrow Mn^{2+}(aq.) + 4H_2O(l)$

$E^\circ = 1.51$ V

$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \rightarrow 2Cr^{3+}(aq.) + 7H_2O(l)$

$E^\circ = 1.38$ V

$Fe^{3+}(aq.) + e^- \rightarrow Fe^{2+}(aq.)$ $E^\circ = 0.77$ V

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq.)$ $E^\circ = 1.40$ V

Identify the only incorrect statement regarding the quantitative estimation of aqueous Fe $(NO_3)_2$.

(a) MnO_4^- can be used in aqueous HCl
(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl
(c) MnO_4^- can be used in aqueous H_2SO_4
(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

36. Given

$$2Cu^+_{(aq)} \longrightarrow 2Cu^{2+}_{(aq)} + 2e \ldots\ldots\ldots\ldots E^\circ_1 = -0.15\ V$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu(s) \ldots\ldots\ldots\ldots E^\circ_2 = 0.325\ V$$

Then the standard e.m.f of the following reaction

$$2Cu^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu(s)$$

will be

(a) 0.175 V (b) 0.35 V
(c) –0.175 V (d) –0.35 V

37. Using the following Latimer diagram for Bromine,

$$pH = 0;\ BrO_4^- \xrightarrow{1.82V} BrO_3^- \xrightarrow{1.50V} HBrO \xrightarrow{1.595V} Br_2 \xrightarrow{1.0652V} Br^-$$

the species undergoing disproportionation is

(a) BrO_4^- (b) BrO_3^-
(c) HBrO (d) Br_2

38. In the electrolysis of $CuCl_2$ solution using Cu electrodes, the weight of Cu anode increased by 2 gram at cathode. At the anode

(a) 0.2 mole of Cu^{2+} will go into solution.
(b) 560 ml O_2 liberate
(c) No loss in weight
(d) 2 gram of copper goes into solution as Cu^{2+}

39. During electrolysis of $CuSO_4$ using Pt-electrodes, the pH of solution

(a) increases
(b) decreases
(c) remains unchanged
(d) cannot be predicted

40. Following are some standard reduction potential values for the given half cell:

(i) $A^{++} + 2e^- \rightleftharpoons A$ $E^0 = 1.27$ V
(ii) $B^+ + e^- \rightleftharpoons B$ $E^0 = -0.7$ V
(iii) $C^{++} + 2e^- \rightleftharpoons C$ $E^0 = -0.54$ V
(iv) $D^+ + e^- \rightleftharpoons D$ $E^0 = 1.05$ V

The combination of which two half cells will give galvanic cell having maximum possible emf.

(a) (i) and (ii) (b) (i) and (iv)
(c) (ii) and (iii) (d) (iii) and (iv)

41. One Coulomb of charge passes through solution of $AgNO_3$ and $CuSO_4$ connected in series and the conc. of two solution being in the ratio 1:2. The ratio of weight of Ag and Cu deposited on Pt electrode is

(a) 107.9 : 63.54
(b) 54 : 31.77
(c) 107.9 : 31.77
(d) 54 : 63.54

42. A solution containing one mole per litre of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$; $Mg(NO_3)_2$ is being electrolysed using inert electrodes. The values of standard electrode potentials (reduction potentials in volts are $Ag/Ag^+ = 0.80$ V, $2Hg/Hg_2^{++} = 0.79$V, $Cu/Cu^{++} = +0.24$ V, Mg/Mg^{++} –2.37 V. With increasing voltage, the sequence of deposition of metals on the cathode will be

(a) Ag, Hg, Cu (b) Cu, Hg, Ag
(c) Ag, Hg, Cu, Mg (d) Mg, Cu,Hg, Ag

43. Equivalent conductance of 1M HCOOH is 12 $ohm^{-1}\ cm^2\ equiv^{-1}$ and that at infinite dilution is 240 $ohm^{-1}\ cm^2\ equiv^{-1}$. Hence % ionization of CH_3COOH is

(a) 4 (b) 5
(c) 2 (d) 1

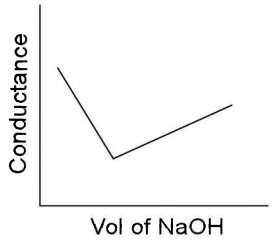
44. Specific conductance of 0.01 M KCl solution is x $ohm^{-1}\ cm^{-1}$. When conductivity cell is filled with 0.01 M KCl the conductance is y ohm^{-1}. When the same cell is filled with 0.01 M H_2SO_4, the observed conductance was Z $ohm^{-1}\ cm^{-1}$. Hence specific conductance of 0.01 M H_2SO_4 is

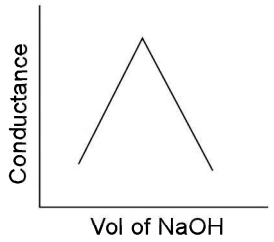
(a) xz (b) $\frac{z}{xy}$
(c) $\frac{xy}{y}$ (d) $\frac{xy}{z}$

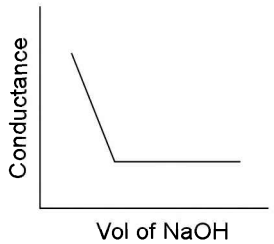
45. The specific conductivity of solution depends upon

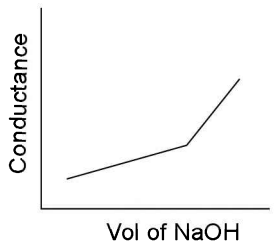
(a) Number of ions as well as mobility of ions
(b) Number of ions per c.c solutin
(c) Number of ions per cc as well as mobilities of ions
(d) Mobilities of ions only

46. HNO_3(aq) is titrated with NaOH(aq) conductometrically, graphical representation of the titration as:

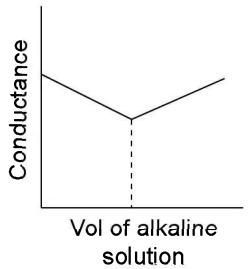
(a)


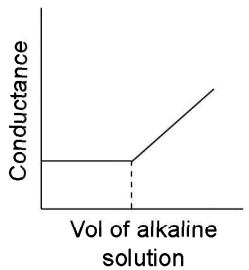
(b)


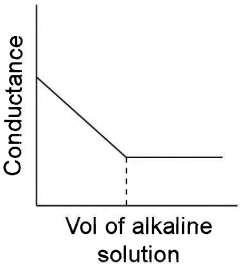
(c)


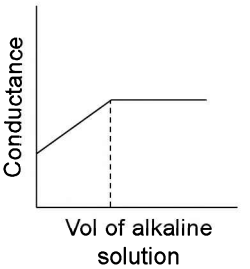
(d)


47. Which of the following plots will obtained for a conductometric titration of strong acid against a weak base?

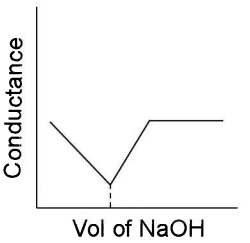
(a)


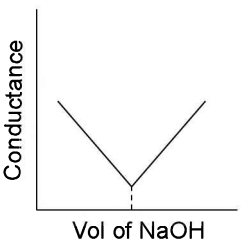
(b)


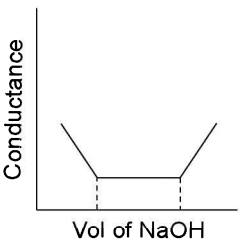
(c)


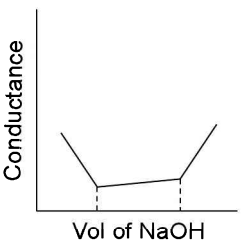
(d)


48. Conductometric titration curve of a equimolar mixture of a HC1 and HCN with NaOH(aq) is:

(a)


(b)


(c)


(d)


ANSWER KEYS

1. (a)	**2.** (a)	**3.** (b)	**4.** (b)	**5.** (a)	**6.** (a)	**7.** (d)	**8.** (b)	**9.** (b)	**10.** (a)
11. (a)	**12.** (d)	**13.** (b)	**14.** (a)	**15.** (b)	**16.** (c)	**17.** (b)	**18.** (d)	**19.** (d)	**20.** (b)
21. (c)	**22.** (c)	**23.** (c)	**24.** (c)	**25.** (b)	**26.** (c)	**27.** (b)	**28.** (b)	**29.** (d)	**30.** (c)
31. (b)	**32.** (d)	**33.** (a)	**34.** (b)	**35.** (a)	**36.** (b)	**37.** (c)	**38.** (d)	**39.** (b)	**40.** (a)
41. (c)	**42.** (a)	**43.** (b)	**44.** (c)	**45.** (c)	**46.** (a)	**47.** (c)	**48.** (d)		

HINTS AND EXPLANATIONS

1. (a) $Fe^{+2} + 2e \longrightarrow Fe,\ \Delta G_1^0 = -2\,Fx_1$ ...(1)

$[\because \Delta G^\circ = -nFe^\circ]$

$Fe^{+3} + 3e^- \longrightarrow Fe,\ \Delta G_2^\circ = -3Fx_2$

$Fe^{+3} + e^- \longrightarrow Fe^{+2},\ \Delta G_3^\circ = -Fx_3$

In order to get (3), subtract (1) from (2)s

$\Delta G_3^\circ = \Delta G_2^\circ - \Delta G_1^\circ$

$-Fx_3 = -3Fx_2 + 2Fx_1$

$x_3 = 3x_2 - 2x_1$

2. (a) Since E_1 and E_2 are oxidation potential. The oxidation reaction for hydrogen electrode is

$$\frac{1}{2}H_2\,(1\text{ atm}) \longrightarrow H^+ e^-$$

$E_{OP} = -0.0591 \log [H^+]$

$E_{OP} = 0.0591\ pH$

$\therefore\ E_{OP} + E_2 = 0.0591\ pH_1 + 0.0591\ pH_2$

$= 0.0591\ (pH_1 + pH_2)$

For acidic buffer of HCN and NaCN,

$$pH = pK_a + \log\frac{[CN^-]}{[HCN]}$$

$$\frac{E_1 + E_2}{0.0591} = pK_a + \log\left(\frac{[CH^-]}{[HCN]}\right)_1 + pK_a + \log\left(\frac{[CN^-]}{[HCN]}\right)_2$$

$$= 2pK_a + \log\frac{x}{y} + \log\frac{y}{x}$$

$$\therefore\ pK_a = \frac{(E_1 + E_2)}{0.0591 \times 2} = \frac{(E_1 + E_2)}{0.1182}$$

3. (b) During discharging, the reaction taking place is

$Pb(s) + PbO_2(s) + 4H^+ + 2SO_4^{2-} \longrightarrow PbSO_4 + 2H_2O$

H_2SO_4 consumed during discharging

$W = ZI.t$

$$= \frac{98}{2 \times 96500} \times 2.5 \times 6 \times 3600$$

$[H_2SO_4] = 0.8165\ M$

$\therefore\ [H_2SO_4] = [H_2SO_4]_{initial} - [H_2SO_4]_{consumed}$

$= 5.00 - 0.8165 = 4.8135\ M$

4. (b) $pH = 14,$

$\therefore\ pOH = 0$

$[OH^-] = 1\ M$

$K_{sp} = [Cu^{+2}]\,[OH^-]^2$

$$[Cu^{+2}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1 \times 10^{-19}}{1} = 1 \times 10^{-19}$$

$Cu^{+2} + 2e^- \longrightarrow Cu$

$$E_{Cu^{+2}/Cu} = E^\circ_{Cu^{+2}/Cu} - \frac{0.0591}{n}\log\frac{1}{[Cu^{+2}]}$$

$$= 0.34 - \frac{0.0591}{2}\log 10^{19}$$

$$= 0.34 - \frac{0.0591 \times 19}{2}$$

$= -0.22\ V$

5. (a) $\Lambda_m^\circ(AgCl) = \dfrac{K \times 1000}{5}$

or $S = \dfrac{K \times 1000}{\Lambda_m^\circ(AgCl)}$

$$= \frac{2.30 \times 10^{-6} \times 1000}{138.2}$$

$= 0.0166 \times 10^{-3}$

$= 1.66 \times 10^{-5}\ M$

6. (a) Current = watt/volt = $\frac{100}{110}$

Amount of electricity

= Q = Current × Time

= $\frac{100}{110} \times 10 \times 3600$

= 32724 C

Atomic mass of Cd = 112.4

Equivalent mass of Cd = $\frac{112.4}{\text{Valency}}$

= $\frac{112.4}{2} = 56.2$

Mass of Cd deposited = $\frac{Q \times \text{Eq.mass}}{\text{Faraday}}$

= $\frac{32724 \times 56.2}{96500}$

= 19.06 g

7. (d) Where K_w is the ionic product of water

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta \Delta G_1^\circ = -RT \ln K_w$

$H^+ + e^- \longrightarrow \frac{1}{2} H_2$; + ; $\Delta G_2^\circ = -nFE^\circ_{H^+/H_2}$

$H^+ + e^- \longrightarrow \frac{1}{2} H_2 + OH^-$;

$\Delta G_3^\circ = -nF\ E^\circ_{H^+/H_2,OH^-}$

Since $E^\circ_{H^+/H_2} = 0$, so $\Delta G_2^\circ = 0$

Thus, $\Delta G_1^\circ = \Delta G_3^\circ$

$-RT \ln K_w = -nFE^\circ_{H_2O|H_2/OH^-}$

$\therefore$ $= E^\circ_{H_2O/H_2,OH} = \frac{RT}{F} \ln K_w$ (since, n = 1)

8. (b) $m = z \times i \times t$

$z = \frac{m}{i \times t}$

Total charge passed through copper voltameter

$= (100 \times 10 \times 10^{-3}) + 2(1/2 + 10 \times 100 \times 10^{-3})$

= Area under the curve = 1 + 1 = 2

Electrochemical equivalent, $z = \frac{m}{2}$

9. (b) $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

According to Nernst equation,

$$E_{red} = E^\circ_{red} - \frac{0.059}{5} \log \left[\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8} \right]$$

Let $[H^+]_{initial} = X$

$$E_{red(initial)} = E^\circ_{red} - \frac{0.0591}{5} \log \left[\frac{[Mn^{2+}]}{[MnO_4^-] \times [X]^8} \right]$$

$[H^+]_{fina} = \frac{X}{100} = \frac{X}{10^2}$

$$E_{red(final} = E^\circ_{red} \frac{-0.5091}{5} \log \frac{[Mn^{2+}] \times 10^{16}}{[MnO_4^-] \times [X]^8}$$

$E_{red(final} - E_{red(initial)}$

$= \frac{-0.5091}{5} \log 10^{16} = -0.1891$ V

This E_{red} decreases by 0.189 V. The tendency of the half cell to get reduced is its oxidizing power. Hence the oxidizing power decreases by 0.189 V.

$\therefore$ (b) is the correct.

10. (a)

11. (a) Na^+ ions are not reduced at cathode and SO_4^{2-} ions are not oxidized at anode

Cathode: $2H_2(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Anode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

$\therefore$ (a) is the correct.

Greater the value of standard reduction potential, greater will be its tendency to undergo reduction. So the sequence of deposition of metals on cathode will be Ag, Hg, Cu. Here, magnesium will not be deposited because its standard reduction potential is negative. So it has strong tendency to undergo oxidation. Therefore, on electrolysis of $Mg(NO_3)_2$ solution, H_2 gas will be evolved at cathode.

$\therefore$ (a) is the correct.

12. (d) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$,

$\Delta G^\circ = -5 \times 1.51$ F

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$,

$\Delta G^\circ = -2 \times 1.23$ F

$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO^{2+}\ 2H_2O$,

$\Delta G^\circ = (-7.55\ F + 2.46\ F) = -5.09$ F

$\therefore$ $E^\circ_{MnO_4/MnO_2} = \frac{-5.09F}{-3F} = +1.696$ V

13. (b) E^0_{RP} for M > ΔE_{RP} for X

$\therefore$ $M^+ + X^- \longrightarrow M + X$ (spontaneous),

$E^0_{cell} = -0.33 + 0.44 = 0.11$V

$\therefore$ Since the e.m.f. is positive, reaction it will be spontaneous

14. (a) $OCl^- \longrightarrow Cl^-$; $E^\circ = 0.94$ V (I)

$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$; $E^\circ = 1.36$ V (II)

Add (I) + (II) $OCl^- \longrightarrow \frac{1}{2}Cl_2$;

$E^\circ = 0.94 - 1.36 = -0.42$ V

15. (b) κ (specific conductance) $= C \times \frac{1}{a}$ $x = y \times \frac{1}{a}$

$\therefore$ Cell constant $\left(\frac{1}{a}\right) = \frac{x}{y}$

$\therefore$ $\kappa(NaCl) = C \times \frac{1}{a} = z \times \frac{x}{y}$ ohm^{-1} cm^{-1}

16. (c) 1 Faraday, that is, 96500 coulombs deposits 1 g equivalent of the substance. Now C × t amount of electricity deposits 'm' g of substance

$\therefore$ 96500 C amount of electricity deposits $\frac{96500 \times m}{C.t}$ equivalent weight.

17. (b) Charge on 6.023×10^{23} electrons = 96500 C

So, 1 coulomb would be the charge on

$\frac{6.023 \times 10^{23}}{96500} = 6.24 \times 10^{18}$ electrons.

18. (d) Since $Ag^+ + e^- \rightarrow Ag$, $Cu^{2+} + 2e^- \rightarrow Cu$, $Au^{3+} + 3e^- \rightarrow Au$, three Faradays of electricity will deposit 3 moles of Ag, 1.5 moles of copper, and 1 mole of gold. Therefore, the molar ratio is 3 : 1.5 : 1 or 6 : 3 : 2.

19. (d) During electrolysis of $CuSO_4$ solution using Cu electrodes, the cell reaction is

Anode: $Cu(s) \longrightarrow Cu^{++} + 2e^-$

Cathode: $Cu^{++}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

The loss in weight of anode is equal to gain in weight of cathode.

20. (b) In presence of inert electrode, the cell reaction is

Anode $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$

Cathode: $Cu^{++}_{(aq)} + 2e^- \longrightarrow Cu(s)] \times 2$

Net cell reaction $2Cu^{++}$ aq. $+ 2H_2O \longrightarrow 4H^+ + 2Cu(s) + O_2\uparrow$

Due to increase in $[H^+]$, pH decreases. $\therefore$ (b)

21. (c) Faraday's IInd Law $\frac{W}{E}$ = constant

So, $\frac{W_{Ag}}{E_{Ag}} = \frac{W_{Cu}}{E_{Cu}}$ $(Ag^+ + e^- \rightarrow Ag, E_{Ag} = \frac{M}{1})$

$\therefore$ $\frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}} = \frac{107.9}{63.54/2}$

$(Cu^{+2} + 2e^- \rightarrow Cu, E_{Cu} = \frac{M}{2})$ $= \frac{107.9}{31.77}$

22. (c) Eq. of Ag = Eq. of Hg^{2+} = Eq. of Hg_2^{2+} or

$\frac{0.216}{108} = \frac{W_{Hg^{2+}}}{a/2} = \frac{W_{Hg_2^{2+}}}{a/1}$; a = 200.6

23. (c) $Cu^{2+} + e^- \rightarrow Cu^+$; $E^\circ = x_1X$; $\Delta G_1^\circ = -Fx_1$ .....(i)

$In^{3+} + 2e^- \rightarrow In^+$; $E^\circ = x_2V$; $\Delta G_2^\circ = -2Fx_2$ .....(ii)

$In^{2+} + e^- \rightarrow In^+$; $E^\circ = x_3V$; $\Delta G_3^\circ = -Fx_3$ ....(iii)

From equation (i) + (iii) – (ii),

$In^{2+} + Cu^{2+} \rightarrow In^{3+} + Cu^+$, $\Delta G^\circ = -Fe^\circ$

Hence,

$\Delta G^\circ = -FE^\circ = \Delta G_1^\circ + \Delta G_3^\circ - \Delta G_2^\circ$

$= -F(x_1 + x_3 - 2x_2)$ or

$E^\circ = x_1 + x_3 - 2x_2$ Volt

24. (c) As per reaction in (c), reduction occurs at iodine electrode and oxidation at Bromine electrode. Hence,

$E^\circ_{Cell} = E^\circ_{I_2/I^-} - E^\circ_{Br_2/Br^-} = 0.54 - 1.09 = -0.55$ V

The negative cell potential suggests the non-spontaneity of the reaction.

25. (b) E_{cell} for the given change

$E_{cell} = \frac{0.059}{2} \log \frac{[H^+] \times P_{1H_2}}{P_{2H_2} \times [H^+]}$

Thus for + ve E_{cell} = $P_{1H_2} > P_{2H_2}$

26. (c) $HA \rightleftharpoons H^+ + A^-$

C O O

C–Cα Cα Cα

or $K = C\alpha^2$ or $25 \times 10^{-6} = 10^{-2} \times \alpha^2$

or $\alpha = 5 \times 10^{-2}$ Also $\alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{19.6}{\lambda_\infty}$

or $\lambda_\infty = \frac{19.6}{5 \times 10^{-2}} = 392$

27. (b) κ (specific conductance) $= C \times \frac{1}{a}\ x = y \times \frac{1}{a}$

$\therefore$ Cell constant $\left(\frac{1}{a}\right) = \frac{x}{y}$

$\therefore$ $\kappa(NaCl) = C \times \frac{1}{a} = z \times \frac{x}{y}$ ohm^{-1} cm^{-1}

28. (b) $\Lambda^{\circ}_{BaSO_4} = \Lambda^{\circ}_{BaCl_2} + \Lambda^{\circ}_{H_2SO_4} - 2\Lambda^{\circ}_{HCl}$

$= (x_1 + x_2 - 2x_3)$

$$\Lambda^{\circ}_{BaSO_4} = \frac{1000 \times \text{sp. conduc tan ce}}{\text{solubility (in saturated solution)}}$$

$$(x_1 + x_2 - 2x_3) = \frac{1000y}{\text{so lubility}}$$

$\therefore$ solubility $(BaSO_4) = \frac{1000y}{(x_1 + x_2 - 2x_3)}$ N

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ $K_{sp}(BaSO_4)$

$= [Ba^{2+}]\ [SO_4^{2-}]\ M^2 = \frac{10^6 y^2}{(x_1 + x_2 - 2x_3)^2}$

29. n_{eq} of Mg/n_{eq} of Al $= \frac{1}{12} \Big/ \frac{10}{9} = 5/x$

$x = 5 \times \frac{10}{9} \times 12 = 66.67$ Rupees

30. (c) As per reaction in (c), reduction occurs at iodine electrode and oxidation at bromine electrode. Hence, $E^{\circ}_{Cell} = E^{\circ}_{I_2/I^-} - E^{\circ}_{Br_2/Br^-} = 0.54 - 1.09 = -0.55$ V

31. (b) E_{cell} for the given change $E_{cell} = \frac{0.059}{2} \log \frac{[H^+] \times P_{1H_2}}{P_{2H_2} \times [H^+]}$

Thus for + ve $E_{cell} = \mathbf{P_{1H_2} > P_{2H_2}}$

32. (d) Hydroquinone is a weak acid. It ionizes in stages:

$H_2Q \rightleftharpoons H^+ + HQ^-$; $K_1 = \frac{[H^+][HQ^-]}{[H_2Q]}$

$HQ^- \rightleftharpoons H^+ + Q^{-2}$; $K_2 = \frac{[H^+][Q^{-2}]}{[HQ^-]}$

Let $[H_2Q]^0$ be the initial concentration of H_2Q. Then by mass balance

$$[H_2Q]^0 = [H_2Q] + [HQ^-] + [Q^{-2}]$$

But, $[HQ^-] = \frac{K_1[H_2Q]}{[H^+]}$; and $[Q^{-2}]$

$$= \frac{K_1K_2[OH_2]}{[H^+]^2}$$

since, $K_1K_2 = \frac{[H^+]^2[Q^{-2}]}{[QH_2]}$.

Thus,

$$[QH_2]^{\circ} = [QH_2] + K_1 \frac{[QH_2]}{[H^+]} + K_1K_2 \frac{[QH]_2}{[H^+]^2}$$

Thus,

$$[QH_2] = \frac{[QH_2]^{\circ}}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}$$

$$E = E^{\circ} + \frac{0.059}{2} \log \frac{[Q][H^+]^2}{[QH_2]}$$

by the above expansion

$$E = E^{\circ} + \frac{0.059}{2} \log \left[\frac{[Q]}{[QH_2]^{\circ}}.[H^+]^2\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)\right]$$

$[Q] = [QH_2]^{\circ}$ $\therefore$ $E = E^{\circ} + \frac{0.059}{2}$ $\log\left([H^+]^2 + K_1[H^+] + K_1K_2\right)$

This equation is to be used in alkaline solution. At every high pH, $K_1K_2 >> [H^+]^2 + K_1[H^+]$ and the equation takes the form

$$E = E^{\circ} + \frac{0.059}{2} \log K_1K_2$$

33. $w = Z\ I\ t$ Eq. mass of water $= \frac{\text{Mol. mass}}{2} = \frac{18}{2}$

$= 9$ $Z = \frac{\text{Eq. mass of water}}{96500} = \frac{9}{96500}$

$$36g = \frac{9}{96500} \times 3 \times t$$

$\therefore$ $t = 128866.7$ s $= 36$ hours

34. $Fe^{3+} + 3e^- \longrightarrow Fe$

$$E = E^{\circ} - \frac{0.059}{n} \log \frac{[Fe]}{[Fe^{3+}]}$$

$$= +0.771 - \frac{0.059}{3} \log \frac{1}{0.1} = +0.75 \text{ V}$$

35. (a) MnO_4^- will oxidize Cl^- ion

According to the equation,

$2MnO_4^- + 16H^+ + 10\ Cl^- \rightarrow 2\ Mn^{2+} + 8H_2O + 5Cl_2$

The cell corresponding to this reaction is as follows:

Pt, Cl_2 (1 atom) $Cl^- \| MnO_4^-, Mn^{2+}, H_2 | Pt$

$E^\circ_{Cell} = 1.51 - 1.40 = 0.11$ V

E°_{Cell} = being +ve, ΔG° = will be –ve hence spontaneous

MnO_4^- will not only oxidize Fe^{2+} ion but also Cl^- ion simultaneously

36. (b) Purpose of the question number 1

1. To show that e.m.f. is an intensive property
2. How to take the 'n' value for cell reaction when $\Delta G = -nFE$

37. (c) If intermediate oxidation state is stronger oxidising agent then next higher oxidation state, than that eintermediate oxidation state will undergo disproportion.

38. (d) During electrolysis of $CuSO_4$ solution using Cu electrodes, the cell reaction is

Anode: $Cu(s) \longrightarrow Cu^{++} + 2e^-$

Cathode: $Cu^{++}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

The loss in weight of anode is equal to gain in weight of cathode.

$\therefore$ (d)

39. (b) In presence of inert electrode, the cell reaction is

Anode $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$

Cathode: $Cu^{++}_{(aq)} + 2e^- \longrightarrow Cu(s)] \times 2$

Net cell reaction $2Cu^{++}$ aq. $+ 2H_2O \longrightarrow 4H^+ + 2Cu(s) + O_2\uparrow$

Due to increase in $[H^+]$, pH decreases.

$\therefore$ (b)

40. (a) Since all the values are standard reduction potential and so the two half cells having maximum and minimum reduction potential values will give a cell of maximum possible emf.

$E^0_{cell} = E^0_{RP(cathode)} - E^0_{RP(anode)}$ $\therefore$ (a)

41. (c) Faraday's IInd Law $\frac{W}{E}$ = constant

So, $\frac{W_{Ag}}{E_{Ag}} = \frac{W_{Cu}}{E_{Cu}}$ $(Ag^+ + e^- \rightarrow Ag, E_{Ag} = \frac{M}{1})$

$\therefore$ $\frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}} = \frac{107.9}{63.54/2}$ $(Cu^{+2} + 2e^- \rightarrow Cu, E_{Cu} = \frac{M}{2}) = \frac{107.9}{31.77}$ $\therefore$ (c)

42. (a) Greater the value of standard reduction potential, greater will be it's tendency to undergo reduction. So the sequence of deposition of metals on cathode will be Ag, Hg, Cu. Here, magnesium will not be deposited because it's standard reduction potential is negative. So it has strong tendency to undergo oxidation. Therefore, on electrolysis of $Mg(NO_3)_2$ solution, H_2 gas will be evolved at cathode.

$\therefore$ (a)

43. (b) $\alpha = \frac{\Lambda_C}{\Lambda_\infty} = \frac{12}{240}$, % ionization $= 100\alpha = 5$

$\therefore$ (b)

44. (c) Cell constant $= \frac{\text{Specific conductance}}{\text{Observed conductance}} = \frac{x}{y}\text{cm}^{-1}$

Specific conductance of 0.01 M $_2SO_4$

= Observed conductance × Cell constant $= z \times \frac{x}{y}$ ohm^{-1} cm^{-1}

$\therefore$ (c)

45. (c) Specific conductance is the conductance per c.c. solution

$\therefore$ (c)

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. If the e.m.f of a galvanic cell is negative, it implies that:

(a) the cell reaction is spontaneous
(b) the cell reaction is non-spontaneous
(c) the cell reaction is exothermic
(d) the cell is working in reverse direction

2. Which of the following statement is correct?

If $E^\circ_{Cu^{2+}|Cu} = 0.34$ V and $E^\circ_{Sn^{2+}|Sn} = -0.136$ V, $E^\circ_{H^+|H_2} = -0.0$ V

(a) Cu^+ ions can be reduced by $H_2(g)$
(b) Cu can be oxidized by H^+

(c) Sn^{2+} ions can be reduced by H_2
(d) Sn can be oxidized by Cu^{2+}

3. The oxidation potential of hydrogen half-cell will be negative if:
(a) $p(H_2) = 1$ atm and $[H^+] = 1$ M
(b) $p(H_2) = 1$ atm and $[H^+] = 2$M
(c) $p(H_2) = 0.2$ atm and $[H^+] = 1$M
(d) $p(H_2) = 0.2$ atm and $[H^+] = 0.2$ M

4. In an electrochemical process, a salt bridge is used:
(a) to maintain electrical neutrality in each solution
(b) to complete the external circuit so that current can flow for long time
(c) to mix the solution of anodic and cathodic compartment
(d) to supply voltage

5. For a reaction in a galvanic cell, the value of $-\Delta G°$ at certain temperature is not necessarily equal to:
(a) $nFE°$ (b) $RT \ln K$
(c) $T.\Delta S° - \Delta H°$ (d) zero

6. When a lead storage battery is discharged
(a) SO_2 is evolved
(b) lead sulphate is produced at both electrodes
(c) sulphuric acid is consumed
(d) water is formed

7. Which of the following statements is/are correct?
(a) The conductance of one cm^3 (or 1 $unit^3$) of a solution is called specific conductance
(b) Specific conductance increases while molar conductivity decreases on progressive dilution
(c) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extraplotation of the plot of Λ_{eq} against $\sqrt{c}$
(d) The conductance of metals is due to the movement of free electrons

8. The values of E^o of some reactions are given

$I_2 + 2e^- \rightarrow 2I^-$ $E^o = 0.54$ volts
$Sn^{+4} + 2e^- \rightarrow Sn^{2+}$ $E^o = 0.152$volts
$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^o = 1.36$ volts
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^o = 0.76$ volts
$Ce^{+4} + e^- \rightarrow Ce^{+3}$ $E^o = 1.6$ volts

Hence
(a) Fe^{3+} oxidizes Ce^{+3}
(b) Ce^{4+} can oxidize Fe^{2+}
(c) Sn^{2+} will reduce Fe^{3+} to Fe^{2+}
(d) Cl_2 will be liberated from KCl by passing I_2.

9. The amount of ion discharged electrolysis is directly proportional to:
(a) Resistance
(b) Time
(c) Current
(d) Chemical equivalent of the ion

10. Which are true for a standard hydrogen electrode?
(a) The hydrogen ion concentration is 1 M
(b) Temperature is 25°C
(c) Pressure of hydrogen is 1 atmosphere
(d) It contains a metallic conductor which does not adsorb hydrogen

ANSWER KEYS

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

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

The cell potential (E_{cell}) of a reaction is related as $\Delta G = -nF E_{cell}$, where ΔG represents max. useful electrical work

n = no. of moles of electrons exchanged during the reaction

for reversible cell reaction

$$d(\Delta G) = (\Delta_r V)\, dp - (\Delta_r S).\, dT$$

at constant pressure $d(\Delta G) = -(\Delta_r S)\, .\, dT$

$\because$ At constant pressure $\Delta G = \Delta H - T\, .\, \Delta S$ ....(1)

$$\therefore \quad \Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_p \qquad \ldots.(2)$$

$\left(\frac{dE_{cell}}{dT}\right)_p$ is known as temperature coefficient of the e.m.f. of the cell

1. The temperature coefficient of the e.m.f. of cell, $\left(\frac{dE}{dT}\right)_p$ is given by:

(a) $\frac{nF}{\Delta S}$ (b) $\frac{\Delta S}{nF}$

(c) $\frac{\Delta S}{nFT}$ (d) $-nFE$

2. At 300 K, ΔH for the reaction

$Zn(s) + AgCl(s) \longrightarrow ZnCl_2(aq) + 2Ag(s)$ is

–218 kJ/mol while the e.m.f. of the cell was 1.015 V. $\left(\frac{dE}{dT}\right)_p$ of the cell is:

(a) -4.2×10^{-4} VK^{-1} (b) -3.81×10^{-4} VK^{-1}

(c) 0.11 VK^{-1} (d) 7.62×10^{-4} VK^{-1}

3. Calculate ΔS for the given cell reaction in Q. no. 2:

(a) –73.53 J/K mol (b) 83.53 J/K mol

(c) 100J/K mol (d) none of these

COMPREHENSION-II

The four elements W, X, Y and Z form diatomic molecules and also form singly charged negative ions. The following observations are made in a series of experiments:

(a) $X^- + Y_2 \longrightarrow 2Y^- + X_2$

(b) $2W^- + Y_2 \longrightarrow$ No reaction

(c) $2Z^- + Y_2 \longrightarrow 2X^- + Z_2$.

Answer the following questions on the basis of the data given in the diagram.

4. Which of the following is the correct order of reduction potential series?

(a) $E_{W_2/W^-} > E_{Y_2/Y^-} > E_{X_2/X^-} > E_{Z_2/Z^-}$

(b) $E_{Y_2/Y^-} > E_{W_2/W^-} > E_{X_2/X^-} > E_{Z_2/Z^-}$

(c) $E_{Y_2/Y^-} > E_{W_2/W^-} > E_{Z_2/Z^-} > E_{X_2/X^-}$

(d) $E_{Z_2/Z^-} > E_{W_2/W^-} > E_{Y_2/Y^-} > E_{X_2/X^-}$

5. Which of the following is the strongest oxidizing agent?

(a) W_2 (b) Y_2

(c) Y_2 (d) Z_2.

6. Which of the following is the strongest reducing agent?

(a) Y^- (b) X^-

(c) W^- (d) Z^-.

COMPREHENSION-III

Question 7 and 8 are based on the following information

Given

$$E^\circ_{Ni^{2+}/Ni} = -0.26 \text{ V}$$

$$E^\circ_{Sn^{2+}/Sn} = -0.12 \text{ V}$$

A solution containing $SnSO_4$(1M) and $NiSO_4$(1M) is electrolysed. (assume neutral aqueous solution)

7. Which of the ions will be deposited preferentially at cathode? (Given pH of pure water = 7) (P_{H_2} = 1 atm)

(a) Ni^{2+} (b) Sn^{2+}

(c) H^+ (d) OH^{--}

8. The concentration of Sn^{2+} when both Ni^{2+} and Sn^{2+} starts depositing at cathode.

(assume $\frac{2.303RT}{F} = 0.06$)

(a) 1 M (b) 10^{-4}M

(c) 10^{-3}M (d) 10^{-8} M

COMPREHENSION

Electrolysis involves electronation and de-electronation at the respective electrodes. Anode of electrolytic cell is the electrode at which de-electronation takes place whereas at cathode electronation is noticed. If two or more ions of same charge are to be electronated or de-electronated, the ion having lesser discharge potential is discharged. Discharge potential of an ion refers for E°_{OP} of E°_{RP} as the case may be. The products formed at either electrode is given in terms of Faraday's laws of electrolysis i.e., $w = \frac{Eit}{96500}$.

9. During electrolysis of $CH_3COONa_{(aq)}$, the mole ratio of gases formed at cathode and anode is

(a) 1 : 2 (b) 2 : 1

(c) 3 : 1 (d) 1 : 3

10. During electrolysis of $HCOONa_{(aq.)}$, the gas liberated at anode and cathode are respectively

(a) H_2, CO_2 and H_2'

(b) H_2, CO_2 and O_2

(c) H_2 and O_2

(d) O_2 and H_2

11. During electrolysis of $CuSO_{4(aq.)}$, the pH of solution becomes

(a) < 7 (b) > 7

(c) $= 7$ (d) ≥ 7

12. 5 litre solution of 0.4 M $CuSO_{4(aq.)}$ is electrolyzed using Cu electrode. A current of 482.5 ampere is passed for 4 minutes. The concentration of $CuSO_4$ left in solution is

(a) 0.16 M (b) 0.32 M

(c) 0.34 M (d) 0.40 M

13. 5 litre solution of 0.4 M $Ni(NO_3)_2$ is electrolyzed using Pt electrodes with 2.4125 ampere current for 1 h? The concentration of $Ni(NO_3)_2$ left is

(a) 0.31 M (b) 0.22 M

(c) 0.26 M (d) 0.40 M

14. The volume of octane required to be used for its combustion by the oxygen liberated during electrolysis of an $NaNO_{3(aq.)}$ by passing 9.65 ampere current for 1 h is

(a) 322.56 mL (b) 32.256 mL

(c) 3.22 mL (d) 1.612×10^2 mL

COMPREHENSION-IV

The case of conductor is nothing but its conductance. Conductance is the conducting power of ions furnished by the electrolyte in the electrolytic conductor. Titration is the process in chemistry in which we measure the unknown strength of a solution by means of standard solution. Similarly there is a term "Conductometric titrations" in which conductance measurements are frequently employed to find the end point or equivalence point acid-alkali and other titrations. This is based upon the concept is that the molar conductance i.e., electrical conductance depends upon the number and the mobility of ions.

As we know that

$$\Lambda_m(\pm) = n\,\upsilon\,(\pm)\,F$$

$$\Lambda_{eq} = (\upsilon \pm)\,F$$

where, n = no. of moles of electrons

$\upsilon\pm$ = velocity of cation or anion

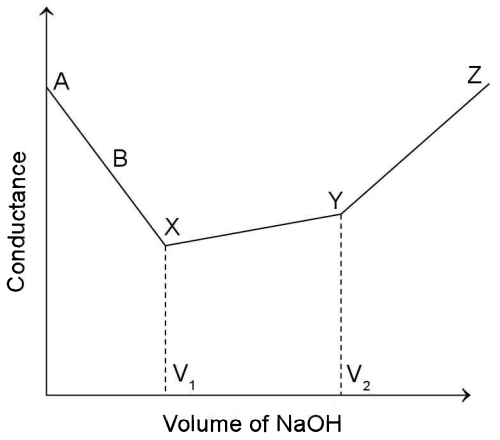
F = amount of charge

Λ_m = molar conductance at a given dilution

Λ_{eq} = equivalent conductance at given dilution

If the velocity of ions decreases, the conductance decreases. Strong acid HCl, taken is conductivity vessel is titrated with strong base NaOH conductometrically taken in burette. As acid is added gradually, fast moving H^+ and OH^- ions are replaced by slow moving Na^+ and Cl^- respectively.

Similarly, when a weak acid i.e., CH_3COOH is titrated with strong base like NaOH. The conductance of CH_3COOH will be low on account of its poor dissociation. On adding base highly ionized sodium acetate is formed and the conductance begins to increase. When the acid is completely neutralized, the further addition of base introduces excess of fast moving OH^- ions. On the basis of the same concepts, a mixture of HCl and CH_3COOH is titrated with strong base NaOH, which is shown by the titration curve showing the variations of conductance of mixture of acids, when definite volume of mixture of acids is titrated by NaOH solution.



Based upon the above write up, answer the following questions:

15. The point of intersection "X" in the above graph represents:

(a) the end point of the reaction of HCl and NaOH solution

(b) the end point of the reaction of CH_3COOH and NaOH

(c) the post-equivalence point of the reaction of CH_3COOH and NaOH

(d) none.

16. Which of the following statements is correct about the graph?

(a) The line AB represents pre-equivalence point of reaction of HCl and NaOH

(b) The line XY represents the post equivalence point of reaction of HCl and NaOH

(c) The line XY represents the equivalence point of the reaction of HCl and NaOH

(d) Both (a) and (b).

17. In the graph, conductance first decreases and reaches minimum thereafter it increases (shown by line AX and XY) because:

(a) slow moving cations and anions are replaced by fast moving anions and cations.

(b) fast moving cations and anions are replaced by slow moving anions and cations.

(c) ionic conductance of H^+ and Na^+ are equal

(d) none of these

18. The sharpness with which the end point "X" may be established depends upon

(a) the concentration of acid

(b) the concentration of base

(c) differences between the conductance of H^+ of HCl and Na^+ of base used.

(d) none of these

19. Which of the following statement(s) are correct about point of intersection of "Y" in the above graph?

(a) It represents the equivalence point of the reaction of HCl and NaOH

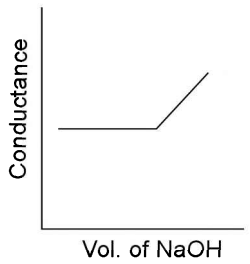
(b) It represents the equivalence point of the reaction of CH_3COOH and NaOH

(c) It represents the post-equivalence of the reaction of CH_3COOH and NaOH

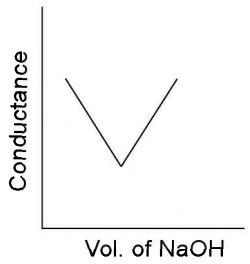
(d) It represents the presence of NaCl and unionised H_2O molecule.

20. CH_3COOH is neutralized by NaOH. Conductometric titration curve will be of the type

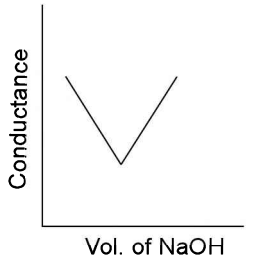
(a)



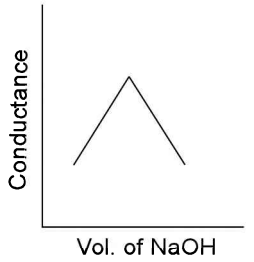
(b)



(c)



(d)



COMPREHENSION-V

One should not get surprised that Ag is the best conductor of electricity. Conductor is concerned with conductance. Conductance (c) is nodiing but it is the conducting powers of ions in solution i.e., in electrolytic conductor or power of flow of electrons in metallic conductor. It is reciprocal of resistance. Conductance in 1 C.C. solution is known as specific conductance (K). The conducting powers of all ions furnished by 1 mole of electrolyte in given volume or dilution, is known as molar conductance (Λ_m). It is related with specific conductance as under

$$\Lambda_m = \frac{1000K}{C_M} \text{ mho } Cm^2 \text{ mol}^{-1}$$

where K is specific conductance; C_M is molar concentration.

In C.G.S. the unit of molar conductance is mho Cm^2 mol^{-1}. In S.I. the unit of molar conductance is Sm^2 mol^{-1} and C_M is the concentration of electrolyte in mol/m^3, where $1m^2$ = 1000 litre and S stands for Siemens.

According to Debye Huckel's Onsagar equation, the molar conductance (Λ_m) in a given dilution related with molar conductance at infinite dilution or at zero concentration at constant temperature as under:

$$\Lambda_m = \Lambda^\circ_m - (A + B\Lambda^0_m)\sqrt{C} \qquad .....(1)$$

This equation is valid for strong electrolyte in which ionisation is complete and even then it is valid in the case

of solution of appreciably low concentration. For H_2O at 25°C, equation (i) reduces into

$$\Lambda_m = \Lambda°_m - (60.2 + 0.229\ \Lambda°_m)$$

For weak electrolyte, the molar conductance at infinite dilution is calculated by Kohlrausch's law. According to this law, at infinite dilution (when dissociation is complete), the molar conductance of an electrolyte is equal to sum of equivalent conductance of cation and equivalent conductance of anion.

For example, for the weak electrolyte A_xB_y,

$= x \times \Lambda°_m$ of cation $+ y \times \Lambda°_m$ of anion.

One can know, α (degree of dissociation), K_a (dissociation constant of acid) and K_{sp} (solubility product of sparingly soluble salt). These are given as under:

(a) $\alpha = \dfrac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}} = \dfrac{\Lambda_m}{\Lambda°_m}$

(b) $K_a = \dfrac{\alpha^2 c}{1-\alpha}$ (for weak acid)

(c) Solubility and solubility product of sparingly soluble salt:

Let us consider sparingly soluble salt AgCl, whose solubility and K_{sp} has to be determined. It will dissociated as under:

$$AgCl\ (s) + H_2O\ (\text{excess}) \rightleftharpoons$$

At t = t Constant

$$Ag^+\ (aq) + Cl^-\ (aq)$$

$$C_M \quad C_M$$

where C_M is the solubility of AgCl in mole/ litre. It is calculated by $\Lambda°_m$ as follows:

$$\Lambda°_m = \frac{1000K}{C_M}$$

or $$\Lambda_m = \frac{1000K}{C_M}$$

($\because$ for sparingly soluble salt, $\Lambda°_m \approx \Lambda_m$)

By knowing the value of K and Λ_m, we calculate C_M and solubility product of AgCl

i.e., $K_{sp\ AgCl} = [Ag^+]\ [Cl^-] = C_M^2$

On the basis of above concepts, a student wish to know various information the given data as under:

Data (i) : At 25° C

K of 0.01 M aq. CH_3COOH solution is

$= 1.63 \times 10^{-2}\ Sm^{-1}$

$\Lambda°_m\ (CH_3COOH) = 390.7 \times 10^{-2}\ Sm^{-1}\ mol^{-1}$

Data (ii): $\Lambda°_m\ (Ca^{+2}) = 1.04 \times 10^{-2}\ Sm^2/\ mol$

$\Lambda°_m(F^-) = 4.8 \times 10^{-3}\ Sm^2 mol^{-1}$

K_{CaF_2} (saturated solution) $= 4.25 \times 10^{-3}\ Sm^{-1}$ at room temp.

K_{H_2O} (used to prepare CaF_2 solution)

$= 2 \times 10^{-4}\ Sm^{-1}$.

On the basis of the above write up, answer the following questions:

21. What is the molar conductance (Λ_m) of CH_3COOH at 25° C from data (i)?

(a) $1.3 \times 10^{-3}\ Sm^2 mol^{-1}$

(b) $1.1 \times 10^{-4}\ Sm^2 mol^{-1}$

(c) $4 \times 10^{-4}\ Sm^2\ mol^{-1}$

(d) $16.3 \times 10^{-4}\ Sm^2\ mol^{-1}$

22. What is the percentage degree of dissociation of CH_3COOH at 25°C from data (i)?

(a) 7% (b) 11%

(c) 9% (d) 4.17%

23. What is the dissociation constant of CH_3COOH at 25°C from data (i)?

(a) 3.5×10^{-4} M (b) 1.82×10^{-5} M

(c) 1.25×10^{-6} M (d) 2.5×10^{-5} M

24. What is the specific conductance due to CaF_2 from data (ii)?

(a) $4.05 \times 10^{-3}\ Sm^{-1}$ (b) $7.05 \times 10^{-3}\ Sm^{-1}$

(c) $4.25 \times 10^{-5}\ Sm^{-1}$ (d) None of these

25. What is the solubility of CaF_2 in g/litre at room temperature according to data (ii)?

(a) 4.9×10^{-3} g/litre (b) 2.58×10^{-2} g/litre

(c) 4.4×10^{-3} g/litre (d) 1.57×10^{-2} g/litre

26. What is the solubility product of saturated solution of CaF_2 at room temperature according to data (ii)?

(a) $2.5 \times 10^{-8}\ M^3$ (b) $3.5 \times 10^{-10} M^3$

(c) $3.32 \times 10^{-11}\ M^3$ (d) $4.42 \times 10^{-12} M^3$

27. For a strong electrolyte if a graph is drawn between $\sqrt{C}$ (in x-axis) and Λ_m (in y-axis) then a straight line will be obtained whose intercept and slope will be respectively?

(a) $\Lambda°_m$, $-(A + B\Lambda°_m)$

(b) $-(A + B\Lambda°_m)$, $\Lambda°_m$

(c) $0, A + BA°_m$

(d) $\Lambda°_m, A + B\Lambda°_m$

28. Which of the following statement(s) is/are correct(s)?

(a) Debye Huckel's Onsagar equation is valid for weak and strong electrolyte both

(b) Debye Huckel's Onsagar equation is valid for strong electrolyte and in case of solution of appreciably low concentration

(c) $\Lambda°_m$ can be obtained by extra-polating $\sqrt{C}$ to zero

(d) Both (b) and (c)

ANSWER KEYS

1. (b)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (b)	**9.** (d)	**10.** (a)
11. (b)	**12.** (d)	**13.** (d)	**14.** (d)	**15.** (a)	**16.** (d)	**17.** (b)	**18.** (b)	**19.** (b)	**20.** (b)
21. (d)	**22.** (d)	**23.** (b)	**24.** (a)	**25.** (d)	**26.** (c)	**27.** (a)	**28.** (d)		

HINTS AND EXPLANATIONS

COMPREHENSION-II

4. (a) For the feasible reaction, the order of reduction potential is as under:

$$E_{W_2/W^-} > E_{Y_2/Y^-} > E_{X_2/X^-} > E_{Z_2/Z^-}$$

5. (a) Since oxidizing agent under reduction.
Thereby higher the reduction potential, stronger is the oxidizing agent.

6. (d) Higher the oxidation potential or lower the reduction potential, higher the reducing power.

COMPREHENSION-V

21. (d) $\Delta_m = \dfrac{K}{C} = \dfrac{1.63\times10^{-2}\,Sm^{-1}}{0.01\times10^3\,mol/m^3}$

$= 16.3 \times 10^{-4}\ S\ m^2\ mol^{-1}$

23. (b) $K = \dfrac{\alpha^2 c}{1-\alpha} = \dfrac{(0.0417)^2 \times 0.01M}{1-0.0417}$

$= 1.82 \times 10^{-5}\ M$

24. (a) $K_{(C_aF_2)} = K_{(CaF_2\ solution)} - K_{H_2O}$

$= 4.25 \times 10^{-3} - 2 \times 10^{-4}$

$= 4.05 \times 10^{-4}\ S\ m^2\ mol^{-1}$

25. (d) $C = \dfrac{K}{\Lambda_m} = \dfrac{4.05\times10^{-3}\,Sm^{-1}}{200\times10^{-4}\,Sm^2\,mol^{-1}}$

$= 2.025 \times 10^{-4}\ mol/dm^3$

$= 2.025 \times 10^{-4}\ 78\ g/litre$

$= 1.58 \times 10^{-2}\ g/litre$

26. (c) $K_{sp} = 4C^3 = 4 \times (2.025 \times 10^{-4}\ M)^3$

$= 3.32 \times 10^{-11}\ M^3$

27. (a)

$\because \quad \Lambda_m = \Lambda°_m - (A + B\Lambda°_m)\sqrt{C}$

$\downarrow\downarrow \quad \downarrow \quad \downarrow$

$y = c \quad m \quad x$

$\Rightarrow$ Intercept $= C = \Lambda°_m$

Slope $= m = -(A + B\ \Lambda°_m)$

MATCH THE COLUMN TYPE QUESTIONS

1. Match the following listed in column I with those listed in column II.

Column I	Column II
(i) Λ_m of KCl increases on dilution	a. is a linear graph
(ii) Λ°_m CH_3COOH increases on dilution	b. is a non-linear graph
(iii) Λ_m of KCl versus (molarity)$^{1/2}$	c. due to increased degree of ionization
(iv) Λ_m of CH_3COOH versus (molarity)$^{1/2}$	d. due to weakening of inter-ionic attractions

2. Match the following:

Column I	Column II
(i) $\Lambda^\circ_m(NaNO_3)$	a. can be obtained by Kohlraush law
(ii) $\Lambda^\circ_m(C_2H_5COOH)$	b. can be obtained by extrapolating Λ_m vs (molarity)$^{1/2}$ graph to zero molarity
(iii) Ionic mobility	c. contribution by the ion to Λ°_m
(iv) Ionic conductance^2	d. velocity of the ion under electric field of 1 V cm^{-1}.

3.

Column I	Column II
(a) If SOP of substance is exist between –1.23 to –0.81 V	(p) Oxidation of substance is not possible
(b) If SOP of substance is exist between –0.81 V to –0.40 V	(q) Possible only in acidic medium
(c) If SOP is less than –1.23 V	(R) Possible in any medium
(d) If SOP is greater than –0.40 V	(s) Oxidation easily takes place

4.

Column I	Column II
(a) $Pt\|Fe^{3+}, Fe^{2+}$	(p) Metal-metal ion half-cell
(b) $Pt\|H_2\|H^+$	(q) Gas-gas ion half-cell
(c) $Pt\|Hg\|Hg_2^{2+}$	(r) half-cell
(d) $Pb\|PbSO_4\|SO_4^{2-}$	(s) Metal Sparing soluble salt half-cell

5.

Column I	Column II
(a) Conductance	(p) Sm^{-1}
(b) Conductivity	(q) S^{-1} m
(c) Molar conductivity	(r) Sm^2mol^{-1}
(d) Resistivity	(s) S

6.

Column-I (Ion)	Column-II (Molar ionic Conductivity(Scm2mol-1))
(a) H^+	(p) 350
(b) Na^+	(q) 50
(c) Li^+	(r) 39
(d) Cs^+	(s) 77

ANSWER KEYS

1. (i)–d; (ii)–c; (iii)–a; (iv)–b
2. (i)–b; (ii)–a; (iii)–d; (iv)–c
3. a→ q; b→ r; c→ p; d→ s
4. a→r; b→q; c→p; d→s
5. a→s; b→ p; c→r; d→q
6. a→ p; b→q; c→r; d→s

TRUE/FALSE TYPE QUESTIONS

1. The electrical conductivity of a solution of acetic acid will be decreased, if a solution of sodium hydroxide is added.
2. In aqueous solution, the limiting molar conductivity of sodium ions is less than that of potassium ions because the sodium ions are more strongly hydrated.
3. E°_{cell} is negative for electrolytic cell.
4. Copper is dissolved at anode and deposited at cathode when Cu electrodes are used and electrolyte is 1 $MCuSO_4(aq)$ solution. because SOP of Cu is less than SOP of water and SRP of Cu is greater than SRP of water.
5. The SRP of three metallic ions A, B, C are –0.3, –0.5, 0.8 volt respectively, so oxidizing power of ions is C > A >B.

ANSWER KEYS

1. F 2. T 3. T 4. F 5. T

ASSERTION/REASON TYPE QUESTIONS

Instructions: In the following questions, an Assertion(A) is given followed by a Reason (R). Mark your responses from the following options.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'
(b) Both Assertion and Reason are true and Reason is not the correct explanation of 'Assertion'
(c) Assertion is true but Reason is false
(d) Assertion is false but Reason is true

1. **Assertion:** On increasing dilution, the specific conductance keep on decreasing.
   Reason: Because the effective number of ions per c.c. of solution decreases.
2. **Assertion:** When the slope of cell potential with respect to temperature is zero at constant pressure, then ΔS is equal to zero.
   Reason: Because $\Delta S_p = nF\left(\frac{dE_{cell}}{d_T}\right)_P$
3. **Assertion:** A saturated solution of KCl is used to make salt bridge in concentration cells.
   Reason: Mobility or velocities of K^+ and Cl^- are nearly same.
4. **Assertion:** We cannot add the electrode potential in order to get electrode potential of third electrode if no. of moles of electrons exchanged are not same.
   Reason: Electrode potential is an extensive property.

ANSWER KEYS

1. (a) 2. (a) 3. (a) 4. (c)

SUBJECTIVE QUESTIONS

1. The following reaction occured in an electrochemical cell

$V^{+2} + VO^{+2} + 2H^+ \rightarrow 2V^{+3} + H_2O$

$E^\circ_{cell} = 0.616$ V

$V^{+3} + Ag^+ + H_2O \rightarrow VO^{+2} + 2H^+ + Ag(s)$

$E^\circ_{cell} = 0.439$ V

Calculate E° for half reaction $V^{+3} + e \rightarrow V^{+2}$

Given $E^\circ_{Ag^+/Ag} = 0.799$ volt.

2. Calculate E^0 of the following half cell reaction at 298 K

$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2NH_3$

$Ag^+ + e^- \longrightarrow Ag,\ E^0_{Ag^+/Ag} = 0.80$ V

$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 = K = 6 \times 10^{-8}$

(Log 2 = .3, Log 3 = .48)

3. At 25°C and at a dilution of 32 litres, the equivalent conductance of a salt of weak base and strong acid is 98.5 $ohm^{-1}\ cm^2$ while that of the strong acid at the same dilution is 383 $ohm^{-1}\ cm^2$. On adding successive quantities of the free base to the solution of the salt, the equivalent conductance could be finally reduced to 89.7 $ohm^{-1}\ cm^2$. Calculate the degree of hydrolysis and the hydrolysis constant.

4. The resistance of a solution 'A' is 50 ohm and that of solution 'B' is 100 ohm, both solutions being taken in the same conductivity cell. If equal volumes of solutions A and B are mixed, what will be the resistance of the mixture using the same cell? (Assume that there is no increase in the degree of dissociation of A and B on mixing)

5. EMF of the following cell is 0.67 V at 298 K

$Pt, H_2 \mid H^+ (pH = X) \parallel 1\ N\ KCl \mid Hg_2Cl_2(s), Hg$

Calculate pH, $E^0_{Cl^-/Hg_2Cl_2,Hg}$ (Calomal electrode) = 0.28 volt

6. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if current efficiency is 50%. If potential drop across the cell is 3.0 volt how much energy will be consumed?

HINTS AND EXPLANATIONS

1. In first cell electrode reactions re:

$V^{+2} \rightarrow V^{+3} = e$ (oxidation)

V^{+4}(from VO^{+2}) $e \rightarrow V^{+3}$ (Reduction)

$V^{+2} + V^{+4} \rightleftharpoons 2V^{+3}$ (Over all process)

$E^\circ_{cell} = E^\circ_{V^{+2}/V^{+3}} + E_{V^{+2}/V^{+3}}$ ...(i)

(oxidn pot (Red pot)

In second cell the electrode processes may be given as—

$V^{+3} \rightarrow V^{+4}$ (from VO^{+2}) $+ e$ (oxid^n)

$Ag^+ + e \rightarrow Ag(s)$

$V^{+3} + Ag^+ \rightleftharpoons V^{+4} + Ag(s)$ (overall process)

$E^\circ_{cell} = E^\circ_{V^{+3}/V^{+4}} + E^\circ_{Ag^+/Ag}$

$0.439 = E^\circ_{V^{+3}/V^{+4}} + 0.799$

$E^\circ_{V^{+3}/V^{+4}} = -0.360$ V

$\therefore\ E^\circ_{V^{+4}/V^{+3}} = 0.360$ V ....(ii)

From Eqs. (i) and (ii) we get

$E^\circ_{cell} = E^\circ_{V^{+2}/V^{+3}} + 0.360$V

$0.616 = E^\circ_{V^{+2}/V^{+3}} + 0.36$ V

$E^\circ_{V^{+2}/V^{+3}} = \mathbf{0.256\ V}\ E^\circ_{V^{+3}/V^{+2}} = \mathbf{-0.256\ V}$

2. The cell uses Ag/Ag^+ electrode as reference half cell

Half cell Reaction E^0

LHS half cell $Ag(s) \rightarrow Ag^+ + e^-\ E^0_{Ag/Ag^+} = -0.8$V

RHS $Ag(NH_3)_2^+ + e^- \longrightarrow Ag(s) + 2NH_3\ E^\circ = xV$

Net $Ag(NH_3)_2^+ \longrightarrow Ag^+ + 2NH_3\ E^0_{cell} = (x - 0.80)$

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6 \times 10^{-8}$$

At equilibrium, $E_{cell} = 0.00$V, K = Keq

$$E^0_{cell} = \frac{0.0591}{n} \log keq$$

$$(x - 0.8\ V) = \frac{0.0591}{1} \log 6 \times 10^{-8}$$

Solving, x = 0.372 V

Hence, E^0 of the half cell reaction is 0.3732 V

3. If h is the degree of hydrolysis of a salt solution at conc. C(M) and if $\Lambda_{soln.}$ be its equivalent conductance, then

$$\Lambda_{soln.} = (1 - h)\,\Lambda_{salt} + h\Lambda_{HA}$$

where Λ_{salt} is the equivalent conductance of unhydrolyzed salt and Λ_{HA} is the equivalent conductance of the strong acid produced by hydrolysis. To measure Λ_{salt} free base is added in sufficient quantity of shift hydrolysis equilibrium to the left. Now on simplificatio

$$h = \frac{\Lambda_{soln.} - \Lambda_{salt}}{\Lambda_{HA} - \Lambda_{salt}}$$

$$\text{So here } h = \frac{98.5 - 89.7}{383 - 89.7} = 0.03$$

Hydrolysis constant $K_h = \frac{h^2C}{1-h}$. Here the salt is at a dilution of 32 litres i.e., 1 equiv/32 litre; so $C = \frac{1}{32}$ (M).

$$\text{Hence } K_h = \frac{(0.03)^2}{(1-0.03)\times 32} = 2.899 \times 10^{-5}.$$

4. Let K_1 and K_2 be the specific conductance of the solutions A and B respectively and the constant of the cell be x.

$\therefore$ For solution A: Sp. Conductance = Conductance x Cell constant

$$K_1 = \frac{1}{50} \times x \qquad \ldots.(1)$$

For solution B: Sp. Conductance $K_2 = \frac{1}{100} \times x$ ....(2)

When equal volumes of A and B are mixed, both the solutions get doubly diluted, hence their individual contribution towards the sp. Conductance of the mixture will be $\frac{K_1}{2}$ and $\frac{K_2}{2}$ respectively and the sp. Conductance of the mixture will be $\frac{1}{2}(K_1 + K_2)$.

$\therefore$ For the mixture: $\frac{1}{2}(K_1 + K_2) = \frac{1}{R} \times x$ .... (3)

(R is the resistance of mixture)

From Eqs. (1), (2) and (3),

R = 66.67 ohm

5. Half Cell reaction

L.H.S. $H_{2(g)} \longrightarrow 2H^+ + 2e^-$ $E^o = 0.00V$

R.H.S. $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$, $E^0_{red} = 0.28$ V

$$H_{2(g)} + Hg_2Cl_2 \longrightarrow 2H^+ + 2Hg(l) + 2Cl^-(aq)$$

$E^0_{cell} = 0.28$ volt

$\therefore$ $K = [H^+]^2\,[Cl^-]^2 = [H^+]^2\,(1)^2 = [H^+]^2$

From Nernst equation

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log[H^+]^2$$

$$0.67 = 0.28 + 0.0591\ pH$$

$$E_{cell} = \frac{E^0_{cell} - 0.28}{0.0591}$$

$$pH = \frac{0.67 - 0.28}{0.059} = 6.6$$

6. $C_6H_5\overset{+3}{N}O_2 + 6H^+ + 6e \longrightarrow C_6H_5\overset{-3}{N}O_2 + 2H_2O$

Change in oxidation no. per mole = 3 – (–3) = 6

$\therefore$ Eq. wt. of nitrobenzene = $\frac{123}{6}$

$\Rightarrow$ $12.3 = \frac{123 \times i_0 \times t \times 50}{6 \times 96500 \times 100}$

($\therefore$ Current efficiency = 50%)

$i_0 t$ (Q) = 115800 coulomb

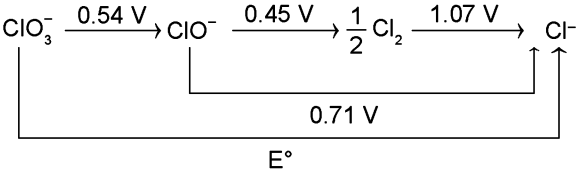
Consumption of energy = Q × N = $\frac{115800 \times 3}{1000}$

= 347.4 kJ

Question Bank

STRAIGHT OBJECTIVE TYPE QUESTIONS

1.



The E° in the given diagram is,

(a) 0.5 (b) 0.6

(c) 0.7 (d) 0.8

2. What is cell entropy change of the following cell?

Pt(s) | $H_2(g)$ | CH_3COOH, HCl || KCl (aq) |Hg_2Cl_2| (s) | Hg

P = 1 atm 0.1M 0.1M

Emf of the cell is found to be 0.045 V at 298 K and temperature coefficient i

3.4×10^{-4} V K^{-1}

Given $Ka_{(CH3COOH)} = 10^{-5}$ M

(a) 60 (b) 65.2

(c) 69.2 (d) 63.5

3. Following cell has EMF 0.7995 V.

Pt | H_2 (1 atm) | HNO_3 (1M) || $AgNO_3$ (1M) | Ag

If we add enough KCl to the Ag cell so that the final Cl^- is 1M. Now the measured emf of the cell is 0.222 V. The K_{sp} of AgCl would be:

(a) $1 \times 10^{-9.8}$ (b) $1 \times 10^{-19.6}$

(c) 2×10^{-10} (d) 2.64×10^{-14}

4. We have taken a saturated solution of AgBr.K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution then the conductivity of this solution in terms of 10^{-7} Sm^{-1} units will be

[Given $\lambda^\circ_{(Ag^+)} = 4 \times 10^{-3}$ Sm^2 mol^{-1} $\lambda^\circ_{(Br^-)} = 6 \times 10^{-3}$ Sm^2 mol^{-1}, $5 \times 10^{-3} Sm^2 mol^{-1}$]

(a) 39 (b) 55

(c) 15 (d) 41

5. At 298K the standard free energy of formation of $H_2O(\ell)$ is – 237.20kJ/mole while that of its ionization into H+ iion and hydroxyl ions is 80 kJ/mole, then the emf of the following cell at 298 K will be

$H_2(g,1 \text{ bar}) | H^+ (1M) || OH^- (1M) | O_2$ (g, 1bar)

(a) 0.40 V (b) 0.81 V

(c) 1.23 V (d) –0.40 V

6. At what $\frac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$ does the following cell have its reaction at equilibrium?

Ag(s) | Ag_2CO_3(s) | Na_2CO_3 (aq) || KBr(aq) | AgBr(s) | Ag(s)

$K_{SP} = 8 \times 10^{-12}$ for Ag_2CO_3 and $K_{SP} = 4 \times 10^{-13}$ for AgBr

(a) $\sqrt{1} \times 10^{-7}$

(b) $\sqrt{2} \times 10^{-7}$

(c) $\sqrt{3} \times 10^{-7}$

(d) $\sqrt{4} \times 10^{-7}$

7. The standard reduction potential of a silver chloride electrode is 0.2 V and that of a silver electrode is 0.79 V. The maximum amount of AgCl that can dissolve in 10^6 L of a 0.1 M $AgNO_3$ solution is

(a) 0.5 mmol (b) 1.0 mmol

(c) 2.0 mmol (d) 2.5 mmol

8. It is observed that the voltage of a galvanic cell using the reaction $M(s) + xH^+ \rightarrow M^{x+} + \frac{x}{2}H_2$ varies linearly with the log of the square root of the hydrogen pressure and the cube root of the M^{x+} concentration. The value of x is

(a) 2 (b) 3

(c) 4 (d) 5

9. Value of Λ_m^∞ for $SrCl_2$ in water at 25°C from the following data:

Concentration (mol/lt)	0.25	1
Λ_m (Ω^{-1} cm^2 mol^{-1})	260	250

(a) 270 (b) 260

(c) 250 (d) 255

10. Which of these ions Cu^+, Co^{3+}, Fe^{2+} is stable in aqueous medium.

Given: $E°_{Cu2+/Cu+} = 0.15$ volt; $E°_{Cu+/Cu} = 0.53$ V; $E°_{Co3+/Co2+} = 1.82$ V; $E°_{Fe3+/Fe2+} = 0.77$ V; $E°_{Fe2+Fe} = -0.44$ V; $E°_{O2,H+/H2O} = 1.23$ V

(a) Cu^+, Co^{3+} (b) Co^{3+}
(c) Cu^+ (d) Co^{3+}, Cu^+, Fe^{2+}

11. For the cell (at 298 K)
$Ag(s) \mid AgCl(s) \mid Cl^-(aq) \parallel AgNO_3(aq) \mid Ag(s)$
Which of the following is correct –

(a) The cell emf will be zero when $[Ag^+]_a = [Ag^+]_c$ ($[Ag^+]$ in anodic compartment = $[Ag^+]$ in cathodic compartment)
(b) The amount of AgCl(s) precipitate in anodic compartment will decrease with the working of the cell.
(c) The concentration of $[Ag^+]$ = constant, in anodic compartment during working of cell.
(d) $E_{cell} = E°_{Ag+ \mid Ag} - E°_{Cl-\mid AgCl\mid Ag} - \frac{0.059}{1}\log\frac{1}{[Cl^-]_a}$

12. Acetic acid is titrated with NaOH solution. Which of the following statement is correct for this titration?

(a) Conductance increases upto equivalence point, then it decreases.
(b) Conductance decreases upto equivalence point, then it increases.
(c) First conductance increases slowly upto equivalence point and then increases rapidly.
(d) First conductance increases slowly upto equivalence point and then drops rapidly.

MULTIPLE CORRECT ANSWER TYPE QUESTIONS

13. In which of the following cell (s) : $E_{cell} = E_{cell}°$?

(a) $Cu(s)|Cu^{2+}(0.01M)||Ag^+(0.1M)|Ag(s)$
(b) $Pt(H_2)|pH = 1\ ||Zn^{2+}(0.01M)|Zn(s)$
(c) $Pt(H_2)|pH = 1\ ||Zn^{2+}(1M)|Zn(s)$
(d) $Pt(H_2)|H^+ = 00.1\ ||Zn^{2+}(0.01M)|Zn(s)$

14 Indicate the ***correct*** statements:

(a) Conductivity cells have cell constant values independent of the solution filled into the cell.
(b) DC (direct current) is not used for measuring the resistance of a solution.
(c) Kohlrausch law is valid both for strong and weak electrolytes.
(d) The k decreases but λ_M and λ_E increase on dilution.

15. The standard redox potential E° of the following systems are

System	E° (volts)
(i) $MnO_4^- + 8H^+ + 5e- \rightarrow Mn^{2+} + 4H_2O$	1.51
(ii) $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$	–0.15
(iii) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^3+ + 7H_2O$	1.33
(iv) $Ce^{3+} \rightarrow Ce^{4+} + e^-$	–1.61

The oxidizing power of the various species are related as

(a) $Cr_2O_7^{2-} > MnO_4^-$
(b) $Ce^{4+} > Sn^{4+}$
(c) $Ce^{4+} > MnO_4^-$
(d) $MnO_4^- > Sn^{4+}$

16. Mark out the correct statement(s) regarding electrolytic molar conductivity.

(a) It increases as temperature increases.
(b) It experiences resistance due to vibration of ion at the mean position.
(c) Increase in concentration decreases the electrolytic molar conductivity of both the strong as well as the weak electrolyte.
(d) Greater the polarity of solvent, greater is the electrolytic molar conduction.

ASSERTION/REASON TYPE QUESTIONS

17. **Statement-1:** In electrochemical cell, we cannot use KCI in the salt bridge if anodic or cathodic compartment consists of Ag^+ of Pb^{2+} ion.
Statement-2: Salt bridge is employed to maintain the electrical neutrality and to minimize the liquid junction potential.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

18. **Statement-1:** Zinc protect the iron better than tin even after it cracks.
Statement-2: $E°_{OPzn} < E°_{OPfe}$ But $E°_{OPSn} > E°_{OPfe}$
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

19. **Statement-1:** On increasing dilution, the specific conductance keep on increasing.
Statement-2: On increasing dilution, degree of ionization of weak electrolyte increases and mobility of ions also increases.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

20. **Statement-1:** For the reaction:
$Ni^{++} + 2e^- \rightarrow Ni$
$Fe^{++} + 2e^- \rightarrow Fe$
$\Rightarrow E°_{Fe++|Fe} < E°_{Ni++|Ni}$ and $E°_{red} > 0$
$\Rightarrow$ So, Fe electrode is cathode and Ni electrodes and Ni electrode is anode.
Statement-2: Because $\Delta G° < 0$ and $E°_{cell} > 0$, so cell is possible.
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

TRUE AND FALSE TYPE QUESTIONS

21. Identity the ture and false statement and answer in given options
1. During electrolysis of 1M NaCl solution Cl2 does not form at the anode.
2. For a concentration cell with its reaction at equilibrium both E_{cell} and $E°_{cell}$ are zero.
3. In a solution of HCN the concentration of CN^- ions is given by 10^{-pH}.

(a) FTF (b) TTT
(c) FFF (d) FTT

22. $KMnO_4$ librates O_2 from water in presence of an acid.
Given, $E°_{MnO4,Mn+2,H+|Pt} = 1.51$ V
$E°_{H+|O2|Pt} = 1.223$ V

23. The standard potentials of some metal-insoluble salt-anoin electrode are as given below

	$E°_{red}$
Ag – AgCl	= 0.222
Ag – AgBr	= 0.03
Ag – AgI	= –0.151
Ag – Ag_2S	= –0.69

Then the K_{SP} values must follow:
K_{SP} (AgCl) > K_{SP} (AgBr) > K_{SP}(AGI) > K_{SP} (Ag_2S)

24. If the E° for $N_2O_4 + 2H^+ + 2e \rightarrow 2HNO_2$ is 1.07 V. Then the standard cell emf of the cell $2N_2O_4 + 2H_2 \rightarrow 4HNO_2$ will be 2.14 volt:

25. At 300 K specific conductivity of ethanol is 4×10^{-10} mho cm^{-1}. The ionic conductance of H^+, $C_2H_5O^-$ at this temperature is 300 and 100 mho cm^2 $equivalent^{-1}$ respectively. Then the negative logarithm of ionic product of alcohol will be 18.

26. Metallic sodium cannot be prepared from electrolysis of an aqueous solution of NaCl because the SRP H_2O < SRP Na^+.

27. The process of AgCN + KCN $\rightarrow$ $K[Ag(CN)_2]$ involves the oxidation of Ag.

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

A fuel cell is a cell that is continuously supplied with an oxidant and a reductant so that it can deliver a current indefinitely

Fuel cells offer the possibility of achieving high thermodynamic efficiency in the conversion of Gibbs energy into mechanical work. Internal combustion engines at best convert only the fraction $(T_2 - T_1)/T_2$ of the heat of combustion into mechanical work.

While the thermodynamic efficiency of the fuel cell is given by, $\eta = \frac{\Delta G}{\Delta H}$, where ΔG is the Gibbs energy change for the cell reaction and ΔH is the enthalpy change of the cell reaction.

A hydrogen-oxygen fuel cell may have an acidic or alkaline electrolyte.

$$Pt|H_2(g)|H^+(aq.)||H_2O(\ell)|O_2(g)|Pt;\ \frac{2.303RT}{F} = 0.06$$

The above fuel cell is used to produce constant current supply under constant temperature & 30 atm constant total pressure condition in a cylinder. If 10 moles H_2 and 5 moles of O_2 were taken initially. Rate of combustion of O_2 is 10 milli moles per minute.

The half cell reactions are

$$\frac{1}{2}O_2(g) + 2H+ (aq) + 2e- \rightarrow H_2O(\ell) \quad E° = 1.246V$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E° = 0$$

To maximize the power per unit mass of an electrochemical cell, the electronic and electrolytic resistances of the cell must be minimized. Since fused salts have lower electrolytic resistances than aqueous solutions, high-temperature electrochemical cells are of special interest for practical applications.

28. Calculate e.m.f. of the given cell at t = 0. (log 2 = 0.3).
(a) 1.255 V (b) 1.35 V
(c) 1.3 V (d) 1.246 V

29. The above fuel cell is used completely as an electrolytic cell with Cu voltameter of resistance 26.94Ω using Pt electrodes. Initially Cu voltameter contains 1 litre solution of 0.05M $CuSO_4$.$[H^+]$ in solution after electrolysis (Assuming no change on volume of solution).
(a) 0.015 M (b) 0.03 M
(c) 0.025 M (d) 0.01 M

30. If $\lambda_m^\infty(Cu^{2+}) = 0.01 S\ m^2\ mole^{-1}$, $\lambda_m^\infty(H^+) = 0.035\ S\ m^2\ mole^{-1}$ and $\lambda_m^\infty(SO_4^{2-}) = 0.016\ S\ m^2\ mole^{-1}$, specific conductivity of resulting solution left in sopper voltameter after above electrolysis is
(a) 2.57 S m^{-1} (b) 1.75 S m^{-1}
(c) 1.525 S m^{-1} (d) 2.25 S m^{-1}

COMPREHENSION-2

REDOX TITRATIONS

Titrations are one of the methods we can use to discover the precise concentrations of solution. A typical titration involves adding a solution from a burette to another solution in a flask. The endpoint of the titration is found by watching a colour change taking place. However, a problem arises when a suitable indicator cannot be found, or when the colour changes involved are unclear. In cases redox potential may sometimes come to the rescue.

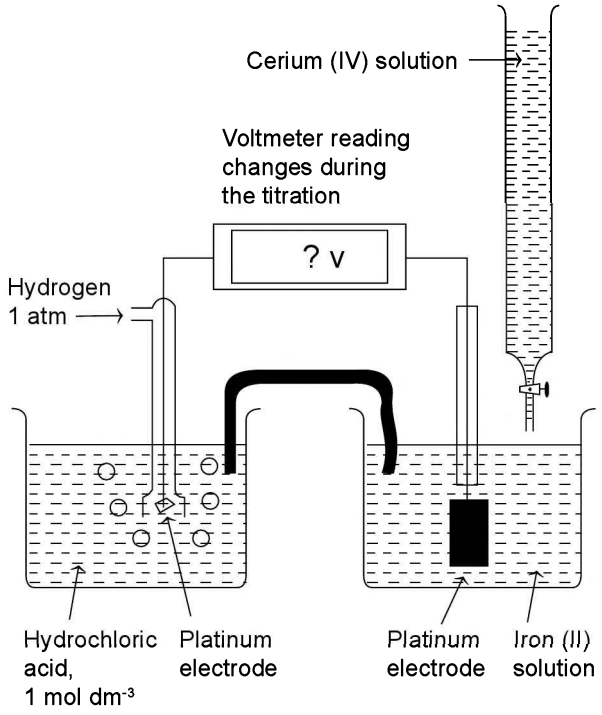


Fig. 1

A particularly well known example (Fig.1) is a method of discovering the concentration of iron in a solution by titrating them with a solution of cerium (IV). The redox potential that are of interest here are $E°_{Fe3+/Fe2+} = +0.77$ V and $E°_{Ce4+/Ce3+} = +1.61$ V. These tell us that cercium (IV) ions are the oxidizing agents, and iron (II) ions are the reducing agent. They should react according to the equation

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$$

Now imagine that we know the concentration of the cerium (IV) ions solution in the burette. We want to measure the concentration of the iron (II) solution. If we add just one drop of the cerium (IV) solution from the bruette, some of the iron (II) ions will be oxidized. As a consequence the beaker would now contain a large number of unreacted ions, but also some iron (III) ions as well. All of the cerium (III). The solution in the beaker now represents an iron(III)/iron(II) half cell, although not at standard conditions. Thus the e.m.f. of the cell will be near, but not equal, to $E°_{Fe3+/Fe2+}$.

	Ions present				Cell	E.m.f./V
	Fe^{2+}	Fe^{3+}	Ce^{3+}	Ce^{4+}		
After the first few drops of Ce^{4+}(aq)	Many	Some	Some	None	Fe^{3-}/Fe^{2-}	A little less than 0.77

Cond.

Near the endpoint	Some	Many	Many	None	Fe^{3+}/Fe^{2+}	A little more than 0.77
Just after endpoint	None	Many	Many	Some	Fe^{4+}/Fe^{3+}	A little more than 1.61

If we continue to add cerium (IV) solution, the number of iron (II) ions is gradually reduced and eventually only a very few are left (Table).At this stage the next few drops of cerium (IV) solution convert all the remaining iron (II) ions into iron (III), and some of the cerium (IV) ions are left unreacted. Once this happens we no longer ions and a smaller number of cerium (IV) ions. The solution in the beaker now behaves as a cerium (IV)/cerium (III) half-cell (although not a standard one).

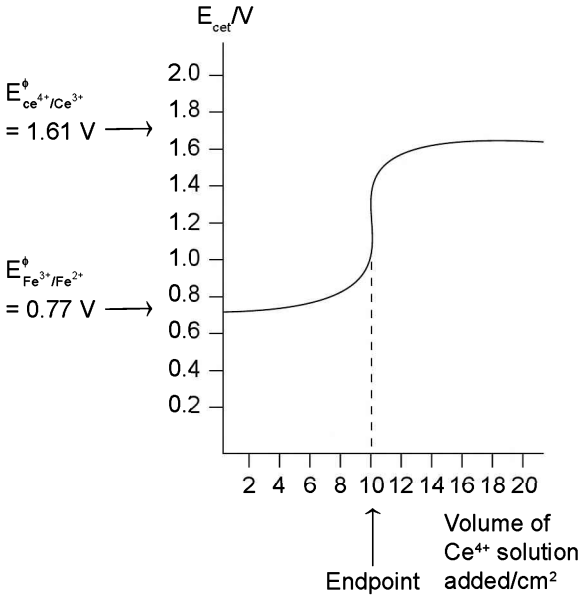


Fig. 2

Just before all the iron (II) ions are converted into iron (III) we have a cell with an e.m.f.of around + 0.77 V. After all the iron (II) ions are oxidised, we have a cell with an e.m.f. of about + 1.61 V. This rapid rise in e.m.f. occurs with the addition of hust one drop of cerium (IV) solution. You should be able to understand why a graph of cell e.m.f. against volume of cerium (IV) solution added looks like that of Fig. 2. The end point of the titration can be read from the graph and the concentration of the iron (II) solution calculated in the usual way.

31. When an ion is converted into a complex ion, the redox potential changes. You can see this in the case of the e.m.f. of the iron (III)/ iron (II) system (+ 0.77 V) and the hexacyanoferrate (III)/ hexacyanoferrate (II) system (+0.36 V). The cyanide ion is said to stabilize the oxidation state of the iorn. If you were to make up a cell

$$\text{Pt(s)}\left|\begin{matrix}Fe(CN)_6^{3-}(aq), Fe(CN)_6^{4-}(aq)\\ 1\text{mol dm}^{-3}\end{matrix}\right\|\left|\begin{matrix}Fe^{3+}(aq), Fe^{2+}(aq),\\ 1\text{mol dm}^{-3}\end{matrix}\right|\text{Pt(s)}$$

What would be the e.m.f. and what would be the cell reaction?

(a) 0.41V, $Fe(CN)_6^{4-}$ (aq.) + Fe^{3+}(aq.) → $Fe(CN)_6^{3-}$(aq.) + Fe^{2+} (aq.)

(b) 0.13V, $Fe(CN)_6^{4-}$ (aq.) + Fe^{3+}(aq.) → $Fe(CN)_6^{3-}$(aq.) + Fe^{2+} (aq.)

(c) 0.41V, $Fe(CN)_6^{3-}$ (aq.) + Fe^{2+}(aq.) → $Fe(CN)_6^{4-}$(aq.) + Fe^{3+} (aq.)

(d) 0.13V, $Fe(CN)_6^{3-}$ (aq.) + Fe^{2+}(aq.) → $Fe(CN)_6^{4-}$(aq.) + Fe^{3+} (aq.)

32. The cell shown below was set up

$$\text{Pt(s)}\left|\begin{matrix}Fe^{3+}(aq), Fe^{2+}(aq),\\ 1\text{mol dm}^{-3}\end{matrix}\right.\left|\begin{matrix}Br(aq),\\ 1\text{mol dm}^{-3}\end{matrix}\right|Br_2(\ell),\left|\right|\text{Pt(s)}$$

What would be the cell e.m.f.? If potassium cyanide solution were added to the left hand half cell (with due care!), what would you expect to happen to the e.m.f. of the cell? $E°_{Br2/Br-}$ = 1.07V and use data of previousquestion, if required.

(a) 0.30 V, emf will increase from 0.30V to 0.41V

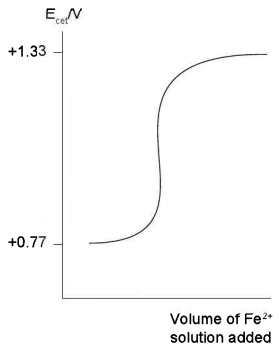
(b) 1.84 V, emf will decrease from 1.84V to 1.43V

(c) 0.30 V, emf will increase from 0.30V to 0.71V

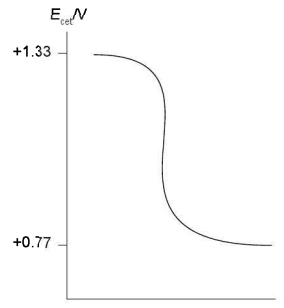
(d) 0.30 V, emf will increase from 0.30V to 0.43V

33. Imagine you were given a solution of potassium dichromate (VI) in a beaker, and a solution of iron (II) sulphate in a burette. You do not know the concentration of dichromate (VI) ions, but the concentration of the iron (II) solution is known. Your task is to carry out a redox titration using the two solutions in order to determine the concentration of dichromate (VI)

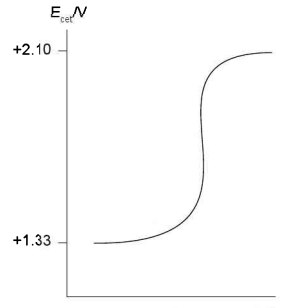
(a)



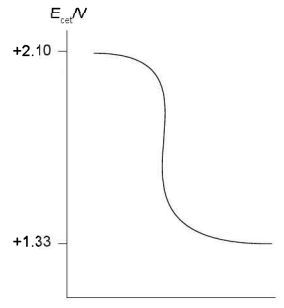
(b)



(c)



(d)



ions. Sketch a graph how the e.m.f. changes in the course of above titration. $E°_{Cr2O2-7/Cr3+}$ = 1.33 V, $E°_{Fe3+/Fe2+}$ = 0.77 V.

COMPREHENSION-3

The molar conductance of NaCl varies with the concentration as shown in the following table.

$\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$

Where λ_m^C = molar specific conductanc

λ_m^∞ = molar specific conductance at infinite diluti

C = molar concentration

Molar Concentration of NaCl	*Molar Conductance In ohm^{-1} cm^2 mole^{-1}*
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell (C) was filled with 25×10^{-4}(M) NaCl solution. The resistance of the cell was found to be 1000 ohm. At infinite dilution, conductance of Cl^- and SO_4^{-2} are 80 ohm^{-1} cm^2 mole^{-1} and 160 ohm^{-1} cm^2 mole^{-1} respectively.

COMPREHENSION-4

METALLURGY OF COPPER

Electrolytic purification of copper is required since the product of the Bessemer convert is impure. Sheets of pure copper are made the cathodes and blister copper is used as the cathodes. The bath contains $CuSO_4$, H_2SO_4 and NaCl. Metallic copper goes into solution as Cu^{+2} ions at the anode and deposited at the cathode. Zinc and iron go into solution and do not deposit at the cathode along with copper. Silver goes into solution as Ag+ ions, but forms sludge in the electrolysis cell. The noble metals such as gold and platinum do not dissolve; they fall to the bottom when released from the copper anode. They help to pay for the copper refining process.

34. In what form will solver be recovered from the plating bath?

(a) Ag^+ (b) AgCl

(c) Ag (d) Ag – Cu alloy

35. The different chemical behaviour of various metal ions (for example only Cu is deposited on the cathode) involved are explainable best using

(a) their amount in impure copper

(b) the electrochemical series

(c) their ionization potentials

(d) their hydration energies

36. The voltage is kept low enough during the operation. This is to ensure that

(a) Fe^{+2} and Zn^{+2} ions are kept in solution only

(b) there is no risk of electric shocks to the plant operators

(c) gold and platinum do not dissolve in solution and are recovered as solids

(d) temperature control is maintained to effect reaction rate control

37. The most important role of various electrolytes added to the electrorefining bath in this case is

(a) to reduce the temperature of bath

(b) to result in good electrical connectivity so as to have high production rates

(c) so that the anode acts as an attackable electrodes

(d) to enhance the viscosity of electrolyte thus preventing leakage from bath.

COMPREHENSION-5

A solution that is relatively resistance to change in pH is called a buffer solution. We can also say that the solution is buffered the simplest way to achieve substantial concentration of both acid and base in the same solution to use a conjugate acid-base pair. The most common form of buffer solution contains a weak acid and its conjugate base or a weak base and its conjugate acid.

By using buffer concept, a student prepare 2L buffer solution of 0.0330 M NaH_2PO_4. The solution is divided in half between the two compartment (each containing 1L buffe) of an electrolysis is carried out for 212 min with a constant current of 1.25 A. [Assumes that $pKa(H_2PO_4^-) = 7.2$]

38. The concentration of $[H^+]$ consumed by HPO_4^{2-} at anode is:

(a) 0.165 M (b) 0.330 M

(c) 1.00 M (d) 0.0825 M

39. pH in 1st compartment cell (at anode) is:

(a) 7.2 (b) 6.72

(c) 7.67 (d) 7.0

MATCH THE COLUMN TYPE QUESTIONS

40. Assume inert electrolyte used in salt bridge in all the given cells is KCl.(K_a of HCOOH = 2×10^{-4})

Column-I	**Column-II**
(a) $Zn \mid ZnSO_4(1M) \mid\mid ZnSO_4(2M) \mid Zn$	(p) Sponataneous cell reaction.
(b) $Cu \mid CuCl_2(1M) \mid\mid CuSO_4(2M) \mid Cu$	(q) Osmotic pressure of cathodic solution is greater than that of anodic solution .
(c) $Ag \mid AgCl(sat.sol.) \mid\mid AgNO_3(1M) \mid Ag$	(r) At equilibrium condition of the cell, freezing point of anodic solution is higher than of cathodic solution
(d) $Pt \mid H_2 \mid HCOOH\ (1M) \mid\mid HCl\ (1M) \mid H_2 \mid Pt$	(s) At equilibrium condition of the cell, boiling point of cathodic solution is higher than that of anodic solution

41. Match the coloumn:

Column-I	**Column-II**
(a) Molten $PbCl_2$ using inert electrode	(p) Metal of salt will reduced
(b) Sodium chloride solution using inert electrode	(q) $H_2O + 2e \rightarrow H_2(g) + 2OH^-$
(c) Silver nitrate solution with silver electrode	(r) Solution becomes basic after electrolysis
(d) Sodium nitrate solution using inert electrode	(s) Solution becomes acidic after electrolysis (t) Solution become acidic after electrolysis

42.

Column – I (Quantities)	**Column – II (Factors on which dependency exist)**
(a) Molar conductance	(p) Temperature
(b) emf of a cell in operation	(q) Concentration of species involved
(c) Electrode potential	(r) Nature of substance involved
(d) Standard reduction potential	(s) Number of electrons lost or gained in the reaction

SUBJECTIVE TYPE QUESTIONS

SHORT SUBJECTIVE

43. In the acid base titration [H_3PO_4(0.1 M) + NaOH (0.1M)] e.m.f of the solution is measured by coupling this electrodes with suitable reference electrode. When alkali is added pH of solution is in accordance with equation, $E_{cell} = E^0_{cell} + 0.059$ pH.

For H_3PO_4 $Ka_1 = 10^{-3}$;
$Ka_2 = 10^{-8}$; $Ka_3 = 10^{-13}$

What is the cell e.m.f. at the llnd end point of the titration if E^0_{cell} at this stage is 1.3805 V.

44. 100 ml, 0.05 M $CuSO_4$ solution is electrolyzed by using current of 0.965 Å for 100 min. Find the pH of solution at the end of electrolysis.

45. The e.m.f. of a cell corresponding to the reaction

$$An + 2H^+(aq) \longrightarrow Zn^{2+}(0.1M) + H_2(g)(1atm)$$

is 0.26 volt at 25° C. Calculate the pH of the solution at the hydrogen electrode

$E^0_{zn^{2+}/zn} = -0.76$ volt and $E^0_{H^+/H_2} = 0$

46. A fuel cell uses CH_4 (g) and forms CO_3^{2-} at the anode. It is used to power a car with 80 Amp. For 0.96 hr. How many litres of CH_4 (g) (stp.) would be required? (V_m = 22.4 L/mol) (F = 96500). Assume 100% effi ciency.

47. Small spherical ball of silver metal used in jewellery having diameter 0.1 cm, which is obtained by the electrolytic deposition. It total number of balls in jewellery is 10,000, then calculate the applied amount of electricity in coulombs, which is used on the depositon on electrodes having entire surface 0.12 m^2. [Density of Ag = 10.5]

It is assumed that 3.5% electricity consumed as wastage during electrolysis and 60% of electrode body immessed in electrode. [Given your answer in multiple of 10^4]

ANSWER KEYS

1. (b)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (b)	**8.** (b)	**9.** (a)	**10.** (b)
11. (c)	**13.** (a, b, d)	**14.** (a, b, c, d)	**15.** (b, c, d)	**17.** (b)	**18.** (c)	**19.** (d)	**20.** (d)	**21.** (a)	
22. True	**23.** true	**24.** False	**25.** True	**26.** False	**27.** False	**28.** (c)	**29.** (a)	**30.** (b)	**31.** (a)
32. (c)	**33.** (b)	**34.** (b)	**35.** (b)	**36.** (a)	**37.** (b)	**38.** (a)	**39.** (b)	**40.** (a, b, c, d)	
41. (a, b, c, d)	**42.** (a, b, c, d)	**46.** (8)	**47.** (5)						

HINTS AND EXPLANATIONS

1. (b) $ClO_3^- + 2H_2 + 4e \rightarrow ClO^- + 4OH^-$; $\Delta G_1°$

$ClO^- + H_2O + e \rightarrow \frac{1}{2}Cl_2 + 2OH^-$; $\Delta G_2°$

$\frac{1}{2}Cl_2 + e \rightarrow Cl^-$; $\Delta G_3°$

$ClO_3^- + 3H_2O + 3e \rightarrow Cl^- + 6OH^-$; $\Delta G°$

$\therefore \Delta G° = \Delta G_1° + \Delta G_2° + \Delta G_3°$

$-6FE° = -4F \times 0.54 - 1F \times 0.45 - 1F \times 1.07$

$\therefore E° = +\frac{3.68}{6} = +0.61$ V

2. (b) considering the cell reaction

$H_2 + 2e \rightarrow 2H^+$

$Hg_2^{2+} + 2e \rightarrow 2Hg\ )\ (\ell) + 2Cl^-(aq)$

$$\Delta S = nF = \left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times 3.4 \times 10^{-4}$$

$= 65.223$ J/K/mole

3. (a) $2Ag^+ + H_2 \rightleftharpoons 2H^+ + 2Ag$

$$E = E° - \frac{0.0591}{2}\log\frac{(H^+)^2}{P_{H2} \times (Ag^+)^2}$$

$$0.222 = 0.7995 - \frac{0.0591}{2}\log\frac{1}{(Ag^+)^2}$$

$(Ag^+) = 10^{-9.8}$

$KsP = (Ag^+)(Cl^-) = (10^{-9.8}) \times (1) = 10^{-9.8}$

(c) Let × gm of Zn deposit on 9 gm of Hg

$$\% \text{ of Zn in Amalgam} = \frac{x}{9+x} \times 100 = 25$$

$\therefore x = 3$ gm

$$\text{Eq. of Zn} = \frac{3 \times 2}{65.4}$$

$$\text{Current} = \frac{6}{65.4} \times \frac{96500}{1000} = 8.85$$

4. (a) The solubility of AgBr in presence of 10^{-7} molar AgNO3 is 3×10^{-7} M.

Therefore, [Br] 3×10^{-4} M^3, $[Ag^+] = 4 \times 10^{-4}$ m^3 and [NO3–] = 10^{-4} m^3

Therefore $K_{total} = k_{Br^-} + K_{Ag^+} + K_{NO_3^-} = 39$ Sm^{-1}

5. (a) Cell reaction

Cathode: $H_2O(\ell) + \frac{1}{2} O_2(g) + 2e^- \rightarrow 2OH^-(aq.)$

Anode: $H_2(g) \rightarrow 2H^+(aq.) + 2e^-$

$$H_2O(\ell) + \frac{1}{2} O_2(g) \rightarrow 2H^+(aq.) + 2OH^-(aq.)$$

Also we have

$$H_2(g)(\ell) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$$

$\Delta G°_f = -237.2$ kj/mol

$$H_2O(\ell) \rightarrow H^+(aq.) + OH^-(aq.)$$

$\Delta G° = 80$ kj/mol

Hence, for cell reaction

$\Delta G° = -77.20$ kj/mole

So, $E = -\frac{77200}{2 \times 96500} = 0.40$ V

6. (b) Anode : $Ag(s) \rightarrow Ag+(aq) + 1e-$

Cathode : $Ag+(aq) + 1e- \rightarrow Ag$

Net : $Ag^+_{(AgBr)} \xrightarrow{1e^-} Ag^+_{(Ag_2Co_3)}$

$$0 = 0 + \frac{0.059}{1} \log \frac{\left(\frac{K_{SP}AgBr}{[Br^-]}\right)}{\sqrt{\frac{K_{SP}Ag_2Co_3}{[CO_3^{2-}]}}}$$

$$\Rightarrow \frac{K_{SP}AgBr}{[Br^-]} = \sqrt{\frac{K_{SP}Ag_2Co_3}{[CO_3^{2-}]}}$$

$$\Rightarrow \frac{4 \times 10^{-13}}{\sqrt{8 \times 10^{-12}}} = \frac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$$

$$\Rightarrow \frac{[Br^-]}{\sqrt{[CO_3^{2-}]}} = \sqrt{2} \times 10^{-7}$$

7. (b) $AgCl + 1e^- \rightarrow Ag + Cl^-$ $\quad E° = 0.2$ V

$Ag \rightarrow Ag^+ + 1e^-$ $\quad E° = -0.59$ V

$AgCl \xrightarrow{1e^-} Ag^+ + Cl^-$ $\quad E° = -0.59$ V

$$E° = \frac{0.059}{n} \log K$$

$$\Rightarrow -0.59 = \frac{0.059}{1} \log K_{SP}$$

$\Rightarrow K_{SP} = 10^{-10}$

Now solubility of AgCl in 0.1 M $AgNO_3$

$S(S + 0.1) = 10^{-10}$

$\Rightarrow S = 10^{-9}$ mol/L

Hence, 1 mole dissolves in 10^9 L solution

Hence, in 10^6 L amount that dissolves in 1 mol.

8. (b) $E_{bck} = \frac{0.059}{2} \log \frac{0.12}{0.08} = 5.19$ mV

9. (a) $\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$

$260 = \Lambda_m^\infty - 0.5\,b$ ... (1)

$250 = \Lambda_m^\infty - b$ ... (2)

On solving (1) & (2), we get

$\Lambda_m^\infty = 270\ \Omega^{-1}\ cm^2 mol^{-1}$

10. (b) If reduction potential of metal ion is greater then O_2/H_2O couple, the ion is stable in water. So Co^{3+} is stable in water

11. (c) Conductivity is high due to $[H^+]$

15. (b, c, d) the SRP should be high for a species to be a good oxidizing agent.

17. (b) Both (S – 1) & (S – 2) are true and (S – 2) is not the correct explanation of (S – 1)

22. **True** The cell for oxidation reaction is,

$Pt \mid O_2 \mid H^+, H_2O \parallel MnO_4^-, Mn^{+2}, H^+ \mid Pt$

$$\therefore E^0_{cell} = E^0_{MnO_4^-, Mn^{+2}, H^+ \mid Pt} - E^0_{H^+ \mid O_2 \mid Pt} = 1.51 - 1.223$$

$= 0.287$ V

Therefore true.

23. **True**

24. **False** $2N_2O_4 + 2H^+ + 2e \rightarrow 2HNO_2$

$H_2 \rightarrow 2H^+ + 2e$

$$N_2O_4 + H_2 \rightarrow 2HNO_2$$

$$\therefore E^0 = E^0_{(N_2O_4 \mid H^+, HNO_2} + E^0_{H_2 \mid 2H^+} = 1.07 \text{ V}.$$

25. **True** $\lambda^\infty = \lambda^\infty_{H^+} + \lambda^\infty_{C_2H_5O^-} = 400$

$$\therefore \lambda = K \times \frac{1000}{C}$$ [C = concentration of C_2H_5OH]

$$\therefore K_{alcohol} = [H^+][OC_2H_5] = (10^{-9})^2$$

$$\therefore pk_{alcohol} = -\log(10^{-18}) = 18$$

26. **False** SRP H_2O > SRP Na^+ so H_2O will be reduced in preference to Na^+ ion.

27. **False** The oxidation number is not changing for Ag.

28. (c) Cell reaction is, $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$

$$E_{cell} = 1.246 - \frac{0.06}{2} \log \frac{1}{P_{H_2} \times \sqrt{P_{O_2}}}$$

$$= 1.246 - \frac{0.06}{2} \log \frac{1}{20\sqrt{10}}$$

$$= 1.246 + \frac{0.06}{2} (1.3 + \frac{1}{2}) = 1.246 + 0.054$$

$= 1.3$ V.

29. (a) $i = \frac{V}{R} = \frac{1.3}{26.94} = 0.04825$ A.

Time of electrolysis $= \frac{5}{10\times10^{-3}} = 500$ minutes.

$Cu^{2+}(aq) + H_2O \rightarrow Cu^{+}(aq) + \frac{1}{2}O_2 + 2H^{+}(aq)$.

$\therefore$ moles of H+ formed $= \frac{ixt}{F} = \frac{0.04825\times500\times60}{96500}$

$= 0.015$ M

30. (b) In resulting solution, $[Cu^{2+}] = 0.0075 = 0.0425$ M, $[H^+] = 0.015$ M and $[SO_4^{2-}] = 0.05$ M.

$\kappa = \kappa Cu^{2+} + \kappa H^{+} + \kappa SO_4^{2-}$

$$= \frac{\lambda^{\infty}_{Cu^{2+}}\times[Cu^{2+}]}{1000} + \frac{\lambda^{\infty}_{H^+}\times[H^+]}{1000} + \frac{\lambda^{\infty}_{SO_4^{2-}}\times[So_4^{2-}]}{1000}$$

$$\frac{0.01\times10^4\times0.0425}{1000} + \frac{0.35\times10^4\times0.015}{1000} + \frac{0.016\times10^4\times0.05}{1000}$$

$= 0.00425 + 0.00525 + 0.008$

$= 0.0175$ S cm^{-1} $= 1.75$ S m^{-1}.

31. (a) $E^0_{cell} = E^0_{Fe^{3+}/Fe^{2+}} - E^0_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = +0.77\,V - 0.36\,V$

$= +41$ V

The reaction is: $Fe(CN)_6^{4-}(aq) + Fe^{3+}(aq) \rightarrow Fe(CN)_6^{3-}(aq) + Fe^{2+}(aq)$

32. (c) $E^0_{cell} = E^0_{Br_2/Fe^{-}} - E^0_{Fe^{3+}/Fe^{2+}} = +1.07$ V $- 0.77 =$ $+0.30$V

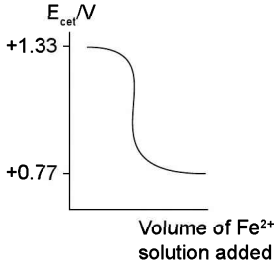
If cyanide ions are added, the left hand half cell would change its e.m.f. to $E^0_{Fe(CN_6^{3-}/Fe(CN)_6^{4-}} = +0.36$. Therefore, the e.m.f. would change to $+0.71$V.

33. (b) After one drop iron (II) solution is added the beaker will contain a mixture of $Cr_2O_7^{2-}$, Cr^{3+} and Fe^{3+} ions. The e.m.f. will be near to $E^{\circ}_{Cr_2O_7^{2-}/Cr^{3+}} = +0.77$. The reaction is:

$6Fe^{2+}(aq) + Cr2O_7^{2-}(aq) + 14H^{+}(aq) \rightarrow$

$6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(I)$

The apparatus would be like that in figure. The graph is shown in figure



34. (b) $Ag^{+} + NaCl \rightarrow AgCl + Na^{+}$.

35. (b) SRP zinc $= -0.76$

SRP iron $= -0.44$

SRP copper $= +0.34$ (highest); Hence, only copper deposits, others do not.

36. (a) Increasing voltage would cause deposition of Fe^{+2} and Zn^{+2} also to occur.

37. (b) Water (pure) is a poor electrical conductor.

38. to 39.

$[H^+] = [OH^-] = \frac{it}{96500} = \frac{1.25\times212\times60}{96500}$

$= 0.165$ M

At anode

$HPO_4^{2-} + H^+$	$\rightleftharpoons$	$H_2PO_4^-$
0.330 M	0.165 M	0.330 M
0.330 M – 0.165 M	0.165 M	0.330 M + 0.165 M
0.165 M		0.495 M

$pH = 7.2 + \log\frac{[HPO_4^{--}]}{[H_2PO_4^-]} = 7.2 + \log\frac{0.165}{0.495}$

$= 7.2 - \log3 = 7.2 - 0.4771 = 6.72$

At cathode

$H2PO_4^- +$	OH- $\rightleftharpoons$	$HPO4^{--} + H_2O$
0.330	0.165	0330
0.330 M – 0.165 M	0	0.330 M + 0.165 M

$pH = 7.2 + \log\frac{0.495}{0.165}$

$pH = 7.2 + \log3 = 7.2 + 0.477$

$pH = 7.67$.

40. (a – p, q, r, s), (b – p, q), (c – p, q, r, s), (d – p, q, r, s)

41. (a – p, s); (b – q, r); (c – p, s); (d – q, s)

(a) $PbCl_2$, Cathode: $Pb^{2+}\,2e^{-} \rightarrow Pb(s)$

Anode: $2Cl^{-} \rightarrow Cl_2(g) + 2e^{-}$

(b) Cathode: $H_2O + 2e \rightarrow H_2(g) + 2\,OH^{-}$

Anode: $2Cl^{-} \rightarrow Cl_2(g) + 2e^{-}$

(OH^{-}) in increased solution become basic

(c) Cathode: $Ag^{+} + e^{-} \rightarrow Ag(s)$

Anode: $Ag(s) \rightarrow Ag^{+} + e^{-}$

Neutral solution

(d) Cathode: $H_2O + 2e \rightarrow H_2(aq) + 2\,OH^{-}$

Anode: $H_2O \rightarrow 1/2\,O_2 + 2H^{+} + 2e^{-}$

Neutral solution

42. (a – p, q, r), (b – p, q, r), (c – p, q, r), (d – r)

43. $pH = \frac{pKa_2 + pKa_3}{2} = 10.5$

$E_{cell} = E^{\circ}_{cell} + 0.059\,pH = 1.3805 + 0.059 \times 10.5 = 2V$.

44. Time taken to electrolyzed Cu-metal completely

$$\frac{ixt}{96500} = \text{equivalents of Cu-deposited}$$

$$\frac{0.965 \times t}{96500} = 0.005 \times 2$$

$t = 1000$ sec.

after 1000 sec pH of solution is not changed because after this time only water is reduced and water is oxidized.

$\therefore$ equivalents of H^+ produced = equivalents of Cu^{2+} ion deposited = 10^{-2}.

pH = - log 10^{-2} = 2.

45. $E^\circ_{cell} = 0.76$ volt

Applying nernst equation

$$E_{cell} = E^\circ_{cell} \frac{-0.0591}{2} \log \frac{[Zn^{2+}][H_2]}{[H^+]^2}$$

$$0.26 = 0.76 \frac{-0.0591}{2} \log \frac{(0.1)(1)}{[H^+]^2}$$

$$\log \frac{0.1}{[H^+]^2} = \frac{2 \times 0.50}{0.0591} \quad \text{or } \log 0.1 - \log [H^+]^2 = 17$$

$$\text{or } 2pH = 17 - \log 0.1$$

$$pH = \frac{18}{2} = 9.$$

46. $CH_4 + 10OH^- \rightarrow CO_3^{2-} + 7H_2O + 8e^-$

$$\text{No. of Faradays required} = \frac{80 \times 3600 \times 0.96}{96500}$$

$$\text{Hence, mol. Of } CH_4 \text{ required } \frac{1}{8} \times \frac{80 \times 3600 \times 0.96}{96500}$$

$$V_{CH_4} = \frac{1}{8} \times \frac{80 \times 3600 \times 0.96}{96500} \times 22.4 \text{ L} = 8.356 = 8.02 \text{ L}$$

$$= 8$$

47. Radius of ball = $\frac{0.1}{2} = 0.5$

Surface area of electrodes = 0.12 m^2 = 1200 cm^2

60% of 1200 = 2000 cm^2.

Weight of jewellery = $\frac{4}{3} \pi r^3 \times 10{,}000 \times \text{density} = \frac{4}{3}$

$\times 3.14 \times (0.05)^3 \times 10000 \times 10.5 = 54.9$ gram

Now amount of electricity in faraday

$$= \frac{\text{wt. of Ag}}{\text{Equivalent wt. of Ag}} = \frac{54.9}{108} = 0.50F = 48250 \text{ coulomb.}$$

$$\text{So applied electricity amount} = \frac{48250 \times 100}{96.5} = 50{,}000$$

coulomb = 5×10^4 coulomb

So, is 5.

SUBJECTIVE ANSWER TYPE QUESTIONS

15. A current of 3.7 ampere is passed for 6 hr between Ni electrodes in 0.5 litre of 2 M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

Sol. The electrolysis of $Ni(NO_3)_2$ in presence of Ni electrode will bring in following changes:

At anode: $Ni \rightarrow Ni^{2+} + 2e$

At cathode: $Ni^{2+} + 2e \rightarrow Ni$

$\because$ Eq. of Ni^{2+} formed = Eq. of Ni^{2+} lost

Thus, there will be no change in concentration of $Ni(NO_3)_2$ solution during elecrolysis, i.e., **it will remain 2 M.**

16. 3 ampere current was passed through an aqueous solution of an unknown salt of Pd for 1 hour. 2.977 g of PD^{n+} was deposited at cathode. Find n. (At. Wt. of Pd =106.4)

Sol. $\because Pd^{n+} + ne \rightarrow Pd$

$$\text{For Pd, } \frac{w}{E} = \frac{i \times t}{96500} \quad \frac{2.977}{106.4/n} = \frac{3 \times 1 \times 60 \times 60}{96500} \quad n = 4$$

17. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25°C?

Assume $[Ni^{2+}] = 1$ M and $P_{H_2} = 1$ atm.

Sol. $Ni \rightarrow Ni^{2+} + 2e \qquad E^\circ_{OP} = 0.236$ V

$2H^+ + 2e \rightarrow H_2 \qquad E^\circ_{RP} = 0$

$\therefore E^\circ_{cell} = 0.236$

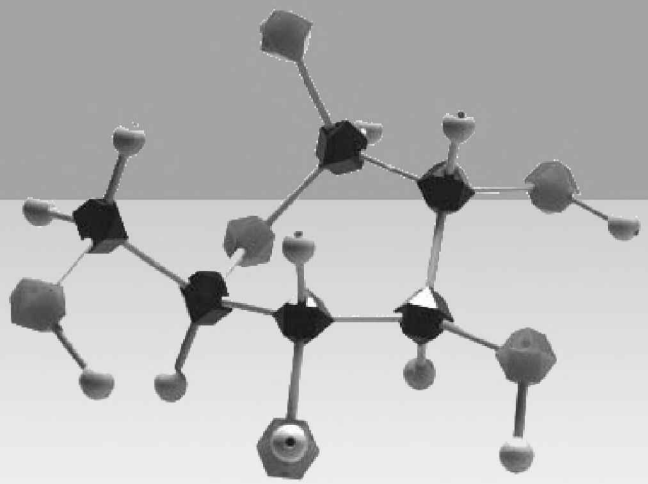
$$\therefore E_{cell} = E^\circ_{cell} + \frac{0.059}{2} \log_{10} \frac{[H^+]^2}{[Ni^{2+}]}$$

$$0 = 0.236 + \frac{0.059}{2} \log_{10} [H^+]^2$$

$$\text{or } -\log H^+ = 4$$

$\therefore$ pH = 4

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CHAPTER 10

Surface Chemistry

INTERFACE OF PHASES

Interface is the boundary between any two phases. Among the three phases, gas, liquid, and solid, five types of interfaces are possible: gas-liquid, gas-solid, liquid-liquid, liquid-solid, and solid-solid. Statistically a surface is only one or two molecules thick. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas.

Remember:

- The bulk phases that we come across in surface chemistry may be pure compounds or solutions.
- Due to complete miscibility, there is no interface between the gases.

Surface science is the study of physical and chemical phenomena that occur at the interface of two phases, including solid-liquid interfaces, solid-gas interfaces, solid-vacuum interfaces, and liquid-gas

The surface of the solid or liquid has a tendency accumulate molecular species when they come in contact. It happens due to unbalanced forces of attraction or free valencies which are present at the solid or liquid surface, have the property to attract and retain the molecules of a gas or a dissolved substance on to their surfaces with which they come in contact.

Since energy is released on account of attraction, the solid acquires a more stable state. These molecular species remain on the surface only and do not penetrate into the bulk. Hence, adsorption may be defined as

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 as compared to that in bulk is called ***adsorption***.

Examples:

1. Dyes get adsorbed on cotton fibres, activated carbon, etc
2. Ammonia gas placed in contact with charcoal gets adsorbed on it.
3. Oxalic acid placed in contact with activated carbon gets adsorbed on it.
4. The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

Adsorbent and adsorbate: The molecular species or substance, which concentrates or accumulates at the surface is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**.

For example, activated charcoal which is finely divided has a tendency to adsorb a number of gases like ammonia, phosgene etc. Here charcoal acts as an adsorbent while gas molecules act as adsorbate. In a similar manner, animal charcoal is used for decolourising a number of organic substances in the form of their solution. The discharge of the colour is due to fact that the coloured component (generally an organic dye) gets adsorbed on the surface of the adsorbent i.e., animal charcoal.

Explanation of Adsorption: As discussed above, the adsorption is a surface phenomenon. The atoms in a solid are held together by certain binding forces which are main van der Waal's forces or may be even chemical forces. The unutilized or unbalanced forces present on the surface (indicated by dotted lines) make it quite active. Moreover, when a solid substance shown in figure 1 (a) is broken into two or more pieces, new surfaces get formed shown in figure 1 (b) i.e., the number of the unbalanced forces becomes more. In other words, the number of active centres or free valencies becomes more by taking the adsorbent in the finely powdered form

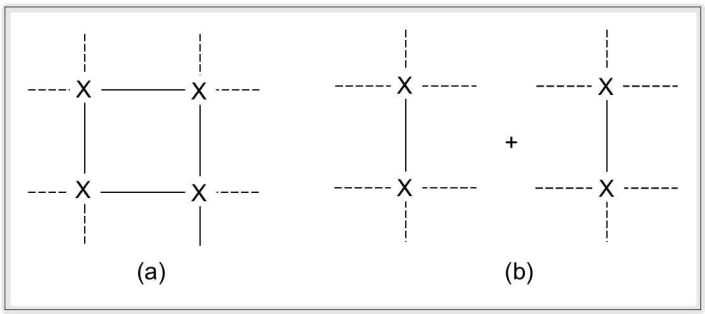


Fig. 10.1 Unbalanced forces on the finely divided solid surface

Due to the unbalanced forces, the atoms or molecules on the surface have a tendency to attract and retain the molecules of the gases or liquids when they come in contact with the surface. This results into higher concentration of any particular species at the surface than in the bulk and this leads to adsorption. The adsorption which are commonly used are activated charcoal, animal charcoal, silica gel and a number of finely divided metals such as Cu, Ni, Pd, etc. Activated charcoal is a powerful adsorbent since it is a microscopic crystalline variety of graphite having a very large surface area.

Desorption

An adsorbed species present on a surface at low temperatures may remain almost indefinitely in that state. As the temperature of the substrate is increased, however, there will come a point at which the thermal energy of the adsorbed species is such that one of several things may occur:

1. a molecular species may decompose to yield either gas phase products or other surface species.
2. an atomic adsorbate may react with the substrate to yield a specific surface compound, or diffuse into the bulk of the underlying solid.
3. the species may desorb from the surface and return into the gas phase.

The last of these options is the desorption process. In the absence of decomposition the desorbing species will generally be the same as that originally adsorbed but this is not necessarily always the case.

Absorption

Absorption is another important phenomenon which is noticed in our daily life. *When the molecules of a substance are uniformly distributed throughout the body of other substance, it is known as* ***adsorption***. For example, when ammonia gas is passed through water, the molecules of ammonia get uniformly distributed in water and we say that ammonia has been absorbed by water.

Difference between adsorption and absorption

On the basis of the above discussion, it appears that adsorption is quite different from absorption. Whereas, adsorption is linked only with the surface of one substance which takes up the particles of the other substance, absorption occurs in the bulk of the substance which absorbs. In order to make a proper distinction between the two, let us place a silica gel and anhydrous calcium chloride in contact with water vapours taken in two separate containers. When silica gel is placed in an environment of water vapours, it simply adsorbs these water vapours. As shown in figure 10.2(a), the water vapours are present in a high concentration at the surface of silica gel whereas, the interior of the gel has no water vapours. On the other hand, when anhydrous calcium chloride is placed in water vapours, it absorbs these.

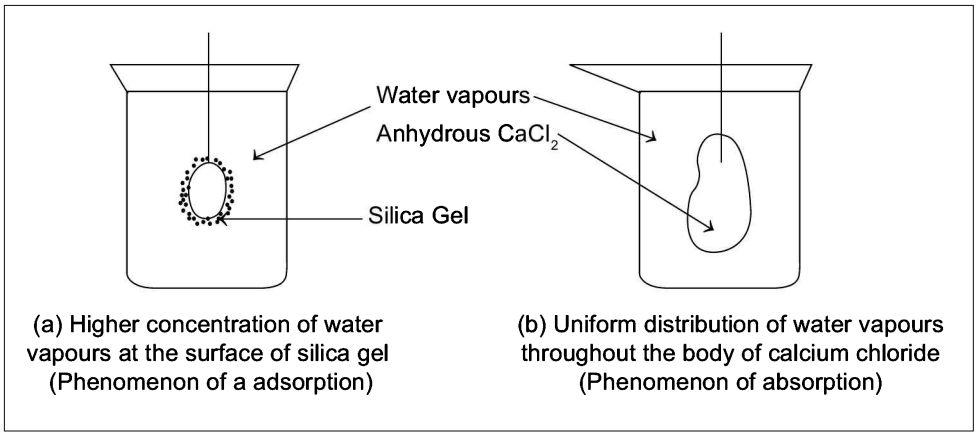


Fig. 10.2

The water vapours uniformly get distributed throughout the body of anhydrous calcium chloride as shown in figure 10.2(b). Thus, silica gel absorbs water vapours while anhydrous calcium chloride absorbs moisture. It is quite obvious that the concentration of the water vapours is mainly on the surface of the gel while these vapours have penetrated into the bulk of the anhydrous calcium chloride. Now, as the adsorption is linked with the surface only, the extent of adsorption depends upon the availability of space on the surface. Therefore, it is expected to be quite fast to start with while its rate must decrease with the passage of time. On the other hand, the absorption must proceed at a uniform speed since it is no way connected with the surface of the substance which absorbs. The main points of distinction between the two phenomenon are listed in a tabular form.

Distinction between absorption and adsorption

Absorption	***Adsorption***
1. It is a phenomenon as a result of which the species of one substance gets distributed uniformly throughout the body of the other substance.	It is the phenomenon as a result of which the species of one substance get concentrated mainly at the surface of the other substance which adsorbs these.
2. The concentration of the same throughout the material.	The concentration on the surface of the adsorbent is different from that in the bulk.
3. It is a bulk phenomenon since it occurs throughout the bulk of the material.	It is only a surface phenomenon since it occurs only at the surface.
4. Absorption proceeds at uniform rate.	Adsorption is rapid in the beginning and its rate slowly decreases with the non-availability of the surface.

Sorption: Some cases are known in which both adsorption and absorption occur together. This means that a particular substance gets distributed throughout the bulk of the other substance but at the same time, its concentration on the surface also increases and is more than in the bulk. However, it is very difficult to make a clear distinction between the two. This is known as ***sorption***. Certain dyes get adsorbed as well as absorbed on the fibres resulting in sorption

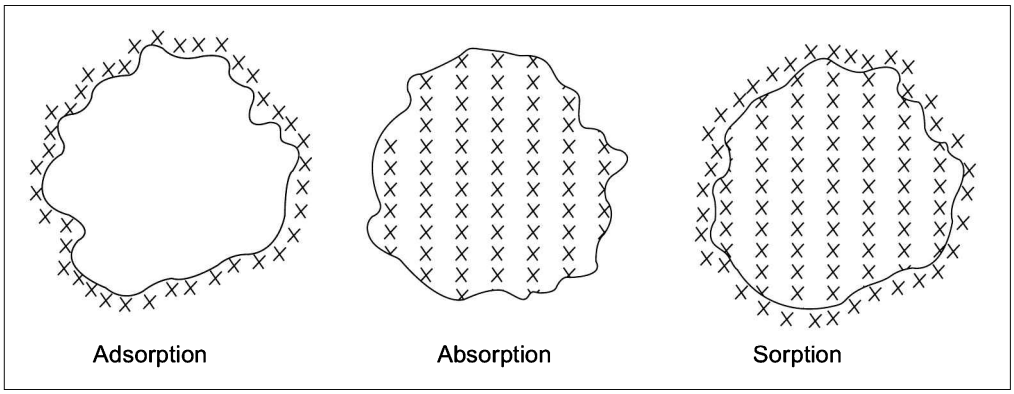


Fig. 10.3

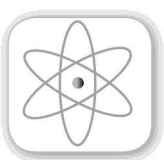
Thermodynamical feasibility of Adsorption: We have studied that the phenomenon adsorption arises because of attraction between he particles or molecules of adsorbent and adsorbate. Therefore, it is exothermic in nature and is accompanied by release in energy known as enthalpy of adsorption (heat of adsorption). It may be defined as

The change in enthalpy taking place for the adsorption of one mole of the adsorbate on the surface of the adsorbent.

The adsorption is also likely to influence the randomness. ($T\Delta S$) factor. The randomness of the adsorbed species on the surface of the adsorbent is likely to decrease i.e., $T\Delta S$ is negative. Let us study the feasibility of the phenomenon in the light of Gibb's Helmholtz equation. Since, ΔH favours while $T\Delta S$ opposes the phenomenon of adsorption, the magnitude of the former must be more. This is feasible only at low temperature and this is what we actually notice. We shall discuss the effect of temperature on the rate of adsorption at a later stage.

$$\frac{\Delta H}{\Delta G} = \underset{(-ve)}{\Delta H} - \underset{(-ve)}{T\Delta S}$$

CLASSIFICATION OF ADSORPTION



Adsorption can be classified into two categories as described below

Positive and Negative Adsorption (Adsorption from Solutions: The Gibbs Equation)
It was pointed out by J. Willard Gibbs (1878) that the concentration of a solute at the surface of a liquid could be greater than in the bulk of the solution. The thermodynamic relationship expressing this behaviour is usually referred to as the **Gibbs adsorption equation.** For a dilute solution of concentration c, this equation is,

$$S = \frac{c}{RT} \cdot \frac{d\gamma}{dc},$$

where S is the excess concentration of solute per cm^2 of surface, as compared with that in the bulk of the solution; $d\gamma/dc$ is the rate of increase of the surface tension of the solution with the concentration of the

solute; R is the familiar gas constant, and T is the absolute temperature. According to the equation, any solute which causes the surface tension of the solvent to decrease, i.e., $d\gamma/dc$ is negative, will have a higher concentration in the surface than in the bulk of the solution, since S will be positive. In other words, a substance which decreases the tension at an interface will concentrate at that interface. If $d\gamma/dc$ is positive, the dissolved substance raising the surface tension, then S will have a negative value; the concentration of the solute will thus be lower in the surface than in the body of the solution. This behaviour, known as **negative adsorption,** has been observed with some electrolytes.

When a finely powdered porous substance, such as charcoal or silica gel, is added to a solution, the area of the interface is very large, and the possible extent of adsorption is considerable. In this case, the Gibbs adsorption equation applies to the surface of contact between the solid and the solution; hence, $d\gamma/dc$ refers, strictly, to the influence of concentration on the solid-liquid interfacial tension. Very little information is available concerning such interfacial tensions, but as an approximation, it is assumed that the influence of concentration is the same as on the corresponding air-liquid surface tension. It may be supposed, therefore, as a rough general rule, that a particular substance will be adsorbed from solution by a solid adsorbent if that substance reduces the surface tension of the solvent.

If substances like dyes, soaps, and detergents are kept in water, their molecules rise and concentrate at the surface and, thus, their concentration is more at the surface and less in the bulk. This is known as positive adsorption.

On the other hand, if substances like KCl and inorganic acids are dissolved in water, these remain more in bulk and their concentration at surface is less. This is negative adsorption.

Physical adsorption: When the particles of the adsorbate are held to the surface of the adsorbent by physical forces such as van der Waal's forces, it is called physical adsorption. This is called physisorption or even van der Waal's adsorption. Since the attractive forces are weak, they can be easily overcome either by increasing the temperature or decreasing the pressure. Therefore, the physisorption can be easily reversed or decreased by either raising temperature or by reducing the pressure of the gas.

Van der Waal's forces are weak but long range forces, hence physisorption can be multilayer adsorption. The enthalpy of adsorption in case of physical adsorption is quite low. It is varies between 20 to 40 kJ mol^{-1}.

Chemical adsorption: When the molecules of the adsorbate and adsorbent are held together by stronger forces similar to the chemical bonds, the adsorption is known as chemical adsorption or **Chemisorption.** This leads to formation of some sort of compound on the surface of the adsorbent. These are known as **surface compounds**. This is further confirmed by the fact that when oxygen is adsorbed on the surface of metal like tungsten or activated charcoal, the molecules which are released from the surface are not of oxygen but those of tungsten oxide in case of metal and of carbon monoxide or carbon dioxide in case of charcoal. Moreover, the enthalpy of adsorption, unlike physical adsorption is also quite high (nearly 400 kJ mol^{-1}) which is almost of the same magnitude that we come across in chemical reactions.

Although, stronger forces similar to the chemical bonds are there ,they are short range forces, hence it is mono layer in nature which means that only the atoms of the molecules present on the surface of the adsorbent are involved in the bond formation.

The important points of distinction between the two types are adsorption are give:



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Difference between Physisorption and Chemisorption

Property	*Physisorption*	*Chemisorption*
1. Nature of forces	Weak van der Waal's forces present.	Strong chemical forces present
2. Heat of adsorption	Low; of the order of 20-40kJ/mol.	High; of the order of 400kJ/mol
3. Temperature	Usually occurs at low temperature	Occurs at high temperature
4. Reversibility	Reversible	Irreversible

(Contd)

Property	Physisorption	Chemisorption
5. Specificit	It is not specific in nature, i.e., all gases are adsorbed on the surface of a solid to the same extent.	It is highly specific in nature and occurs only when there is bond formation between adsorbent and adsorbate molecules.
6. Nature of molecular layers	Forms multi-molecular layers	Forms mono-molecular layer
7. Extent of adsorption	The extent of adsorption is directly related with the case of liquefaction of the gas.	There is no correlation between extent of adsorptiona and the ease of liquefaction of the gas.
8. Activation energy	It does not involve appreciable activation energy. In most cases, the activation energy required is almost nil.	It generally requires appreciable activation energy since a chemical reaction is to take place.
9. State of adsorbate	Same state as in the bulk.	State of adsorbate molecules may be quite different from that in the bulk.

Factors Influencing Adsorption of Gases by Solids

When a gas is not involved in the formation of any compound with the surface of the adsorbent, it represents adsorption.Gases are adsorbed on the surface of either finely divided metals such as Ni, Pt, Fe, Pd etc. or porous solids such activated charcoal or as activated charcoal, animal charcoal, silica gel, alumina etc. The extent of adsorption depends upon a number of factors which are briefly discussed

1. Nature of gas or adsorbate

The only criteria for the extent of adsorption is the magnitude of the attractive forces which exist between the particles of the adsorbent and adsorbate. For example, under given conditions of temperature and pressure, the easily liquefiable gases like NH_3, HCl and CO_2 are adsorbed to greater extent than the gases like H_2, O_2 and N_2 which are liquefied with difficult . The former being heteroatomic in nature, have a greater magnitude of the attractive forces as compared to the latter.

In general, the ease of the liquefaction of gases can be compared in terms of their **critical temperatures**. The critical temperature of a gas may be defined as

the minimum temperature above which a gas cannot be liquefied however large its pressure may be

Thus, the greater the value of critical temperature, easier will be the ease of liquefaction of the gas and more will be the extent of its adsorption on a particular solid. The critical temperatures of different gases along the extent of their adsorption in cc in one gram of the activate charcoal (adsorbent) are listed.

Gas	H_2	N_2	CO	CH_4	CO_2	HCl	NH_3	SO_2
Critical temperature (K)	33	126	134	190	304	324	406	430
Amount adsorbed (in cc)	4.7	8.0	9.3	16.2	48	72	18	380

—— Extent of adsorption increases ⟶

Note: This does not apply to chemisorption since adsorption can occur only when specific bonds are formed between the molecules of adsorbate and adsorbent. Thus, chemisorption is of selective nature.

The nature of adsorbent which is normally a solid is linked with its surface area.

- Charcoal, silica gel and alumina are regarded as good adsorbents because of their porous nature and large surface area.
- Metals acting as adsorbent are also taken in finely divided form so that large surface area may be available for adsorption of the gases.
- Transition metals are also good choice for chemisorption because they can offer vacant 'd' orbitals.

2. Effect of temperature (Adsorption Isobar)

The curves between x/m (amount of the gas adsorbed per unit mass of adsorbent) and the temperature at constant pressure for the two types of adsorption are as follows:

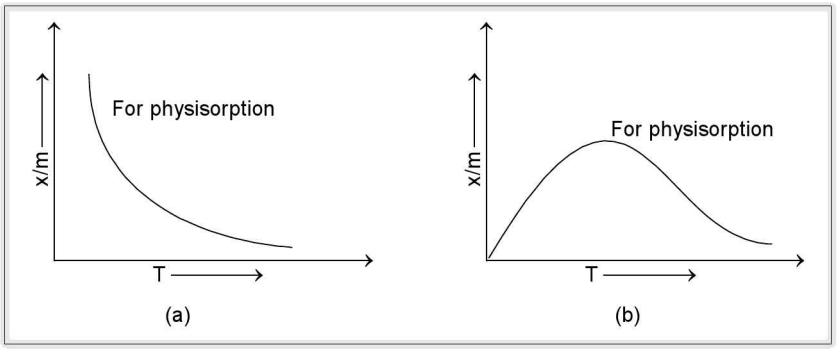


Fig. 10.4 Adsorption isobars for (a) Physical adsorption and (b) Chemisorption

From the curves, it is evident that the extent of adsorption decreases with rise in temperature in case of physical adsorption or physisorption. This is quite expected also because adsorption is of exothermic nature. Therefore, the reverse process i.e., desorption is endothermic in nature. As the temperature is increased, the process desorption i.e., reverse process is favoured. In other words, the extent of adsorption of the gas on the surface of the solid decreases with rise in temperature.

$$\text{Gas} + \text{solid} \Leftrightarrow \text{Gas adsorbed } \Delta H = -\text{ve}$$

The similar trend is expected in chemisorption also but here the adsorption is initially shown to increase with the rise in temperature and then follows the same trend. This may be attributed to the fact that the energy supplied by the initial rise in temperature provides the molecules of the adsorbate the desired activation energy so that proper bonds could be formed with the particles of the adsorbent. When all the species of the adsorbate have been properly oriented, a further rise in temperature will decrease the extent of adsorption as in case of physical adsorption.

3. Effect of Pressure

The extent of the adsorption is generally expressed as x/m where m is the mass of the adsorbent and x is the mass of the adsorbate when equilibrium has been attained. If we plot a graph between x/m and the pressure p of the gas at a constant temperature, the curve is called adsorption isotherm.

A simple type of adsorption isotherm (i.e., the relation between the pressure of the gas (adsorbate) and the amount (x/m) of it adsorbed on the surface of adsorbent is shown in figure 3

At the equilibrium pressure, p_s, x/m reaches its maximum value i.e., no more adsorption takes place even if the pressure is further increased. This rate is also called saturation state in adsorption and the corresponding pressure (p_s) is regarded as *saturation.*

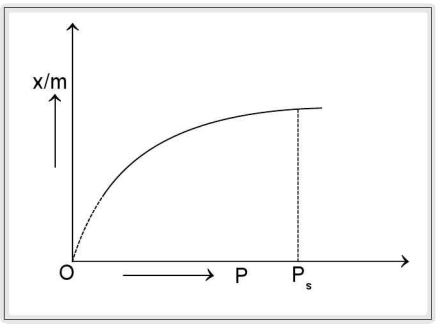


Fig. 10.5 Adsorption isotherm

pressure. Such isotherms are considered when the adsorbate simply forms a unimolecular layer on the surface of adsorbent.

So we observe that, an increased pressure of a gas or vapour, or an increase in the concentration of solute causes increased adsorption. The increase of adsorption with increased pressure is experimentally found not to be proportional to pressure but is somewhat less; and so, Freundlich (1909) puts the adsorption proportional to a fractional power of pressure. On the basis of experimental studies, **Freundlich** gave a relation between the amount of the gas adsorbed (x) per unit mass of the adsorbent (m) and the pressure (p). This is known as **Freundlich's adsorption isotherm** because the graph has been plotted at constant temperature.

The relationship can be expressed by the following equation:

$$\frac{x}{m} = KP^{\frac{1}{n}}$$

where *x* is the mass of the gas adsorbed on mass *m* of the adsorbent at pressure *P*, *k* and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

(i) ***At low pressure:***
From the adsorption isotherm (Figure 10.5), it is clear that at low pressure, the graph is almost straight. This means that x/m is directly proportional to the pressure. This may be expressed as,

$$n \approx 1 \Rightarrow \frac{x}{m} = KP^{\frac{1}{n}} \approx KP$$

(ii) ***At intermediate range of pressure,*** x/m, will depend upon the power of pressure which lies between 0 to 1 i.e., fraction power of pressure. This may be expressed as,

$$\frac{1}{m} \propto p^{1/n} \text{ or } \qquad \frac{x}{m} = K_{P^{1/n}}$$

(iii) ***At high pressure:*** The value of x/m becomes almost constant, i.e., it does not change with the change in pressure. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.
Where n is a constant (whole number) which depends upon the nature of adsorbate and adsorbent.

The constants K and n can be determined as follows:

Taking logarithsm on both sides of equation, we get,

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log p$$

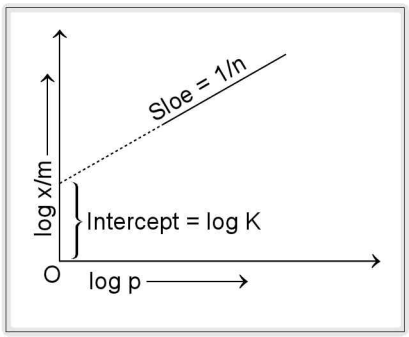


Fig. 10.6 Liner graph between log x/m and log p

Thus, if we plot a graph between log (x/m) and long p, a straight line will be obtained. Thus, slope of the line (figure 6) is equal to 1/n and the intercept on long (x/m) axis will correspond to log k.

The same equation can be applied to adsorption from solution, provided we substitute x/m (amount adsorbed per unit mass) for V and c (= equilibrium, i.e., final concentration) in place of , when we get,

$$\left.\begin{array}{l}\text{Freundlich Adsorption isotherm}\\ \text{(by solids from solution).}\end{array}\right\} : \left(\frac{x}{m}\right) = kc^n \ (n < 1)$$

or, $\log (x/m) = \log k + n \log c$

i.e., if log (amount adsorbed) be plotted against log c, a straight line of slope less than one would be obtained–which is approximately true in most cases.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Langmuir Adsorption Isotherm

Remember:

- **It is based upon the 'adsorption-desorption equilibrium'**
  Adsorption process represents two opposing tendencies i.e., condensation (or adsorption) of the gas molecules on the surface of the solid and evaporation (or desorption) of these molecules back to the gaseous state.

  The rate of condensation of a gas is proportional to the uncovered surface of the adsorbent while that of evaporation to its covered surface.

  To start with, the entire surface of the solid (adsorbent) is uncovered and the rate of condensation is very high while that of evaporation is negligible. With the passage of time, more and more of the surface becomes covered. As a result, the rate of condensation decreases while that of evaporation increases till the two are equal.
- It is applicable to unimolecular adsorption only.
- The layer of the adsorbed gas is only one molecule thick i.e., it is unimolecular in nature. Since, this type of adsorption is noticed only in case of chemisorption. Langmuir adsorption isotherm is applied only to chemisorption.
- **It has been assumed that enthalpy of adsorption is itself independent of coverage.**

Langmuir Isotherm-derivation from kinetic considerations

The equilibrium that may exist between gas adsorbed on a surface and molecules in the gas phase is a dynamic state, i.e., the equilibrium represents a state in which the rate of adsorption of molecules onto the surface is exactly counterbalanced by the rate of desorption of molecules back into the gas phase. It should therefore be possible to derive an isotherm for the adsorption process simply by considering and equating the rates for these two processes.

Expressions for the rate of adsorption and rate of desorption,

$$R_{ads} = \frac{f(\theta).P}{\sqrt{2\pi mkT}} \exp(-E_a^{ads}/RT)$$

$$R_{des} = P.f'(\theta).\exp\left(\frac{-E_a^{des}}{RT}\right)$$

Equating these two rates yields an equation of the form:

$$\frac{P.f(\theta)}{f'(\theta)} = C(T) \qquad [1]$$

where the terms $f(\theta)$ and $f'(\theta)$ contain the pre-exponential surface coverage dependence of the rates of adsorption and desorption respectively and all other factors have been taken over to the right hand side to give a temperature-dependent "constant" characteristic of this particular adsorption process, $C(T)$.

We now need to make certain simplifying assumptions ... the first is one of the key assumptions of the Langmuir isotherm.

Adsorption takes place only at specific localized sites on the surface and the saturation coverage corresponds to complete occupancy of these sites.

Let us initially further restrict our consideration to a simple case of **reversible molecular adsorption**. i.e.,

$$\mathbf{S} + \mathbf{M}_{(g)} = \mathbf{S} - \mathbf{M}$$

where, **S** represents a vacant surface site and **S – M** the adsorption complex.

Under these circumstances it is reasonable to assume coverage dependencies for rates of the two processes of the form:

Adsorption, $f(\theta) = c\,(1-\theta)$ i.e., proportional to the fraction of sites that are unoccupied.

Desorption, $f'(\theta) = c'\theta$ i.e., proportional to the fraction of sites which are occupied by adsorbed molecules.

where, θ is the fraction of sites occupied at equilibrium.

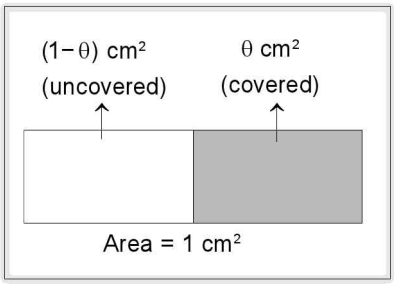


Fig. 10.7

***Note**: These coverage dependencies are exactly what would be predicted by noting that the forward and reverse processes are elementary reaction steps, in which case it follows from standard chemical kinetic theory that*:

1. *the forward adsorption process will exhibit kinetics having a first order dependence on the concentration of vacant surface sites.*
2. *the reverse desorption process will exhibit kinetics having a first order dependence on the concentration of adsorbed molecules.*

Substitution into equation [1] then yields,

$$\frac{P.(1-\theta)}{\theta} = B(T)$$

where, $B(T) = (c/c).C(T)$. After rearrangement this gives the Langmuir Isotherm expression for the surface coverage

$$\boxed{\theta = \frac{bP}{1+bP}}$$

where, b ($= 1/B(T)$) is a function of temperature and contains an exponential term of the form

$$b = \ldots\ldots \exp\left[(E_a^{des} - E_a^{ads})/RT \right] = \ldots\ldots \exp\left[-\Delta H_{ads}/RT \right]$$

Consequently, *b* can only be regarded as a constant with respect to coverage if the enthalpy of adsorption is itself independent of coverage-this is the second major assumption of the Langmuir Isotherm.

$$\therefore \quad \frac{x}{m} \propto \theta \propto \frac{bP}{1+bP} \quad \text{or,} \quad \theta = \frac{K_3 bP}{1+bP} = \frac{aP}{1+bP}$$

Here, is a constant and is equal to $k_3 b$

$$\text{Thus, } x/m = \frac{aP}{1+bp} \qquad \text{(Langmuir Adsorption Isotherm)}$$

Case 1: At low pressure

$$\text{At low pressure } bP<<1 \Rightarrow (1+bp) \approx 1 \Rightarrow x/m = \frac{aP}{1+bp} \approx aP$$

Hence, the variation of $\frac{x}{m}$ with P will be linear at low pressure.

Case 2: At moderate pressure

At moderate pressure no approximation can be made. So,

$$x/m = \frac{aP}{1+bp}$$

So, the extent of increase of of $\frac{x}{m}$ with P will be little less as compred to that increase at low pressure region.

Case 3: At very high pressure

$$\textbf{At very high pressure } bP>>1 \Rightarrow (1+bp) \approx bP \Rightarrow x/m = \frac{aP}{1+bp} \approx \frac{aP}{bP} = \frac{A}{B} = \text{CONSTANT}$$

Validity of the Langmuir Adsorption Isotherm

According to adsorption isotherm,

$$x/m = \frac{aP}{1+aP} \qquad \text{or} \qquad \frac{x/m}{P} = \frac{a}{1+bP}$$

Taking reciprocal,

$$\frac{P}{x/m} = \frac{1+bP}{a} = \frac{1}{a} + \frac{b}{a}P$$

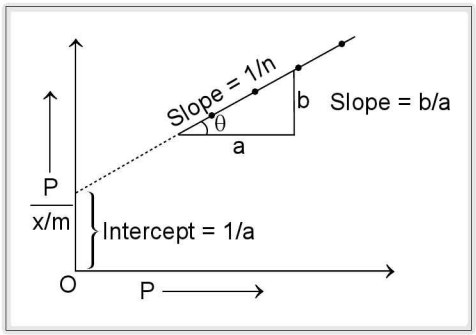


Fig. 10.8 Graph between P/x/m and P in representing Langmuir Adsorption isotherm

Since a and b are constant, a graph between $\frac{P}{x/m}$ and P must be straight line. The slope is equal to b/a and intercept on Y-axis is equal to 1/a.

Langmuir adsorption isotherm is applicable to the adsorption from the solutions in the same way as from the gases. The effect of temperature is also similar. However, equilibrium concentration (C) is used in place of equilibrium pressure and the mathematical expressions for the isotherm is:

$$\frac{x}{m} = \frac{aC}{1+bC} \qquad \text{(Langmuir Adsorption Isotherm)}$$

Note that extent of adsorption and rate of adsorption have different variation with θ

$$\frac{x}{m} \propto \theta \quad \text{but} \quad \text{rate} \propto (1-\theta)$$



Worked-out Examples

1. In an actual experiment, 1.0 g of active charcoal was found to need 155 cm^3 of N_2(STP) to form a mono-molecular layer. The cross-section of a nitrogen molecule is 16.2 $\overset{\circ}{A}^2$, Calculate the surface area.

Solution Number of molecules in 155 cc N_2 = (155/22, 400) × N_0(Avogadro No.)

∴ Total Area = (155/22, 400) × $6.02 \times 10^{23} \times 16.2 \times 10^{-20}$ m^2

$= 674.8\ m^2$ ($\because$ $1\ \overset{\circ}{A} = 10^{-10}$ m)

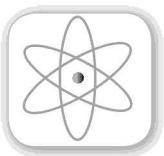
∴ Surface Area = 674.8 m^2g^{-1}.

2. When 5.19×10^{-5} g of palmitic acid ($C_{15}H_{31}COOH$), in the form of a dilute solution in benzene, was spread on the surface of water, it could be compressed to an area of 265 sq cm before the resisting force increased sharply. Calculate the area occupied by a single molecule in the closely packed layer.

Solution The molecular weight of palmitic acid is 256, and hence the 5.19×10^{-5} g contain $5.19 \times 10^{-5}/256$ moles, or $6.02 \times 10^{23} \times 5.19 \times 10^{-5}/256$ individual molecules, since there are 6.02×10^{23}, i.e., the Avogadro number, molecules per mole of any substance. The area occupied by these molecules in the closely packed monolayer is 265 sq cm;
hence,

$$\text{Area per single molecule} = \frac{265 \times 256}{6.02 \times 10^{23} \times 5.19 \times 10^{-5}} = 21.7 \times 10^{-16} \text{ sq cm.}$$

APPLICATIONS OF ADSORPTION

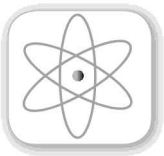


Some of the important applications of adsorption are given below:

1. **In gas masks** Activated charcoal is generally used in gas masks to adsorb poisonous and toxic gases from air. These masks are commonly used by the miners because there are poisonous gases like CO, CH_4 etc., in the atmosphere in the coal mines. Therefore, these masks help to purify the air for breathing.
2. **In dyeing of cloth** Mordants such as alums are used in dyeing of cloth. They adsorb the dye particles which, otherwise, do not stick to the cloth.
3. **In dehumidizers** Silica gel is commonly used to adsorb humidity or moisture from air. This is necessary for storage of delicate instruments which might otherwise be damaged by moisture.
4. **Removal of colouring matter** Many substances such as sugar, juice and vegetable oils are coloured due to the presence of impurities. They can be decolourised by placing in contact with adsorbents like activated charcoal or fuller's earth. This method is commonly used in the manufacture of cane sugar. The coloured sugar solution is treated with animal charcoal or activated charcoal.
5. **Heterogeneous catalysis** The phenomenon of adsorption is useful in the heterogeneous catalysis. The metals such as Fe, Ni, Pt, Pd, etc., are used in the manufacturing processes, such as Contact process, Haber process and the hydrogenation of oils. Its use is based upon the phenomenon of adsorption.

6. **In ion–exchange resins** The organic polymers containing groups like – COOH, – SO_3H and – NH_2 etc., possess the property of selective adsorption of ions from solutions. These are quite useful in the softening of water.
7. **In adsorption indicators** Many adsorption indicators are being used in volumetric analysis, example dyes such as eosin and fluorescein are used as adsorption indicators
8. **In qualitative analysis** Certain qualitative tests such as the lake test for the confirmatio of Al^{3+} ions are based upon adsorption i.e., $Al(OH)_3$ has the capacity to adsorb the colour of blue litmus from the solution.
9. **Chromatographic analysis** Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields
10. **Production of high vacuum** The adsorption of air in liquid air helps to create a high vacuum in a vessel. This process is used in high vacuum instruments as Dewar flask for storage of liquid air or liquid hydrogen.

COLLOIDAL STATE



1. **True solution** is one phase system. Hence, it is homogeneous beyond the dimension of molecules, atoms and ions. It contains small solute particles (molecules or ions) dispersed uniformly throughout the solvent.

   For example, the solution of sodium chloride in water. The particle size is less than 1 nm. The particles of a solute in a true solution are invisible even under microscope and its particles can pass through ordinary filter paper as well as through animal membrane
2. **Suspension** is a heterogeneous mixture which contains small insoluble particles. The particle size is more than 100 nm.

   For example, dirt particles in water. The particles of a suspension may be visible to the naked eye or under a microscope. The particles of a suspension can neither pass through an ordinary filter paper nor through animal membrane.
3. **Colloidal solution** is a heterogeneous solution which contains particles of intermediate size.
   For example, milk. The particles of a colloidal solution have diameters between 1 to 100 nm. Such particles cannot be normally seen with a naked eye. However, light reflected by them can be seen under a ultra-microscope. The particles of a colloidal solution can pass through ordinary filter paper but not through animal membrane.

   Thus, colloidal solutions are intermediate between true solutions and suspensions. In other words, the size of dispersed particles in colloidal solutions is more than that of solute particles in a true solution and smaller than that of a suspension.

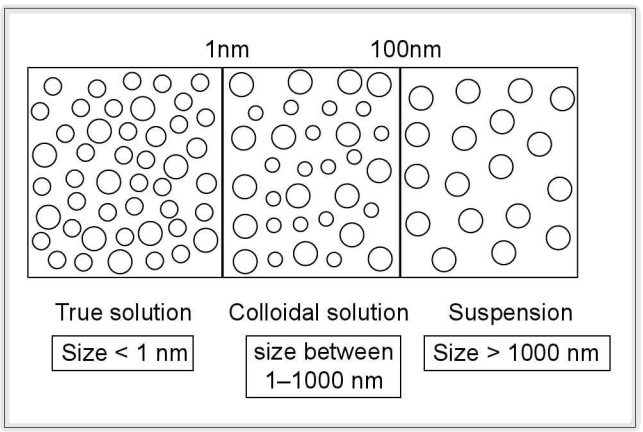


Fig. 10.9

Actually, there can be two types of substances on the basis of their diffusion through parchment membrane.

1. **Crystalloids:** The one having faster rate of diffusion.
2. **Colloids:** The one having slower rate of diffusion.

However, this classification has now historical importance and was rejected because some substances diffuse rapidly in water but slowly in alcohol medium (example NaCl), whereas, some substances diffuse slowly in water but rapidly in alcohol medium (example soaps). Therefore, a new term **colloidal state** was preferred.

Distinguishing features in suspension, colloids and true solution

Property	*Suspension*	*Colloid*	*Solution*
Particle size	$> 10^{-5}$ cm or 10^3Å or 100 mμ	10^{-7} to 10^{-5} cm or 10Å to 10^3Å or 1 mμ to 100 mμ	$<10^{-7}$ cm or 10Å or 1 mμ
Visibility	Visible with naked eye	Images are visible under ultra microscope	Not visible with any of the optical means
Separation			
(a) with filter paper	Possible	Not possible	Not possible
(b) with membranes	Possible	Possible	Not possible
Diffusion	Does not diffuse	Diffuses very slowly	Diffuses readily
Setting or sedimentation	Settles under influence of gravity	Settle under centrifuge	Does not settle
Nature	Heterogeneous	Heterogeneous	Heterogeneous
Appearance	Opaque	Turbid	Clear

Phase of Colloids

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.

(a) **Dispersed Phase:** It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the former acts as a dispersed phase.

(b) **Dispersion Medium:** It is normally the component present in excess and is just like a solvent in a solution.

The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

Types of colloidal system

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various types alongwith their characteristic names are given in table.

Colloids can be classified as follows

Medium/Phases		***Dispersed Phase***		
		Gas	***Liquid***	***Solid***
Continuous Medium	Gas	**None** (All gases are mutually miscible)	**Liquid Aerosol** Examples: fog, mist, hair sprays	**Solid Aerosol** Examples: smoke, cloud, air particulates
	Liquid	**Foam** Example: whipped cream	**Emulsion** Examples: milk, **mayonnaise**, hand cream	**Sol** Examples: pigmented ink, blood
	Solid	**Solid Foam** Examples: aerogel, styrofoam, pumice	**Gel** Examples: agar, gelatin, jelly, silicagel, **opal**	**Solid Sol** Example: cranberry glass

In some cases, a colloid can be considered as a homogeneous mixture. This is because the distinction between "dissolved" and "particulate" matter can be sometimes a matter of approach.

Classification of colloids

Colloids can be can be classified in a number of ways based upon some of their important characteristics.

(a) **Based upon appearance:**

(i) A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols. If the dispersion medium is water. When the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called alcosols or benzosol. They have fluid-like appearance.

(ii) Colloidal systems in which the dispersion medium is a gas are called aerosols.

(iii) Colloids in which the dispersion medium is a solid are called gels, example cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

(b) **Based upon charge:**

The colloids can be classified into positive or negative colloids according to the charge present on the dispersed phase particles. Metal hydroxides are generally positively charged while metal sulphides carry a negative charge.

(c) **Based on interaction or affinity of phases:** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types:

(i) **Lyophilic Colloids:** The colloidal system in which the particle of dispersed phase have great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence, lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.

(ii) **Lyophobic colloids:** The colloidal system in which the dispersed phase have no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.

Lyphilic Colloids

1. **Association Colloids:** Soap and detergent when dissolved in water show the aggregation and form colloidal particles called micelles.

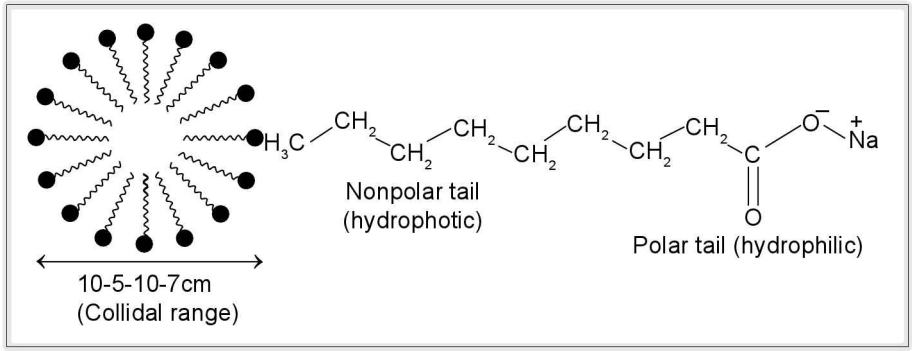


Fig. 10.10

2. **Macromolecular Colloids:** Large polymer molecular when dissolved in a liquid molecularly dissolve. Very high molecular mass of polymer gives colloidal dimension to its molecule.

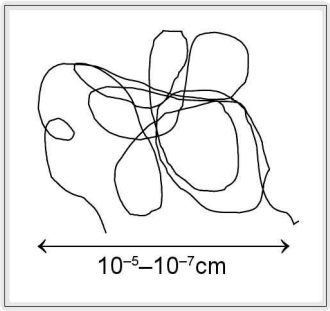


Fig. 10.11

When a polymer (a high molecular weight substance) is placed in a solvent, it dissolves at molecular level but because of high molecular mass (1000 times or even more for example, compared to low molecular weight materials), the polymer molecule itself becomes of the size comparable to the colloidal range. Such lyophilic colloids, which are molecular solutions of polymers are called macromolecular colloids. Apart from this class of lyophilic colloids, the solution of soaps and detergents in water from lyophilic colloidal dispersions. When placed in water, a soap or detergent dissolves at molecular level and forms true solutions. However, if the concentration of soap is high, hundred of molecules of soap aggregate together by physical forces and form a colloidal entity called Micelle.

The formation and properties of micelles will be dealt later in this unit. Soaps and detergents for their aggregation behaviour that leads to colloidal solutions are also known as Association colloids. Thus, colloidal solutions of soap and detergents and those of high mol mass polymeric materials (example, starch, gelatin, gums) in water are collectively known as hydrophilic solutions.

No special method is employed in making of a lyophilic dispersion (simple dissolution is enough). For example, gelatin, agar-agar, starch etc., when mixed with hot water get converted into sols. In principle, any molecular solution of a high polymer in any solvent can be called as a sol. Lyophilic sols (of association colloids) can be made by simply dissolving soaps and detergents in above certain concentration. These solutions are thermodynamically stable and cannot be coagulated (to create dispersed phase material from dispersion medium i.e., precipitation or breaking up of solid).

In the table, following two types of sols are distinguished from one another.

Lyophilic and lyophobic sols

Property	*Lyophilic Sols*	*Lyophobic Sols*
Nature	Dispersed phase has more affinity for dispersion medium	Dispersed phase has less affinity for dispersion medium.
Preparation	Need no special methods for preparation. Adding of the material in solvent gives the sols. For example adding starch in water gives starch sol	Simple mixing does not produce sols. Special methods (dispersion or condensation) are necessary.
Concentration	Sols have higher concentration of dispersed phase.	Sols have lower concentration of dispersed phase.
Stability	Thermodynamically more stable systems	Thermodynamically less stable systems. Coagulate with time.
Solvation	Dispersed phase particles are highly solvated	Dispersed phase particles are not solvated.
Viscosity	Viscosity of sols are often higher than the viscosity of dispersion medium.	Almost same as that of dispersion medium.
Surface tension	Surface tensions of sols are much lesser than the surface tensions of dispersion medium	Almost same as that of dispersion medium.
Reversibility	Reversible with temperature.	Irreversible.
Charge	The charge on dispersed phase particles depends upon pH of medium.	Independent of pH of medium.
Tyndall effect	Less scattering of light.	More scattering of light.
Coagulation by electrolytes	Very high concentration of salt is required for phase separation.	A small amount of salt is required for their coagulation.

The lyophobic sols consist the colloidal particles in the form of aggregates of small molecules or atoms (gold, sol, sulphur sol, As_2S_3) sol etc., are some examples) which are held together by van der Waals forces. These are thus also called as multimolecular colloids.

Interaction between colloid particles

The following forces play an important role in the interaction of colloid particles:

- Excluded volume repulsion: This refers to the impossibility of any overlap between hard particles.
- Electrostatic interaction: Colloidal particles often carry an electrical charge and therefore attract or repel each other. The charge of both the continuous and the dispersed phase, as well as the mobility of the phases are factors affecting this interaction.
- Van der Waals forces: This is due to interaction between two dipoles that are either permanent or induced. Even if the particles do not have a permanent dipole, fluctuations of the electron density gives rise to a temporary dipole in a particle. This temporary dipole induces a dipole in particles nearby. The temporary dipole and the induced dipoles are then attracted to each other. This is known as van der Waals force, and is always present (unless the refractive indexes of the dispersed and continuous phases are matched), is short-range, and is attractive.
- Entropic forces: According to the second law of thermodynamics, a system progresses to a state in which entropy is maximized. This can result in effective forces even between hard spheres.
- Steric forces between polymer-covered surfaces or in solutions containing non-adsorbing polymer can modulate interparticle forces, producing an additional steric repulsive force (which is predominantly entropic in origin) or an attractive depletion force between them. Such an effect is specifically searched for with tailor-made superplasticizers developed to increase the workability of concrete and to reduce its water content.

Preparation of Colloids: The two different techniques that can be employed to obtain a lyophobic sol are condensation methods and dispersion methods. In condensation method, as the name suggests, the atoms and molecules of the substance condense (aggregate) leading to the particles of colloidal dimension. The condensation can be brought about by both physical and chemical means.
The physical methods are illustrated below:

(i) **By exchange of solvent:** A true solution of a solute in a solvent when mixed with another liquid (which is miscible with the solvent but does not dissolve solute in it) then a colloidal system is produced. For example, sulphur is molecularly dissolved in alcohol; an addition of excess amount of water to this solution produces colloidal solution of sulphur in water.

(ii) **By excessive cooling:** Cooling sometimes produces colloidal dispersions. An example of the method is to produce colloidal solution of ice in organic solvents like ether, chloroform etc., by freezing a mixture of solvent and water.

Preparation of Sols: Using Chemical Methods, a sol can be prepared by hydrolysis, reduction, oxidation, double decomposition etc.

(i) **By hydrolysis:** Addition of drop by drop of an aqueous solution of $FeCl_3$ on boiling hydrolysis of $Fe(OH)_3$ solution.

$$FeCl_3 + 3H_2O \longrightarrow \underset{sol}{Fe(OH)_3} + 3HCl$$

(ii) **By reduction:** Gold sol can be prepared on reducing a solution of gold (III) chloride with formaldehyde and tannic sol.

$$2AuCl_3 + 3HCHO + 3H_2O \longrightarrow \underset{sol}{2Au} + 3HCOOH + 6HCl$$

Gold sol can be prepared by reducing $AuCl_{3(aq)}$ by hydrazine or $SnCl_2$.

$$4AuCl_3 + 3NH_2NH_2 \longrightarrow \underset{sol}{4Au} + 3N_2 + 12HCl$$

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{sol}{2Au} + SnCl_4$$

(iii) **Oxidation:** Sulphur sols are obtained when H_2S gas is bubbled through the solution of an oxidizing agent like Br_2, HNO_3, Mn^{2+} etc., where H_2S is oxidized to elemental sulphur.

$$H_2S + Br_2 \longrightarrow 2HBr + \underset{sol}{S}$$

$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + \underset{sol}{S}$$

Therefore, during 2nd group analysis of mixture, by passing H_2S in cold solution of mixture sometimes (if it contains an oxidant) leads to the formation of white, grey turbidity of sulphur sols instead of precipitates of 2nd group sulphides.
A colloidal solution of sulphur can also be obtained by adding dilute HCl to sodium thiosulphate.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O + \underset{sol}{S}$$

(iv) **Double Decomposition:** This method is often used to prepare various colloidal solutions. Sulphide sols are often obtained by this method. For example, on passage of H_2S through cold aqueous solutions of $AsCl_3$, $CdCl_2$, $Hg(CN)_2$, their sulphide sols are formed.

$$2AsCl_3 + 3H_2S \longrightarrow \underset{sol}{As_2S_3} + 6HCl$$

$$CdCl_2 + H_2S \longrightarrow \underset{sol}{CdS} + 2HCl$$

$$Hg(CN)_2 + H_2S \longrightarrow \underset{sol}{HgS} + 2HCN$$

Also, dropwise addition of $FeCl_3$ solution to solution of sodium ferrocyanide gives Prussian blue sol.

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_4] + 12NaCl$$

Silver chloride sols and Barium sulphate sols are formed by allowing the following reactants to react in cold, dilute conditions.

$$AgNO_3 + NaCl \longrightarrow \underset{sol}{AgCl} + NaNO_3$$

$$BaCl_2 + H_2SO_4 \longrightarrow \underset{sol}{BaSO_4} + 2HCl$$

The dispersion methods (paricle's size is decreased to colloidal dimension) employed for make lyophobic sols involve the following techniques.

(i) **By Grinding:** The coarse particles of dispersed phase in presence of dispersion medium are grinded into smaller colloidal size particles in grinding machines such as mixie or colloidal mill (figure). These fine particles can then be stabilized by an stabilizer, for example, gum, tannin etc.

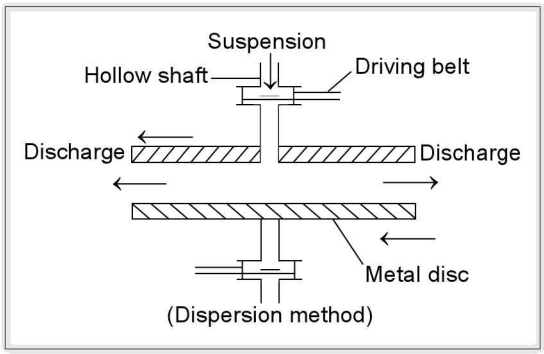


Fig. 10.12

(ii) **By Bredic's Arch Method:** This is a simple method (Figure 10.13) for preparing metal sols (example, gold sol) and involves an electric are between the two metal rods partly dipped into the water as dispersion medium. The high electric tears the particles from rod (or wires) which are of colloidal size and remain dispersed in dispersion medium.

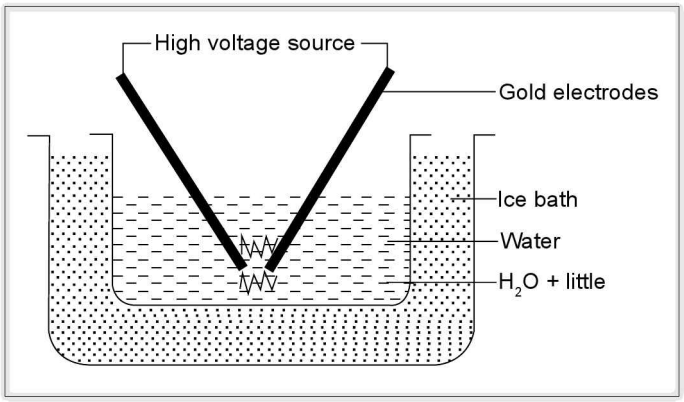


Fig. 10.13

The heat generated during the process is removed by putting system under ice cold water. Little amount of KOH in water prevents growth of sol particles and stabilizes the dispersion. Purple of Cassuis (Au sol in water) sol is obtained by this method.

(iii) **Peptization**

1. The phenomenon of converting fresh precipitate into colloidal state by the action of solute or solvent is known as peptization. The solute or solvent used are known as peptizing agent.
2. For example,
   (a) Freshly precipitated $Fe(OH)_3$ turns into in colloidal state by the action of $FeCl_3$.

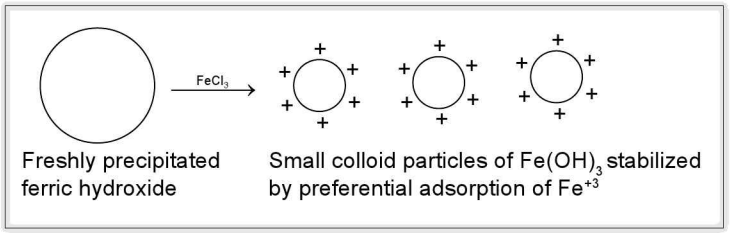


Fig. 10.14 Peptization – A method for the preparation of a sol

   (b) Freshly precipitated stannic acid can be peptized by $NH_{3(l)}$ or HCl_{aq}.
   (c) Freshly precipitated HgS, CdS and NiS can be peptized by H_2S.
   (d) Peptization of albumin in water of nitrocellulose in acetone or ethyl alcohol to form collodion.
3. The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added–particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles. A coarse suspension of silver chloride on shaking with electrolytes produces AgCl sol. Shaking of AgCl suspension with $AgNO_3$ solution produces positively charged AgCl sol due to adsorption of Ag^+ ions whereas shaking of AgCl suspension with HCl produces negatively charged AgCl sol due to adsorption of Cl^- ions.

Purification of Sols:

Sols so obtained are contaminated with two types of impurities and need purification

(a) **Insoluble impurities:** These are removed by simple filtrati n of impure sols. Impurities are retained on filter paper and sols are filtere

(b) **Soluble Impurities:** The soluble impurities either of molecular nature or of ionic nature in colloidal solutions need special methods for their removal from sols.

Following techniques are used for this purpose:

Dialysis: The separation of soluble impurities from a colloidal solution on the basis of their different rates of diffusion through parchment membrane is known as dialysis.

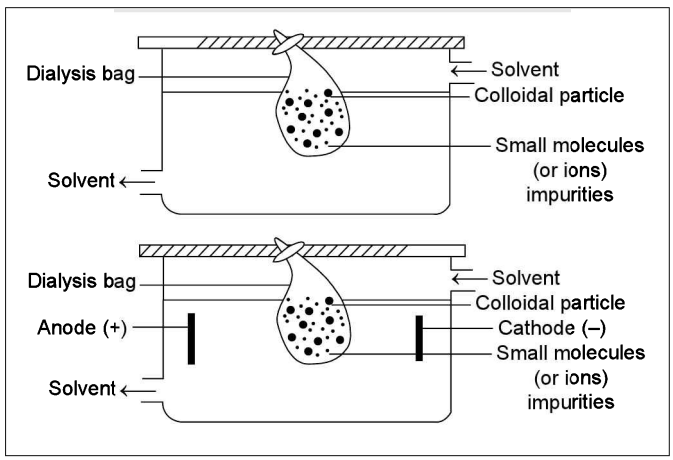


Fig. 10.15 (a)

This can be done by using a semipermeable bag. It has small pores which allows the small molecular/ ionic species to pass through but not the colloidal particles which are larger in size as compared to the membrane pores. Thus, a colloidal solution is filtered in the bag (figure (a)) which is tied on the mouth and suspended in the liquid (the dispersion medium). Slow diffusion of molecules/ions from colloidal solution to the outer medium purifies the sol

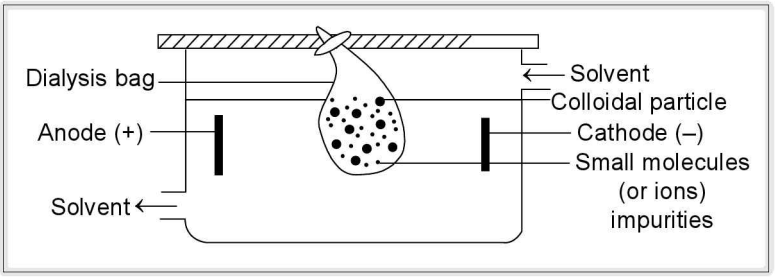


Fig. 10.15 (b)

In case of ionic nature of impurities, dialysis can be speeded up by taking an advantage of electricity and the process is known as electrodialysis (figure (b))

Properties of Colloids: Due to their small size, these colloidal solutions remain stable over a long period of time as they do not settle down under earth's gravity (sedimentation rate is very slow). At the same time, most lyophobic colloids are stable due to the surface charge or a layer of a protective material on to the surface of colloidal particles. This surface modification does not allow the isolated particles to come close to each other, colloid and form bigger particles. However, as the systems are associated with large surface area and consequently large surface free energy, these systems have to break one day. Thus, lyophobic colloids are thermodynamically unstable systems.

Large surface area provides a tremendous adsorption capacity to the colloidal particles. This property is utilized, for example, to remove poisonous gases by use of colloidal charcoal in gas masks and removal of effluents like dyes etc, from waste wate .

Following are some characteristic properties of colloidal solutions.

Properties of colloidal solutions

(1) **Physical properties:**

(i) **Heterogeneity:** Colloidal solutions are heterogeneous in nature consisting of two phases viz., the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filter - tion clearly indicate the heterogeneous character of colloidal system. Recent investigations, showed that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.

(ii) **Filterability:** Colloidal particles readily pass through orginary filter papers. It is because the size of the pores of the filter paper is la ger than that of the colloidal particles.

(iii) **Non-setting nature:** Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitel . Thus there is no effect of gravity on the colloidal particles.

(iv) **Colour:** The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors:

(a) Size and shape of colloidal particles.
(b) Wavelength of the source of light.
(c) Method of preparation of the colloidal solution.
(d) Nature of the colloidal solution.
(e) The way an observer receives the light, i.e., whether by reflection or by transmission
(f) Stabilization of a colloidal dispersion (peptization)

Stabilization serves to prevent colloids from aggregating. Steric stabilization and electrostatic stabilization are the two main mechanisms for colloid stabilization. Electrostatic stabilization is based on the mutual repulsion of like electrical charges. In general, different phases have different charge affinities, so that a electrical double layer forms at any interface. Small particle sizes lead to enormous surface areas, and this effect is greatly amplified in colloids. In a stable colloid, mass of a dispersed phase is so low that its buoyancy or kinetic energy is too weak to overcome the electrostatic repulsion between charged layers of the dispersing phase. The charge on the dispersed particles can be observed by applying an electric field: All particles migrate to the same electrode and therefore must all have the same sign charge

Stability: Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

Examples:

(i) Finest gold is red in colour. As the size of particles increases, it becomes purple.
(ii) Dilute milk gives a bluish tinge in reflected light whereas, reddish tinge in transmitted light.

(2) **Mechanical Properties**

(a) **Brownian movement:** Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownian movement.

Robert Brown first observed this motion with pollen grains suspended in wate .

Cause of movement: Brownian movement is due to bombardment of the dispersed particles by molecules of the medium. The Brownian movement (figure) depends upon the size of sol. particles. With the increase in the size of the particle, the chance of unequal bombardment decrease, and the Brownial movement too disappears. It is due to the fact that the suspension fails to exhibit this phenomenon.

It should be noted that Brownian movement does not change with time but changes with temperatures.

Following are the important characteristic conclusions regarding Brownian motion of particles.

(i) Brownian motion is observed upto a particle size of 0.5 microns.
(ii) The smaller the particle, the more rapid is the movement.
(iii) The movement is independent of λ of light used and time of illumination.
(iv) The movement does not change with time and exist till last.
(v) The movement depends upon temperature; the intensively of the movement increases with increasing temperature.
(vi) The movement is due to the bombardment of solvent of the movement increases with increasing temperature.

Importance

(i) Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus, it confirms kinetic theor .
(ii) Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.
(iii) Brownian movement helps to calculate the Avogadro's number (Detail beyond the scope).

Sedimentation: Heavier sol particles tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

Optical properties (tyndal effect)

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light (figure). This effect is called Tyndall effect. The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wavelength of the visible

light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since, maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.

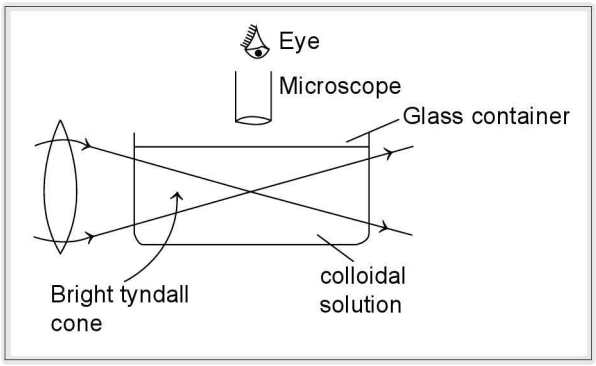


Fig. 10.16

The Tyndall effect is observed under the following conditions:

(i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.

(ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultramicroscope and in determining the number of colloidal particles in a colloidal solution.

(4) **Electrical Properties:**

The two electrical properties of colloidal solutions are:

(a) **Electrophoresis or Cataphoresis:** In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.

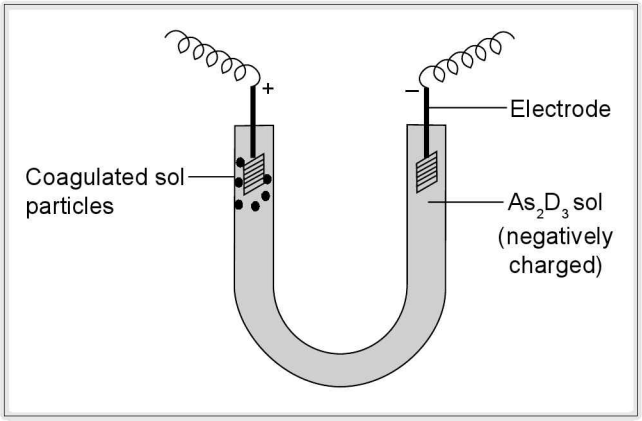


Fig. 10.17

The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositively cha ged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode. This shows that ferric hydroxide sol. particles are positively charged.

The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

Electrophoresis is the motion of dispersed particles relative to a fluid under the influence o a spatially uniform electric fiel . This electrokinetic phenomenon was observed for the first time in 1807 by Reuss, who noticed that the application of a constant electric fiel caused clay particles dispersed in water to migrate. It is ultimately caused by the presence of a charged interface between the particle surface and the surrounding fluid

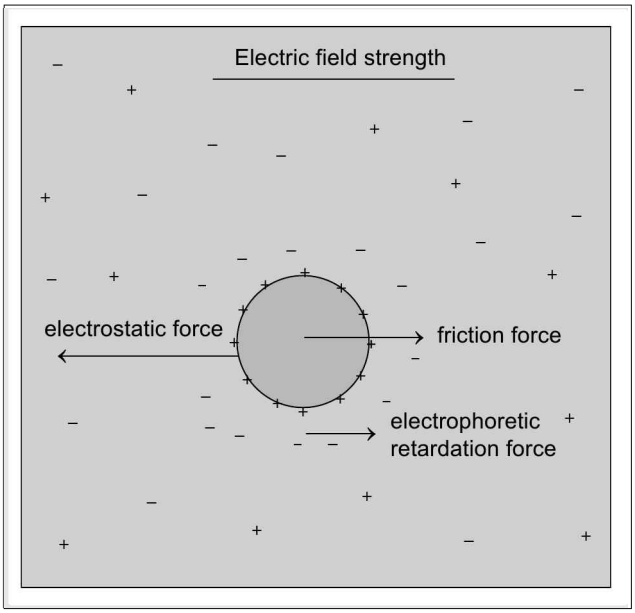


Fig. 10.18 Illustration of electrophoresis

Origin of charge: Various reasons have been given regarding the original of charge on the colloidal particles. These are given below:

(i) **Frictional electrification:** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.

(ii) **Dissociation of the surface molecules:** It leads to electric charge on colloidal particles. For example, an aqueous solution of a soap (sodium palmitate) dissociates into ions.

$$\underset{\text{sod. palmitate}}{C_{15}H_{31}COONa} \rightarrow C_{15}H_{31}COO^- + Na^+$$

The Na^+ ions pass into the solution while $C_{15}H_{31}COO^-$ ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of colloidal size bear negative charge.

(iii) **Preferential adsorption of ions from solution:** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus, AgCl particles can adsorb Cl^- ions from chloride solutions and Ag^+ ions; the sol. will be negatively charged in the first case and positively cha ged in the second case.

(iv) **Capture of electron:** It is from air during preparation of sol. by Bredig's arc method.

(v) **Dissociation of molecular electrolytes on the surface of particles:** H_2S molecules get adsorbed on sulphides during precipitation. By dissociation of H_2S, H^+ ions are lost and colloidal particles become negatively charged.

Electrical charged sols

Positively charged sols	Negatively charged sols
1. Ferric hydroxide, aluminium hydroxide	Metals such as Pt, Au, Ag, Metals sulphides Example, arsenius sulphide.
2. Basic dyes such as methylene blue	Starch, clay, silicic acid.
3. Haemoglobin	Acid dyes, such as eosin.

(b) **Electro-osmosis:** The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosi

Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol particles.

Example, if the dispersion medium moves towards the cathode (negative electrode), the sol particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.

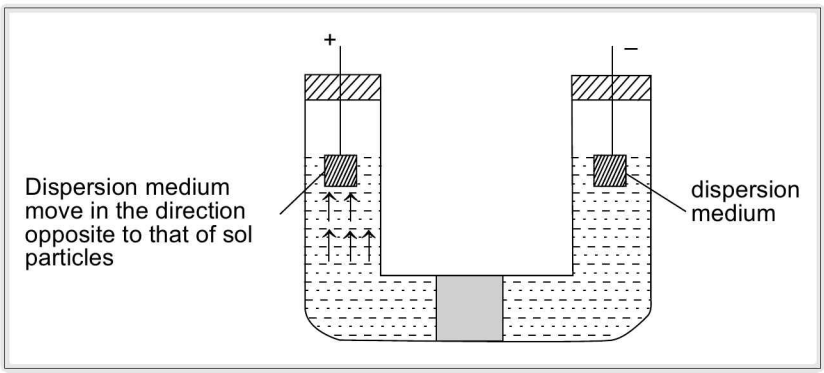


Fig. 10.19

Electric Double Layer

The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve or – ve charges respectively. The charged layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles i.e., one due to absorbed ions and the other due to oppositely charged ions forming a diffused layer. This layer consists of ions of both the signs, but its net charge is equal and opposite to those absorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite change is called electrokinetic potential or zeta potential.

A **double layer** (**DL**, also called an **electrical double layer**, **EDL**) is a structure that appears on the surface of an object when it is placed into a liquid. This object might be a solid particle, a gas bubble, a liquid droplet, or a porous body. It consists of two parallel layers of ions. The first layer

is the surface charge (either positive or negative) and coincides with the surface of the object. The other layer is in the fluid, and electrically screens the first layer. This second layer is diffuse, because it forms from free ions in the fluid under the influence of electric attraction and thermal motion, and is thus called the **diffuse layer**.

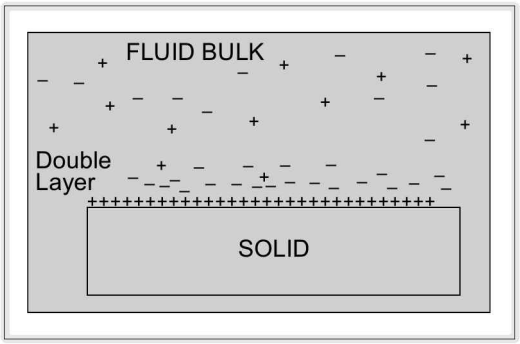


Fig. 10.20

Schematic of double layer in a liquid at contact with a solid. Depending on the nature of the solid, there may be another double layer (unmarked on the drawing) inside the solid.

Interfacial DL is usually most apparent in systems with a large ratio of surface area to volume, such as colloid or porous bodies with particles or pores (respectively) on the scale of microns or even nanometers. However, the importance of DLs extends to other systems, example, DL is fundamental to the electrochemical behaviour of electrodes.

The DL plays a fundamental role in many real-world systems. For instance, milk exists only because fat droplets are covered with a DL that prevent their coagulation into butter. DLs exist in practically all heterogeneous fluid-based systems, such as blood, paints, inks, ceramic slurries and cement slurries.

The DL is closely related to electrokinetic phenomena and electroacoustic phenomena.

(c) **Coagulation:** The colloidal sols are stable due to the presence of electric charges on the colloidal particles. Because of the electrical repulsion, the particles do not come close to one another to form precipitates. The removal of charge by any means will lead to the aggregation of particles and hence, precipitation will occur immediately.

This process by means of which the particles of the dispersed phase in a sol are pecipitated is known as coagulation.

If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called flocculation

Most of the sols are coagulated by adding an electrolyte of opposite sign. This is due to the fact that the colloidal particles take up the ions of electrolyte whose charges are opposite to that on colloidal particles with the result that charge on the colloidal particles is neutralized. Thus coagulation takes place. For example, arsenius sulphide sol. (negatively charged) precipitated by adding barium chloride solution. It is due to the fact that the negatively charged particles of the sol. take up barium ions and get neutralized which lower the stability. As a result, precipitation takes place.

It is observed that different amounts of different electrolytes is required to bring coagulation of a particular solution.

The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called coagulation value or flocculation value of the electrolyte for the sol

The reciprocal of coagulation value is regarded as the coagulating power.

For example, the coagulation values of NaCl, $BaCl_2$ and $AlCl_3$ for arsenic sulphide sol. are 51, 0.69 and 0.093 millimoles/litre respectively. Thus their coagulating powers are, 0.0196, 1.449 and 10.75 respectively.

The coagulation values of a few electrolytes for negatively charged arsenic sulphide and positively charged ferric hydroxide sol are given in table given below. The valency of the coagulation ion (the ion whose charge is opposite to that of the colloidal particles) is also given.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Coagulation values of different electrolytes

Coagulation values of cations and anions are reported in the given table.

For negatively charged sols			*For positively charged sols*		
Electrolyte	***Positive ion***	***Coagulation value***	***Electrolyte***	***Negative ion***	***Coagulation value***
$FeCl_3$	Fe^{3+}	0.136	KCl	Cl^-	103
$CaCl_2$	Ca^{2+}	0.649	KNO_3	NO_3^-	131
$BaCl_2$	Ba^{2+}	0.691	K_2SO_4	SO_4^-	0.22
KCl	K^+	49.5	K_2CrO_4	CrO_4^{2-}	0.33
NaCl	Na^+	51.0	$K_4[Fe(CN)_6]$	[Fe(CN)6]4-	0.06

From the above table, it is clear that the coagulating power of Al^{3+} ions in precipitating the arsenic sulphide sol is approximately 550 times more than that of sodium (Na^+) or potassium (K^+) ions. Again, it is observed that the negatively charged arsenic sulphide sol is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Destabilizing a Colloidal Dispersion (Flocculation)

Unstable colloidal dispersions form floc as the particles aggregate due to interparticle attractions. In this way, photonic glasses can be grown. This can be accomplished by a number of different methods:

- Removal of the electrostatic barrier that prevents aggregation of the particles. This can be accomplished by the addition of salt to a suspension or changing the pH of a suspension to effectively neutralize or "screen" the surface charge of the particles in suspension. This removes the repulsive forces that keep colloidal particles separate and allows for coagulation due to van der Waals forces.
- Addition of a charged polymer flocculant. Polymer flocculants can bridge individual colloidal particles by attractive electrostatic interactions. For example, negatively-charged colloidal silica or clay particles can be flocculated by the addition of a positively-cha ged polymer.
- Addition of non-adsorbed polymers called depletants that cause aggregation due to entropic effects.
- Physical deformation of the particle (example, stretching) may increase the van der Waals forces more than stabilization forces (such as electrostatic), resulting coagulation of colloids at certain orientations.

Unstable colloidal suspensions of low-volume fraction form clustered liquid suspensions, wherein individual clusters of particles fall to the bottom of the suspension (or float to the top if the particles are less dense than the suspending medium) once the clusters are of sufficient size for the Brownian forces that work to keep the particles in suspension to be overcome by gravitational forces. However, colloidal suspensions of higher-volume fraction form colloidal gels with *viscoelastic* properties. Viscoelastic colloidal gels, such as bentonite and toothpaste, flow like liquids under shear, but maintain their shape when shear is removed. It is for this reason that toothpaste can be squeezed from a toothpaste tube, but stays on the toothbrush after it is applied.

Hardy-Schulze rules: H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol:

(1) Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation. Example, the negative charged sol is best coagulated by cations and a positive sol. is coagulated by anions.

(2) The charge on coagulating ion influences the coagulation of sol. In general, the coagulating power of the active ion increases with the valency of the active ion. After observing the regularities concerning the sign and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows: "Higher is the valency of the active ion, greater will be its power to precipitate the sol."

Thus, coagulating power of cations is in the order of $Al^{3+} > Ba^{2+}$ or $Mg^{2+} > Na^{+}$ or K^{+}. Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$.

Some other methods of coagulation:

Apart from the addition of electrolyte, coagulation can also be carried out by following methods:

(i) **By persistent dialysis:** It has been observed that traces of electrolytes are associated with the solution due to which it is stable. If the solution is subjected to prolonged dialysis, the traces of electrolytes are removed and coagulation takes place.

(ii) **By mutual coagulation of colloids:** When two sols of oppositively charges are mixed together in a suitable proportion, the coagulation takes place. The charge of one is neutralized by the other. For example, when negatively charged arsenic sulphide sol. is added to positively charged ferric hydroxide sol., the precipitation of both occurs simultaneously.

(iii) **By electrical method:** If the electrical charge of lyophobic sol. is removed by applying any electric field such as in electrophoresis, they also precipitate out.

(iv) By excessive cooling or by excessive heating.

(v) **Colligative properties:** Colloidal solutions too exhibit colligative properties such as osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point. But the effect of colloidal particles on colligative properties except osmotic pressure is very small. This is due to the large size of colloidal particles. The number of colloidal particles produced by a given mass of colloid is much less than the number produced in a molecular solution, containing the same mass of solute. Hence, the colligative effect in colloidal solutions is too less.

5. Protective colloids

Lyophilic sols are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic sols are more easily coagulated by the addition of suitable electrolyte. To avoid the precipitation of lyohobic sol. by the addition of electrolyte, some lyophilic colloid is added to it. Such lyophilic colloid is called protective colloid and the action of lyophilic colloid by the electrolytes is known as protective anion. The substances commonly used as protective colloids are gelating, albumin, gum arabic, casein, starch, glue etc. A gold sol. containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the sol.

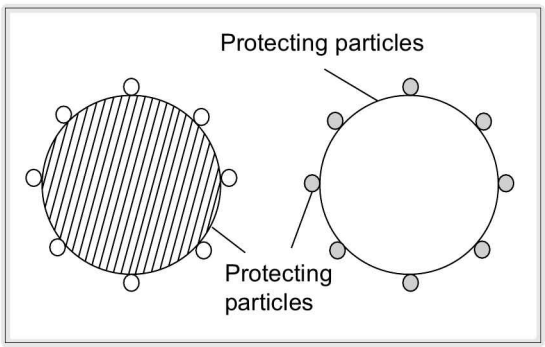


Fig. 10.21

Explanation: The particles of the protective colloid get adsorbed on the particles of the lyophobic colloid, thereby forming a protective layer around it (figure). The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.

According to a recent view, the increase in stability of the lyophobic colloid is due to the mutual adsorption of the lyophilic and lyophobic colloids. It is immaterial which is adsorbed on which. In fact, the smaller particles, whether of the protective colloid or the lyophobic colloid, are adsorbed on the bigger particles.

Gold number: The protective power of the lyophilic colloids is expressed in terms of gold number a term introduced by Zsigmondy.

Gold number is the number of milligram of the protective colloid which prevent the coagulation of 10 ml of red gold sol. when 1 ml of a 10 per cent solution of sodium chloride is added to it.

Thus, smaller the gold number of lyophilic colloid, the greater is the protective power.

The protective power was also measured in terms of Congo Rubin number, which may be defined as

"The amount of protective colloid in milligrams which prevents colour change in 100 ml of 0.01% congo rubin solution to which 0.15 gram equivalent of KCl is added when observed after 10-16 minutes."

Isoelectric point of colloid

The hydrogen ion concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e., uncharged) is known as isoelectric point of the colloid. At this point, lyophilic colloid is expected to have minimum stability because at this point particles have no charge. The isoelectric point of gelatin is 4.7. This indicates that at pH = 4.7, gelating has no electrophoretic motion. Below 4.7, it moves towards the cathode and above 4.7 it moves forwards the anode. It is not always true, example, silicic acid has been found to have maximum stability at the isoelectric point.

Emulsions

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets whose diameter, in general, exceeds 0.1 m.

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium. Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquid is water and the other liquid is oil. Here, the term 'oil' is used to represent all organic substances which are soluble in water.

The emulsion are classified as:

(1) **Oil in water type emulsion (O/W):**
(2) **Water in oil type:**

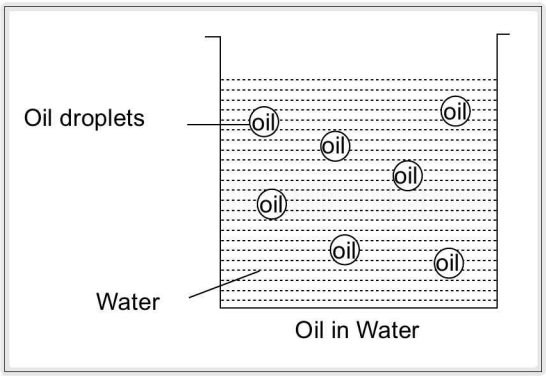


Fig. 10.22

(1) **Oil in water type:** In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream, etc.

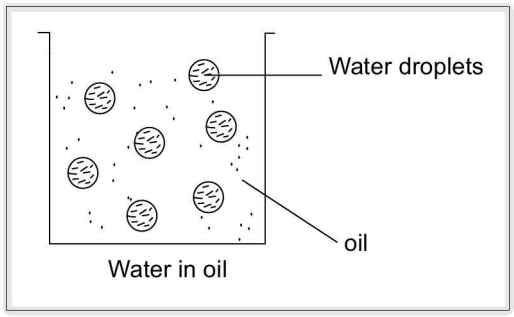


Fig. 10.23

(2) **Water in oil type:** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsions can be interconverted into each other by changing the concentration of one of the liquids.

Distinction between two types of emulsions: The two types of emulsions may be distinguished from each other in a number of ways.

(1) **Dye test:** It involves the addition of oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion and it the emulsion remains colourless, it is oil-in-water type emulsion.
(2) **Conductivity test:** It involves the addition of electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of electrolyte, it is oil-in-water type emulsion and it conductivity is very small, it is water-in-oil type emulsion.
(3) **Dilution test:** As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is water-in-oil type.

Preparation of emulsion (Emulsification) Emulsification is the process which involves the preparation of emulsion. Generally, an emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layers upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers. To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance which stabilizes the emulsion is called emulsifier or emulsifying agent. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence, milk is a fairly stable emulsion.

Function of emulsifier: The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus helps the intermixing of two liquids. For example, a molecule of a soap or detergent (emulsifier) gets concentrated at the interface between oil and water. The polar end of the emulsifier is in water and non-polar end is in oil as shown in figur

In a soap, RCOONa, R is the non-polar end, whereas COO^{-} Na^{+} is the polar end.

Properties of emulsion:

(i) The size of particles of the dispersed phase of an emulsion is usually larger than in sols.
(ii) Like colloidal particles, emulsions exhibit properties such as Tyndall effect, Brownian movement (provided the particles are not too large), electrophoresis, coagulation, etc.

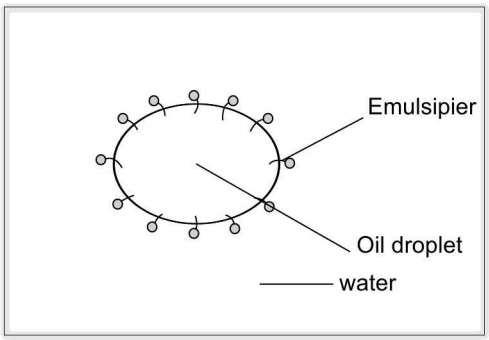


Fig. 10.24

Demulsification: The process which involves the breaking of an emulsion into two separate liquid layers is called demulsification. The following methods may be used to bring demulsification

(1) **Chemical Methods:** An emulsion may be demulsified by adding a chemical substance whose action on the dispersed phase and the dispersion medium is opposite to that of the original emulsifying agent used to produce the stable emulsion.
(2) **Centrifugation:** Cream is separated from milk by the centrifugal method.
(3) **Cooling:** Fat can be removed from milk by keeping it in a refrigerator for a few hours.
Demulsification:
Besides the above noted methods of demulsification, the following methods have also been developed:
(i) Suitable centrifugal action-milk cream is separated from milk by centrifugation.
(ii) Application of electric field-electrophoresis
(iii) Addition of an electrolyte having multivalent opposite charge than that on the dispersed phase.
(iv) Chemical destruction of stabilizer.
(v) Distilling off of one of the components, usually water.
(vi) Addition of demulsifi rs like alcohol, phenol etc.

Uses of emulsion

(1) Many pharmaceutical preparations—medicines, ointments, creams and various lotions are emulsions. It is believed that medicines are more effective and easily assimilated by the body tissues when they are in colloidal form i.e., emulsion.
(2) All paints are emulsions.
(3) The digestion of fat in the intestines is helped by emulsification. A little of the fat forms a medium soap (emulsifier) with the alkaline solution of the intestine and this soap emulsifier the rest of the fats, thus making it easier for the digestive enzymes to do their metabolic functions.
(4) Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil in water emulsion.
(5) Milk is an emulsion of liquid fats in water.
(6) In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore go on the surface due to formation of foams while the other impurities are left at the bottom of the vessel.
(7) The emulsion of asphalt in water is used in road making and building.

Gels

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are: boot polishes, jelly, gum arabic, agar agar, processed cheese and silicic acid.

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids which accumulate on its surface. This action of gels is known as Synresis or Weeping. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

Gels are divided into two categories i.e., elastic gels and non elastic gels. The two categories differ from their behaviour towards dehydration and rehydration as under.

A **gel** (from the lat. *gelu*—freezing, cold, ice or *gelatus*—frozen, immobile) is a solid, jelly-like material that can have properties ranging from soft and weak to hard and tough. Gels are defined as a substantially dilute crosslinked system, which exhibits no flow when in the steady-state. By weight, gels are mostly liquid, yet they behave like solids due to a three-dimensional crosslinked network within the liquid. It is the crosslinks within the fluid that give a gel its structure (hardness) and contribute to stickiness (tack).

Elastic gels	***Non-elastic gels***
1. They change to solid mass on dehydration which can be changed back to original.	1. They change to solid mass on dehydration which cannot be changed back to original form by addition of water followed by warming. form with water.
2. They absorb water when placed in it with	2. They do not exhibit imbibation. simultaneous swelling. This phenomenon is called imbibation.

7. Uses of colloids

(1) **Medicines:** The medicines containing gold, silver or calcium etc., in colloidal form are more effective and easily assimilated by the human systems.

(2) **Dyes:** In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.

(3) **Rubber industry:** Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.

(4) **Smoke screens:** Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage

(5) **Formation of delta:** The river waver carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.

(6) **Purification of water:** The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e., Al^{3+} ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.

(7) **Artificial rain:** Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.

(8) **Smoke precipitation:** Smoke coming out of the chimney is industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus, they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).

In Cottrell precipitator, the smoke is made to pass through chambers fitted with highly electrically charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure)

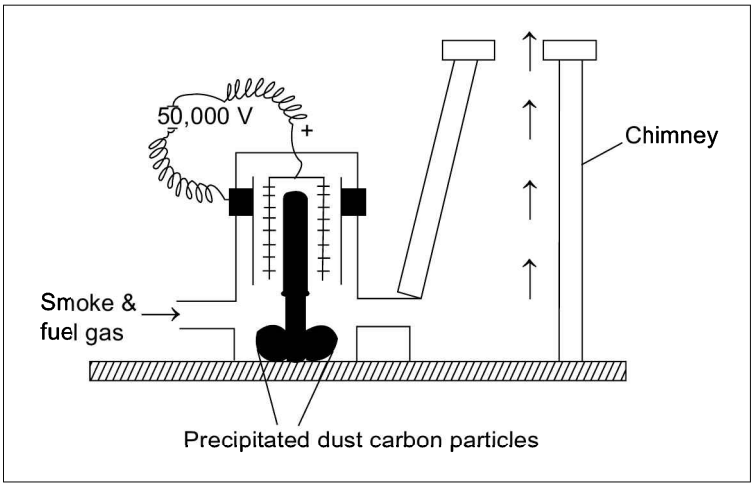


Fig. 10.25

(9) **Sewage disposal:** Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus, do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When electric field is created, then the dust particles are coagulated on the oppositely charged electrodes. The deposit may be utilized as a manure.

(10) **Cleaning action of soap and detergent:** Soap solution may be used to wash off the dirt sticking to the fabric, in the presence

(i) it forms a collodial solution in water (miscelles), removes dirt by simple adsorption of oily substance and thus washes away.

(ii) it decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached alongwith the only material.

ONE CORRECT OPTION TYPE QUESTIONS

1. For adsorption, the thermodynamic requirement is that
(a) ΔH must be negative
(b) ΔS must be negative
(c) ΔG must be negative
(d) ΔH, ΔS and ΔG must be negative

2. A white precipitate of $Sn(OH)_4$ is peptized with dil. HCl. The sol particle will carry
(a) Positive charge
(b) Negative charge
(c) Sometimes positive and sometimes negative charge
(d) No charge

3. According to Hardy-Schulze law the co-agulating power of Al^{3+},Zn^{2+},Na^{+} ions will be nearly in the ratio
(a) 1:2:3 (b) 3:2:1
(c) 1^6:2^6:3^6 (d) 3^6:2^6:1

4. Mayonniase represents
(a) a sol (b) an aerosol
(c) a foam (d) an emulsion

5. Select the correct statement(s),
(a) A hydrophilic colloid is a colloid in which there is a strong attraction
(b) A hydrophobic colloid is a colloid in which there is a lack of attraction between the dispersed phase and water.
(c) Hydrophobic sols are often formed when a solid crystallizes rapidly from a chemical reaction or a supersaturated solution
(d) All of the above

6. Protein solutions are
(a) hydrophobic in nature
(b) hydrophilic
(c) both (a) and (b)
(d) None of the above

7. A colloid of gold particles is
(a) hydrophobic in nature
(b) is a sol (of solid dispersed in water)
(c) both (a) and (b)
(d) None of the above

8. Some of the properties given below are for colloids sols
I : Viscosity same as that of the medium
II : Extensive hydration takes place
III : Particles migrate either towards cathode or anode in an electric fiel
IV : Particles cannot be detected even under ultra-microscope
Select the properties which are for lyophilic colloidal sols.
(a) I, II (b) III, IV
(c) I, III (d) II, IV

9. Some of the following are suspensions:
I : Fog
II : Air
III : Blood
IV : Paint
V : Aerosol sprays
VI : Pearl
True suspensions are:
(a) I, II, III (b) III, IV, V
(c) I,III,V (d) I,II,V

10. Some of the following are true solutions:
I : Air
II : Sea water
III : Gasoline
IV : Wine
V : Pearl
VI : Blood
Select true solutions:
(a) I, II, III, IV (b) II, III, IV, V
(c) I, IV, V, VI (d) II, IV, VI

11. Which types of solutions is not filtrable through filter paper and parchment membrane both?
(a) True solutions and colloidal sol
(b) Colloidal sol and suspension
(c) True solution and suspension
(d) Suspension only

12. Select the correct statement(s),
(a) The process of dialysis is similar to osmosis, except that both solvent and small solute particles can pass through the semipermeable dialysis membrane
(b) Proteins can be purified by dialysis
(c) Hemidialysis is used to cleanse the blood of patients whose kidneys have malfunctioned
(d) All of the above

13. A reddish brown sol (containing Fe^{3+}) is obtained by:
(a) the addition of small amount of $FeCl_3$ solution to freshly prepared $Fe(OH)_3$ precipitate
(b) the addition of $Fe(OH)_3$ to freshly prepared $FeCl_3$ solution

(c) the addition of NH_4OH to $FeCl_3$ solution dropwise
(d) the addition of NaOH to $FeCl_3$ solution dropwise

14. If dilute HC1 is added to a precipitate of stannic oxide:
(a) $SnCl_2$ and $SnCl_4$ are formed
(b) a stable sol of stannic oxide is formed
(c) $Sn(OH)_2$ is formed
(d) Sn_2O_3 is formed

15. Collodion is obtained:
(a) when cellulose nitrate is peptised by organic solvents as ethanol
(b) when high electric current is passed between metal electrodes
(c) colloidal sol is heated
(d) aq NaOH is added to cellulose nitrate

16. Hemidialysis is used to:
(a) separate colloidal sol from water
(b) separate charged and uncharged particles
(c) cleanse the blood of patients whose kidneys have malfunctioned
(d) None of the above

17. Select the incorrect statement(s).
(a) Surface active agents like soaps and synthetic detergents are micelles.
(b) Soaps are emulsifying agents.
(c) $C_{17}H_{35}$ (hydrocarbon part) and —COO^- (carboxylate) part of stearate ion ($C_{17}H_{35}COO^-$) both are hydrophobic.
(d) All are incorrect statements

18. Select the correct statement(s) about phospholipids.
(a) In aqueous solution, they form micelles.
(b) They form bilayers.
(c) They are principal components of cell membranes.
(d) All of the above are correct statements

19. Intensity of the scattered light depends on the difference between ..... of dispersed pnase and dispersion medium:
(a) densities (b) refractive indices
(c) viscosity (d) surface tension

20. Which is kinetic phenomenon?
(a) Brownian motion (b) Tyndall effect
(c) Both (a) and (b) (d) None of these

21. Following are some of the properties of the colloidal sols
I: Tyndall effect
II: Brownian motion
III: Maxwell distribution of molecules
These valid properties are:
(a) I, II, III (b) I, II
(c) I, III (d) II, III

22. Potential difference of the electrical double layer formed in a colloidal sol is called:
(a) EMF
(b) Zeta potential
(c) Brownian potential
(d) Nernst potential

23. SnO_2 is taken in basic medium and current is passed. Colloidal sol migrates towards:
(a) anode (+ plate) (b) cathode (+ plate)
(c) both (a) and (b) (d) None of these

24. Fixed parts of a colloidal sol of AgI are respectively [AgI] Ag^+ and [AgI] I^- in presence of:
(a) KI and $AgNO_3$ (b) KI and KI
(c) AgI and KI (d) $AgNO_3$ and KI

25. Which pair is correctly matched?
(a) $[Fe(OH)_3] : Fe^{3+}$
(b) $[As_2S_3] : As^{3+}$
(c) $[SnO_2] : SnO_3^{2-}$ in acidic medium
(d) [AgI] : I^- in excess of $AgNO_3$

26. Zeta potential or electrokinetic potential is dependent on:
(a) viscosity
(b) dielectric constant
(c) velocity of the colloidal particles when an electric field is applied
(d) All of the above

27. Colloidal sulphur particles are negatively charged with $S_2O_3^{2-}$ and other ions on the surface of sulphur. Hence, most effective electrolyte in coagulating colloidal sulphur is:
(a) NaCl (b) $MgCl_2$
(c) $A1C1_3$ (d) Na_2SO_4

28. Aluminium hydroxide forms a positively charged sol. Which of the following ionic substances should be most effective in coagulating the sol?
(a) NaCl (b) $Fe_2(SO_4)_3$
(c) $CaCl_2$ (d) K_3PO_4

29. Graph between log $\frac{x}{m}$ and log P is a straight line inclined at an angle $\theta - 45°$. When pressure of 0.5 atm and log k = 0.699, the amount of solute adsorbed per g of adsorbent will be
(a) 1 g/g adsorbent
(b) 1.5 g/g adsorbent
(c) 2.5 g/g adsorbent
(d) 0.25 g/g adsorbent

30. Flocculation value of a coagulating electrolyte is expressed in:
(a) millimol L^1
(b) mol L^{-1}
(c) mg K^{-1}
(d) microgram mL^{-1}

31. Gold number of some lyophilic sols are:

I. Casein	:	0.01
II. Haemoglobin	:	0.03
III. Gum arable	:	0.15
IV. Sodium oleate	:	0.40

Which has maximum protective power?
(a) I (b) II
(c) III (d) IV

32. Gold number of haemoglobin is 0.03. Hence, 100 mL of gold sol will require haeomoglobin so that gold is not coagulated by 10 mL of 10% NaCl solution:
(a) 0.03 mg (b) 30 mg
(c) 0.30 mg (d) 3mg

33. What happens when gelatin is added to gold sol?
(a) Gold sol is destabilised and peptisation occurs
(b) Gold sol is stabilised and no coagulation takes place
(c) Gold sol is destabilised and coagulation takes place
(d) Gold sol is stabilised and peptisation takes place

34. Which is not the correct matching of emulsions?
(a) Milk : O/W
(b) Cold cream : W/O
(c) Butter : O/W
(d) Vanishing cream : O/W

35. Coagulation or demulsification can be done by some of the methods given below:
I. by addition of a substance which would destory the emulsifier
II. by addition of an electrolyte which would destroy the charge
III. by heating, freezing and centrifuging
Select correct methods:
(a) I, II (b) I, II, III
(c) II only (d) III only

36. Water carrying impurities is purified by addition of potash alum. $A1^{3+}$ of the potash alum causes:
(a) peptization of negatively charged turbidity
(b) coagulation of negatively charged turbidity
(c) peptization of positively charged turbidity
(d) coagulation of positively charged turbidity

37. Artificial rain is caused by spray of:
(a) electrified sand or salt
(b) neutral salt or sand
(c) negatively charged sand or salt
(d) positively charged sand or salt

38. Artificial smoke screens are made by:
(a) aluminium oxide (b) lead oxide
(c) sodium oxide (d) titanium oxide

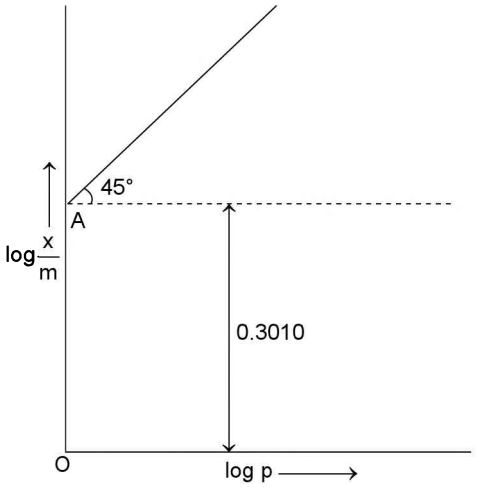
39. Milk is an emulsion of fat dispersed in water. It is stabilized by:
(a) casein – a lyophilic colloidal sol
(b) casein – a lyophobic colloidal sol
(c) lactose – a lyophilic colloidal sol
(d) lactose – a lyophobic colloidal sol

40. There are certain properties related to adsorption:
I. reversible
II. formation of unimolecular layer
III. low heat of adsorption
IV. occurs at low temperature and decreases with increasing temperature
Which of the above properties are for physical adsorption?
(a) I, II, III (b) I, III, IV
(c) II, III, IV (d) I, III

41. Select the correct statement(s):
(a) Residual force-field on a surface is responsible for adsorption.
(b) Rate of adsorption is very rapid in the beginning but decreases until equilibrium is attained.
(c) Desorption and adsorption are two opposite terms.
(d) All of the above are correct statements

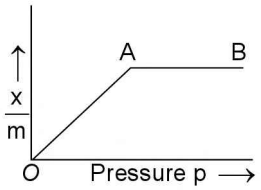
42. Surface area per gram of the adsorbent is called
(a) molar surface area
(b) normal surface area
(c) specific surface area
(d) equivalent surface area

43. Graph between $\log\left(\frac{x}{m}\right)$ and log p is a straight line at angle 45° with intercept OA as shown. Hence, $\left(\frac{x}{m}\right)$ at a pressure of 0.2 atm is:



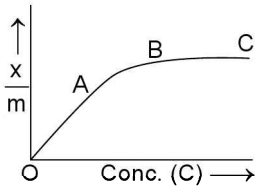
(a) 0.2 (b) 0.4
(c) 0.6 (d) 0.8

44. In the following isotherm:



(a) $\frac{x}{m} \propto p^{o}$ when point A is reached
(b) desorption may start along AB
(c) $\frac{x}{m} \propto p^{1/n}$ along OA
(d) All of the above

45. When saturation is attained in terms in terms of adsorption, variation of $\left(\frac{x}{m}\right)$ and C (concentration) is given by the portion of the isotherm

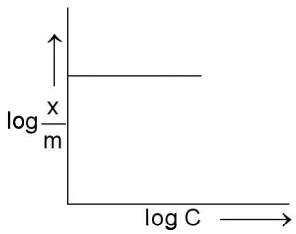


(a) OA (b) OB
(c) AB (d) BC

46. Lake test of aluminium ion is based on adsorption of blue litmus on:
(a) solid surface of Al
(b) solid surface of $Al(OH)_3$
(c) solid surface of Al_2O_3
(d) solid surface of $AlCl_3$

47. 50 mL of 1 M oxalic acid (molar mass = 126) is shaken with 0.5 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. What is the amount of oxalic acid adsorbed per gram of carbon?
(a) 3.15 (b) 1.575
(c) 6.30 (d) 12.60

48. For the adsorption of solution on a solid surface $\frac{x}{m} = kC^{1/n}$. Adsorption isotherm of $\log\left(\frac{x}{m}\right)$ and log C was found of the type



This is when:
(a) C = 0 (b) $\frac{1}{n} = 0$
(c) C = constant (d) C = 2 M

49. In the following reactions, catalysts used have been shown above the arrow. Which of these are not the suitable catalysts?

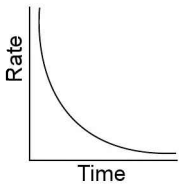
I. $2H_2O_2(aq) \xrightarrow{I^-(aq)} 2H_2O(l) + O_2(g)$

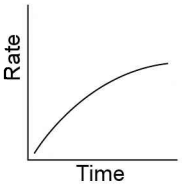
II. $HCl(g) + O_2(g) \xrightarrow{NO(g)} 2H_2O(l) + Cl_2(g)$

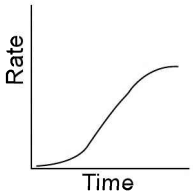
III. $2H_2(g) + O_2(g) \xrightarrow{MnO_2} 2H_2O(l)$

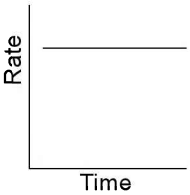
(a) I, II (b) II, III
(c) I, III (d) I, II, III

50. When MnO_4^- is added to oxalic acid, rate of the reaction with time (oxidation of MnO_4^- by oxalic acid) may follow graph:

(a) 

(b) 

(c) 

(d) 

51. Aqueous solution of $FeCl_3$ is yellow and that of $FeCl_2$ is very light green (appears colourless).

$$\underset{\text{yellow}}{Fe^{3+}} + e^- \longrightarrow \underset{\text{colourless}}{Fe^{2+}}$$

Yellow solution changes to colourless by reduction on:

(a) passing H_2 gas into it
(b) adding Zn pieces into it
(c) both (a) and (b)
(d) None of the above

52. What are the products X, Y, Z (aliphatic class) in:

$$CO + H_2 \xrightarrow{Ni} X$$

$$CO + H_2 \xrightarrow{Cu} Y$$

$$CO + H_2 \xrightarrow{ZnO + Cr_2O_3} Y?$$

(a) CH_3OH is all cases
(b) CH_3OH, HCHO, CH_4
(c) CH_4, HCHO, CH_3OH
(d) CH_4, CH_3OH, HCHO

53. $RCOCl + H_2 \xrightarrow{S \text{ in quinoline}} A$, A is:

(a) RCH_2OH (b) RCHO
(c) RCOOH (d) RCOOR

54. List A is for the names of the processes and List B is for the catalysts used.

	List A		**List B**
I:	Ostwald	P	Ni
II:	Steam hydrocarbon re-forming	Q	NO
III:	Fischer-Tropsch	R	Pt
IV:	Lead-chamber	S	Co/Al_2O_3

Correct matching is:

	I	II	III	IV
(a)	P	Q	R	S
(b)	R	P	S	Q
(c)	R	P	Q	S
(d)	P	R	Q	S

55. When $FeCl_3$ solution is added to NaOH a negatively charged sol is obtained. It is due to the

(a) Presence of basic group
(b) Preferential adsorption of OH^- ions
(c) Self dissociation
(d) Electron capture by sol particles

56. Following reaction is catalysed by MnO_2:

$$KClO_3 \xrightarrow{\Delta} HCl + 3O_2$$

If reaction mixture is plunged into water at the intermediate state, sometime solution appears green. This indicates the formation of the intermediate:

(a) KCl (b) $KMnO_4$
(c) K_2MnO_4 (d) Mn_2O_4

57. Following are the terms about activity and selectivity:

I: Activity is the ability of catalysts to accelerate chemical reactions and selectivity is the ability of catalysts to direct reaction to yield particular products.

II: Activity is the ability of catalysts to direct reaction to yield particular products and selectivity is the ability of catalysts to accelerate chemical reactions.

Select the correct term:

(a) I (b) II
(c) I and II both (d) none of these

58. Example of intrinsic colloid is:

(a) As_2S_3 sol (b) S sol
(c) Egg albumin (d) $Fe(OH)_3$ sol

59. Arsenic (III) sulphide forms a sol with a negative charge.

Which of the following ionic substances should be most effective in coagulating the sol?

(a) KCl (b) $MgCl_2$
(c) $Al_2(SO_4)_3$ (d) Na_3PO_4

60. If a freshly formed precipitate of SnO_2 is peptised by a small amount of NaOH, these colloidal particles may be represented as:

(a) $[SnO_2]\ SnO_3^{2-} : 2Na^+$
(b) $[SnO_2]\ Sn^{4+} : O^{2-}$
(c) $[SnO_2]\ Na^+ : OH^-$
(d) $[SnO_2]\ Sn^{4+} : OH^-$

ANSWER KEYS

1. (d)	**2.** (a)	**3.** (d)	**4.** (d)	**5.** (d)	**6.** (a)	**7.** (c)	**8.** (d)	**9.** (b)	**10.** (a)
11. (d)	**12.** (d)	**13.** (a)	**14.** (b)	**15.** (a)	**16.** (c)	**17.** (c)	**18.** (d)	**19.** (b)	**20.** (a)
21. (b)	**22.** (b)	**23.** (a)	**24.** (d)	**25.** (a)	**26.** (d)	**27.** (c)	**28.** (d)	**29.** (c)	**30.** (a)
31. (a)	**32.** (c)	**33.** (b)	**34.** (c)	**35.** (b)	**36.** (b)	**37.** (a)	**38.** (d)	**39.** (a)	**40.** (b)
41. (d)	**42.** (c)	**43.** (b)	**44.** (d)	**45.** (d)	**46.** (b)	**47.** (c)	**48.** (b)	**49.** (b)	**50.** (c)
51. (b)	**52.** (c)	**53.** (b)	**54.** (b)	**55.** (b)	**56.** (c)	**57.** (a)	**58.** (c)	**59.** (c)	**60.** (a)

HINTS AND EXPLANATIONS

1. (d) On the basis of equation, $\Delta G = \Delta H - T\Delta S$ can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in adsorption which is a spontaneous process.
ΔS is negative
ΔH is sufficiently negative and as a result ΔG is also negative.

2. (a) $Zn(OH)_4 + 4HCl \longrightarrow SnCl_4 + 4H_2O$
$[Zn(OH)_4]Sn^{4+} \vdots 4Cl^-$ (Positive charge)

29. (c) $\frac{x}{m} = k \cdot P^{1/n}$ since log k = 0.699, hence k = 5
Hence, k = 5
slope $= \frac{1}{5} = \tan 45° = 1$
thus, $\frac{x}{m} = 5 \times 0.5$
$= 2.5$ g/g adsorbent

55. (b) $FeCl_2 + 3NaOH \longrightarrow Fe(OH)_3 + 3NaCl$
$NaOH \longrightarrow Na^+ + OH^-$
OH^- ions having similarity with $Fe(OH)_3$ will be adsorbed on the surface of $Fe(OH)_3$ to form an electrical double layer.

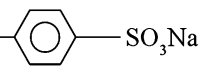
$$Fe(OH)_3 \left| \begin{matrix} OH^- \\ OH^- \\ OH^- \end{matrix} \right| \begin{matrix} Na^+ \\ Na^+ \\ Na^+ \end{matrix}$$

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. 1 mol of [AgI] Ag^+ sol is coagulated by:
(a) 1 mol of KI (b) 500 mL of 1 M K_2SO_4
(c) 1 L of 1 M KI (d) none of these

2. An emulsifier is an agent which:
(a) accelerates the dispersion
(b) homogenizes an emulsion
(c) stabilizes an emulsion
(d) acids the flocculation of an emulsion

3. On adding $AgNO_3$ solution into KI solution, a negatively charged colloidal sol is obtained when they are in:
(a) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.1 m KI
(b) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.2 M KI
(c) 100 mL of 0.2 M $AgNO_3$ + 100 mL of 0.1 M KI
(d) 100 mL of 0.15 $AgNO_3$ + 100 mL of 0.25 M KI

4. There is no scum formation when hard water is being used. The washing powder can be:
(a) $C_{17}H_{35}COONa$
(b) 
(c) both (a) and (b)
(d) None of these

5. Which of the following statements are true for hydrophilic sols?
   (a) They do not require electrolytes for stability.
   (b) Their coagulation is reversible.
   (c) Their viscosity is of the order of that of water.
   (d) Their surface tension is usually lower than that of dispersion medium.
6. Which one of the following statements are incorrect?
   (a) Brownian movement is more pronounced for smaller particles than for bigger ones.
   (b) Sols of metal sulphides are lyophilic.
   (c) Schulze-Hardy law states, the bigger the size of the ion, the greater is its coagulating power.
   (d) One would expect charcoal to adsorb chlorine more strongly than hydrogen sulphide.
7. Reactions in zeolite catalyst depend on
   (a) pores (b) apertures
   (c) size of cavities (d) pressure
8. Which is/are correct statement about the role of a catalyst in a reaction?
   (a) It is reactant in a rate-determining step and then a product of some subsequent step and then a product of some subsequent step.
   (b) It provides an alternate mechanism with a lower energy of activation.
   (c) In increases the rate of chemical reaction but does not itself undergo a permanent change during the course of the reaction.
   (d) It increases quantity of the product.
9. Colloidal solutions of gold prepared by different methods are of different colours because of:
   (a) different diameters of colloidal gold particles
   (b) variable valency of gold
   (c) different concentration of gold particles
   (d) impurities produced by different methods

ANSWER KEYS

1. (a, b, c) **2.** (b) **3.** (b, d) **4.** (b) **5.** (a, b, d) **6.** (b, c, d) **7.** (a, b, c) **8.** (a, b, c) **9.** (a)

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

The following passage describes characteristics of colloids. Answer the questions at the end of it.

Lyophilic colloidal sols are much more stable than lyophobic colloidal sols. This is due to the extensively salvation of lyophilic colloidal sols, which forms a protective layer outside it and thus prevents it from forming associated colloids.

Lyophilic colloidal sols also protect lyophobic colloidal sols from precipitation by the action of electrolytes. This is due to formation of a protective layer by lyophilic sols outside lyophobic sols. Lyophilic colloidal sols are called protective sols. Gelatin (lyophilic) protects gold sol (lyophobic) from coagulation on the addition of sodium chloride solution.

- Protective powers of different colloidal sols are measured in terms of 'gold number' (Zsigmondy).
  It is defined as the amount of protective sol in milligrams that prevents the coagulation of 10 mL of a given gold sol on adding 1 mL of 10 per cent solution of sodium chloride. Thus, smaller the gold number of a lyophilic sol, the greater is the protective power.

1. 0.025 g of starch sol is required to prevent coagulation of 10 mL gold sol when 1 mL of 10% NaCl solution is present. What is gold number of starch sol?
   (a) 0.025 (b) 2.5×10^{-5}
   (c) 0.25 (d) 25
2. Gold number of haemoglobin is 0.03. Hence, 100 mL of gold sol will require_____haemoglobin so that gold is not coagulated by 10 mL of 10% NaCl solution.
   (a) 0.03 mg (b) 30 mg
   (c) 0.30 mg (d) 3 mg
3. $[Ag]I^-$ colloidal sol can be coagulated by the addition of a suitable cation. 1 mol of $[AgI]I^-$ requires mol of $AgNO_3$, $Pb(NO_3)_2$ and $Fe(NO_3)_3$ as:

(a) 1, 1, 1 (b) 1, 2, 3

(c) 1, $\frac{1}{3}, \frac{1}{3}$ (d) 6, 3, 2

4. Small quantity of $FeCl_3$ solution is added to freshly prepared and well washed $Fe(OH)_3$ ppt.

(a) $Fe(OH)_3$ is dissolved forming $FeCl_3$

(b) a reddish brown positively charged sol $[Fe(OH)_3]$ Fe^{3+} is formed due to peptization

(c) a reddish brown negatively charged sol $[Fe(OH)_3]$: 3 Cl^- is formed due to peptization

(d) $Fe(OH)_3$. $FeCl_3$ (a double salt) is formed

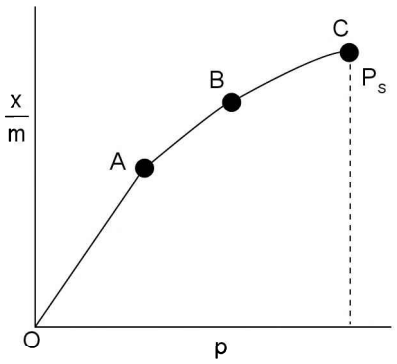
COMPREHENSION-II

A graph between x/m and the pressure P of the gas at a constant temperature is called adsorption isotherm. Where x is the number of moles of the adsorbate and m is the mass of the adsorbent. Adsorption isotherms of different shapes have been experimentally observed. According to Frundlich adsorption isotherm,

$$x/m = kP^{1/n}$$

where k and n are constant parameters depending upon the nature of the solid and gas.

5. In the given isotherm, select the incorrect statement:



(a) $\frac{x}{m} \propto p^{1/n}$ along OA

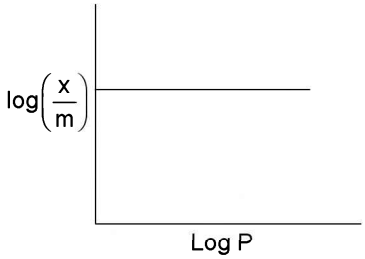
(b) $\frac{x}{m} \propto p^o$ when point B is reached

(c) $\frac{x}{m}$ does not increase as rapidly with pressure along BC due to less surface area available for adsorption

(d) Nature of isotherm is different for two gases for same adsorbent

6. Adsorption between of $\log\left(\frac{x}{m}\right)$ and log P was found of the type:

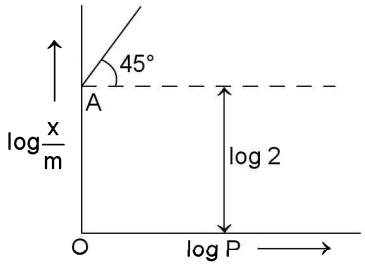
This is true when:



(a) P = 0 (b) P = 1

(c) $\frac{1}{n} = 1$ (d) $\frac{1}{n} = \infty$

7. Graph between $\log\left(\frac{x}{m}\right)$ and log P is a straight line at angle 45° with intercept OA as shown. Hence, $\left(\frac{x}{m}\right)$ at a pressure of 2 atm is:



(a) 2 (b) 4

(c) 8 (d) 1

COMPREHENSION-III

Coagulation is the process by which the dispersed phase of a colloid is made to aggregate and thereby separate from the continuous phase. The minimum concentration of an electrolyte in milli-moles per litre of the electrolyte solution which is required to cause the coagulation of colloidsl sol is called coagulation value.

Therefore, higher is the coagulating power of effective ion, smaller will be the coagulation value of the electrolyte.

$$\text{Coagulation value} \propto \frac{1}{\text{coagulating power}}$$

The coagulation values of different electrolytes are different. This behaviour can be easily understood by Hardy-Schulze rule which states.

"The greater is the valency of the effective ion greater is its precipitating power."

8. Which one has the highest coagulating power?
   (a) K^+ (b) Ca^{2+}
   (c) Al^{3+} (d) Sn^{4+}

9. As_2S_3 sol is negatively charged, capacity to precipitate it is highest in
   (a) K_2SO_4 (b) Na_3PO_4
   (c) $AlCl_3$ (d) $CaCl_3$

10. The ability of an ion to bring coagulation of a given colloid depends upon
    (a) the sign of its charge
    (b) magnitude of its charge
    (c) both magnitude and sign
    (d) None of these

11. The coagulation of colloidal particles of the sol can be caused by
    (a) heating
    (b) adding electrolyte
    (c) adding oppositely charged sol
    (d) All of these

ANSWER KEYS

1. (d) **2.** (c) **3.** (c) **4.** (b) **5.** (b) **6.** (c) **7.** (b) **8.** (d) **9.** (c) **10.** (c) **11.** (d)

MATCH THE COLUMN TYPE QUESTIONS

1. Following are the various types of colloids. Match column X with column Y.

	X (Colloids)		Y(Classification
I	rain cloud	A	sol
II	milk of magnesia	B	aerosol
III	soap suds	C	gel
IV	butter	D	foam

2. Match List I with List II:

	List I (term)		List II (related property)
A.	Coagulation	1.	Scattering of light
B.	Lyophilisation	2.	Washing of precipitate
C.	Peptisation	3.	Purification of colloids
D.	Tyndall effect	4.	Electrolyte

ANSWER KEYS

1. (I)-(b);(II)–(a); (III)–(d); (IV)–(c) **2.** (a)-(4);(b)–(3); (c)–(2); (d)–(1)

TRUE/FALSE TYPE QUESTIONS

1. Colloids, on account of their extremely small dimensions, have large surface area per unit mass and these are good adsorbents.
2. Soaps and detergents lower the interfacial surface tension between oil and water.
3. The addition of electrolyte deactivates enzymes due to coagulation.
4. Tyndall's cone has bluish colour.
5. A resultant mixture of 10 mL of 1 M KI and 5 mL of 1 M $AgNO_3$ is the positively charged colloidal sol.
6. The formation of micelles takes place below Kraft temperature.

ANSWER KEYS

1. T 2. T 3. T 4. T 5. F 6. F

ASSERTION/REASON TYPE QUESTIONS

INSTRUCTIONS: In the following questions, an Assertion (A) is given followed by a Reason (R). Mark your responses from the following options.

(a) Both Assertion and Reason are true and Reason is the correct explanation of 'Assertion'
(b) Both Assertion and Reason are true and Reason is not the correct explanation of 'Assertion'
(c) Assertion is true but Reason is false
(d) Assertion is false but Reason is true

1. **Assertion (A):** In the presence of promoter, the activity of the catalyst is enhanced.
   Reason (R): The promoter increases the surface area of the catalyst and thus, enhancing the number of active centres.
2. **Assertion (A):** Colloidal AgI is prepared by adding $AgNO_3$ in slight excess to KI solution. When subjected to an electric field, the colloidal particles migrate to the anode.
   Reason (R): Colloidal particles adsorb ions and thus, becomes electrically charged.
3. **Assertion (A):** The adsorption of a vapour on a clean surface is a spontaneous process.
   Reason (R): Change in the entropy of the process is highly positive.
4. **Assertion (A):**AgI changes to positively charged colloidal sol in presence of KI.
   Reason (R): It is due to adsorption of I^- on AgI.
5. **Assertion (A):** Proteins, starch and rubber are lyophilic colloids.
   Reason (R): They have strong interaction with the dispersion medium.

ANSWER KEYS

1. (a) 2. (a) 3. (b) 4. (d) 5. (a)

SUBJECTIVE QUESTIONS

1. The layer of fat in the pans used for preparing soaps can be removed by adding boiling washing soda solution. How will you account for it?
2. SnO_2 forms a positively charged colloidal sol in the acidic medium and negatively charged sol in the basic medium. Explain.
3. The coagulation values of the electrolytes $AlCl_3$ and NaCl for As_2S_3 sol are 0.093 and 52 respectively. How many times $AlCl_3$ has greater coagulating power than NaCl?
4. What happens when persistent dialysis of a colloidal solution is carried out?

HINTS AND EXPLANATIONS

1. Washing soda (Na_2CO_3) gets hydrolyzed to form NaOH as follows:

$$Na_2CO_3 + H_2O \xrightarrow{\text{(boil)}} 2NaOH + H_2O + CO_2$$

NaOH reacts with fat which is a triglyceride to form soap and glycerol by saponification reaction. The soap thus formed helps in cleaning the pan.

2. SnO_2 is amphoteric in nature which means that it can react with both acis and bases. With an acid such as HCl, if forms $SnCl_4$. The Sn^{4+} ions are adsorbed on the surface of SnO_2 to give a positively charged colloidal sol.

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

$$SnO_2 + Sn^{4+} \longrightarrow \underset{\text{Positively charged}}{[SnO_2]Sn^{4+}}$$

Similarly, with base like NaOH, if forms sodium stannate (Na_2SnO_3). The stannate ions get adsorbed on the surface of SnO_2 to give negatively charged colloidal sol.

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3$$

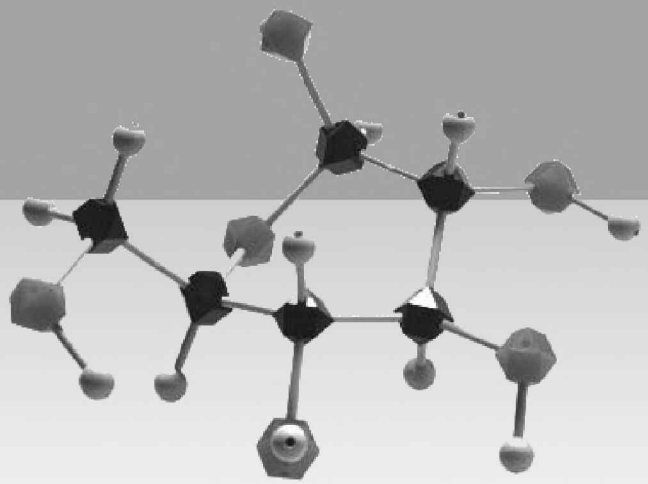
$$SnO_2 + SnO_3^{2-} \longrightarrow \underset{\text{negatively charged}}{[SnO_2]SnO_3^{2-}}$$

3. It may be noted that the coagulating powers of the electrolytes are inversely proportional to their coagulating values. Thus,

$$\frac{\text{Coagulatign power of } AlCl_3}{\text{Coagulating power of NaCl}} = \frac{52}{0.093} = 559$$

Thus, coagulating power of $AlCl_3$ is 559 times more than that of NaCl.

4. The stability of a colloidal sol is due to the presence of a small amount of the electrolyte. On persistent dialysis, the electrolyte is completely removed. As a result, the colloidal sol becomes unstable and gets coagulated.



CHAPTER 11

Solid State

CRYSTALLINE AND AMORPHOUS STATE

Both solids and liquids are called CONDENSED STATE OF MATTER. This indicates that the molecules, atoms or ions that make up a solid are closely packed, they are held together by strong cohesive forces and cannot move at random. Solids occur either in the crystalline or in the amorphous state. CRYSTALS have definite geometrical shape and are bounded by plane faces. Examples of crystals are alum, diamond, salts etc., whereas powdery precipitate, glass, resins, stiff jellies etc., are examples of amorphous solids.

Difference Between Amorphous and Crystalline Solids

Amorphous solids

(i) They do not have sharp melting point.

(ii) An amorphous substance does not have any pattern of arrangement of molecules or atoms i.e., it does not have any geometrical shape. It has been found that even if some orderly arrangement of molecules or atoms exists in a few amorphous substances, it does not extend more than a few Angstrom units. Thus, unlike solids, amorphous substances do not have long range order.

(iii) Amorphous substances differ from solids and in fact resemble liquids in an important respect. The properties such as electrical conductivity, thermal conductivity, mechanical strength and refractive index are the same in all directions. Amorphous substances are said to be isotropic. Liquids and gases are also isotropic.

(iv) These are super cooled liquid or pseudo solids.

(v) They do not have well defined planes. They do not have symmetry.

(vi) They undergo an irregular cut.

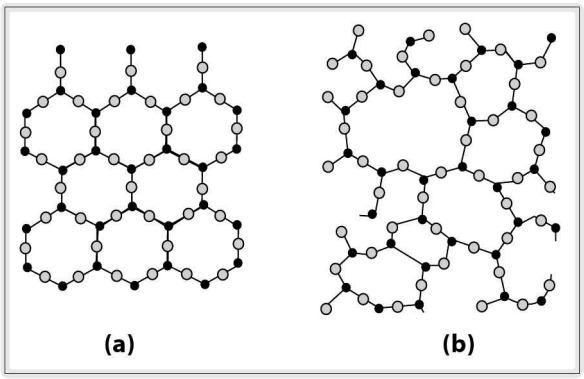


Fig. 11.1 To dimensional structure of (a) quartz (crystalline) and (b) quartz glass (amorphous)

(vii) Following is the cooling curve for amorphous solid:

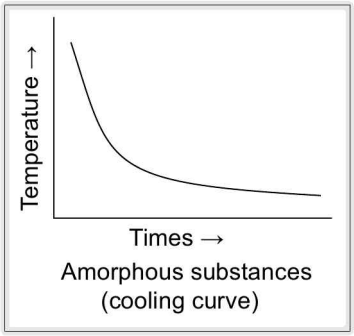


Fig. 11.2

Crystalline solids

(i) They have sharp melting point.

(ii) Crystalline solids are anisotropic, i.e., their physical properties are different in different directions. For example, the velocity of light passing through a solid varies with the direction in which it is measured. Thus, a ray of light entering crystalline solid may split up into two components each following a different velocity. This phenomenon is known as double refraction. Thus, anisotropy in itself is a strong evidence for the existence of ordered molecular arrangements in such materials.

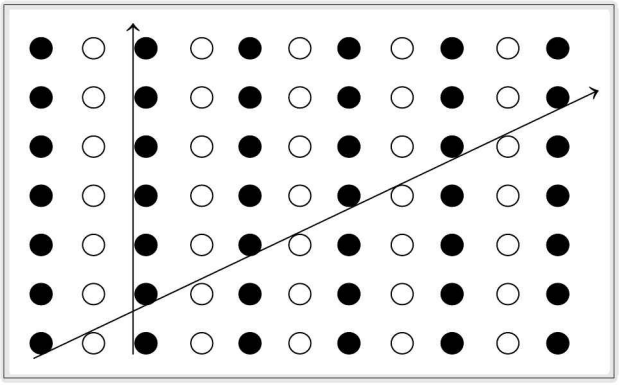


Fig. 11.3 Anisotropic behaviour of solids

(iii) They have a symmetry in structure.
(iv) They under go a clean cleavage.
(v) Following is the cooling curve for crystalline solid.

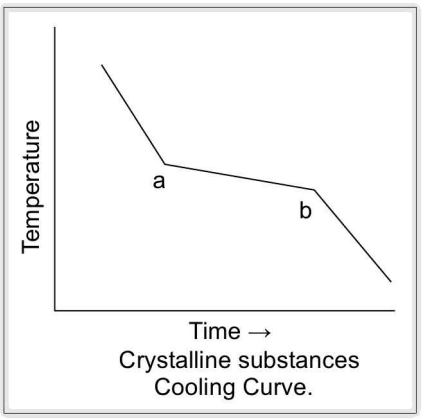


Fig. 11.4

POLYMORPHISM AND ALLOTROPY

The same substance, elementary or compound, may exist in more than one crystalline modification. This phenomenon is called polymorphism and in the case of elements it is customary to refer to it as allotorpism and allotropy.

Polymorphism

Various cases of polymorphism are well-known. For example, common ice may be made to crystallize in a number of modifications (at lest six), called ice I, ice II and so on, if the external pressure is increased. The existence of mercuric iodide in the yellow and the red modifications, the occurrence of silicon dioxide as quartz, flint, opal, sand, agate, etc., the existence of ammonium nitrate in five well-characterised polymorphic forms, and similar other phenomena are examples of polymorphism. The different crystalline forms of the same substance are called polymorph.

Each polymorphic form of a substance is thermodynamically stable within a particular temperature and pressure range, and the transformation from one form to another takes place at any given pressure at a fixed temperature known as the transition temperature of transition point.

Comparison between transition point and melting point

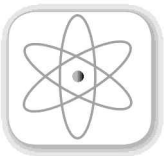
In an extended sense, the term transition point includes melting or boiling point, because melting is really a reversible transition or phase change. There is no basic distinction between the two. The following analogies are to be noted:

(i) At the melting point or transition temperature, both forms are equally stable, having the same vapour pressure (same chemical potential), and can co-exist side by side.
(ii) The transition point and the melting point are perfectly well-defined temperatures, whose values are changeable with external pressure according to similar rules.
(iii) The transition from one modification to another, as well as the melting of a crystal takes place with either evolution or absorption of heat; such changes are also usually attended with volume change.

(iv) It is usually possible to superheat or supercool one modification above or below the transition point easily, but it is less easy to supercool a liquid below the melting point and is almost impossible to superheat a solid above the melting point.

(v) A dissolved foreign material depresses the M.P. and also changes the transition temperature according to the same basic rule (i.e., if the solute dissolves in the phase stable at higher temperature, the transition point is lowered and vice versa).

MITCHERLICH'S LAW OF ISOMORPHISM



That the structure of a crystal is in some way related to its chemical composition was first recognized by Mitcherlich (1819) who stated this in his law of isomorphism in the following way: "The same number of atoms combined in the same manner produces the same crystalline form: the crystalline form is independent of the chemical nature of the atoms and is determined solely by their number and mode of combination."

Substances crystallizing in the same crystalline form are called isomorphous. Examples of isomorphism among compounds of similar structure investigated by the discoverer of the law are the alkali metal phosphates and arsenates. Also, other cases of isomorphism are well-known. Thus, common alum, ferric alum and chrome alum have similar structure, K_2SO_4, $M_2(SO_4)_3$, $24H_2O$ and are also isomorphous, crystallizing in the octahedral form (cubic system). The sulphates of zinc, iron etc., ($FeSO_4$, $7H_2O$ etc.) crystallize in the same crystalline form.

Classification of Crystaline Solids

Types of solid

(i) ***Ionic solid***

Constituent Particles– Positive and negative ions

Bonding/Attractive Forces– Electrostatic force of attraction

Examples– NaCl, ZnS, Na_2O, CaF_2

Physical Nature– Hard and rigid but brittle and they shatter easily by hammering. By hammering, a layer of ions slips away from their oppositely charged neighbours and brings them closer to ions of like charge. The increase of electrostatic repulsions along the displaced plane causes the crystal to break.

Electrical conductivity– Insulators in solid state but conductors in molten state and in aqueous solutions

Melting Point– High melting points

(ii) ***Metallic solids***

Constituent Particles– Positive ions in a sea of delocalized electrons

Bonding/Attractive Forces– Metallic bond results from the simultaneous attraction between mobile valence electrons and positively charged kernels present in the electron sea.

Examples– Fe, Cu, Ag, Mg

Physical Nature– Hard with high tensile strength (they can be stretched without braking) but malleable (can be beaten into sheets) and ductile (can be drawn into wires). The hardness and tensile strength can be explained in terms of strong electrostatic force of attraction between the kernels and mobile electrons. When stress is applied on the metal surface, the kernels present in a layer slip over the other layer. This causes deformation in the shape of crystal. The mobile electrons still keep on attracting each other only there is a shift in the position of the kernels from one lattice site to the other.

Electrical conductivity– Excellent conductors in solid state as well as in molten state. There is no current in a conductor in the absence of electric field although the free electrons are in motion. This is because in the absence of electric field, the electrons are in random motion and at any instant the number of electrons moving through any section from left to right is the same as the number of electrons crossing from right to left. Therefore, the net flow of electrons is zero and thus no current flows through the conductor. On applying the electric field, all the electrons are directed in one direction and, therefore, current flows through the current. Conductivity of metals decreases with increase in temperature.

Melting Point– Fairly high

(iii) ***Molecular solids***

Constituent Particles – Molecules

Bonding/Attractive Forces– There can be three types:

(a) Non-polar solid (Dispersion or london force)

(b) Polar solid (Dipole-dipole interactions)

(c) Hydrogen bonded solid (Hydrogen bonding)

Examples– (a) Non-polar solid (Ar, CCl_4, H_2, I_2, CO_2,)

(b) Polar solid (HCl, SO_2)

(c) Hydrogen bonded solid (H_2O(ice))

Physical Nature– (a) Non-polar solid –Soft as there is weak dispersion or london force

(b) Polar solid –Soft as there is weak dipole-dipole interactions

(c) Hydrogen bonded solid –Hard as there is stronger hydrogen bonding

Electrical conductivity– They are all insolator (no mobile electrons or ions)

Melting Point– (a) Non-polar solid –Very low

(b) Polar solid –Low

(c) Hydrogen bonded solid –Low

(iv) ***Covalent or network solids***

Constituent Particles – Constituent items

Bonding/Attractive Forces– Covalent bonding

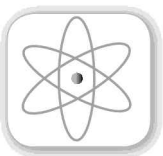
Examples– SiO_2 (quartz), SiC, C (diamond), AlN, C (graphite)

Physical Nature– The atoms interlocked by a network of covalent bonds produce a crystal which is considered to be a single giant molecule. These crystals are very hard (graphite is soft).

Electrical conductivity– They are all insulators (graphite is conductor–exception)

Melting Point– Very high melting points.

SPACE LATTICE AND UNIT CELL



Lattice It is the imaginary collection of infinite number of points in space with a regular and repeating arrangement geometry Thus, a regular three dimensional arrangement of points in space is called a space lattice.

The characteristics of a crystal lattice are as follows:

(a) Each point in a lattice is called lattice point or lattice site.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

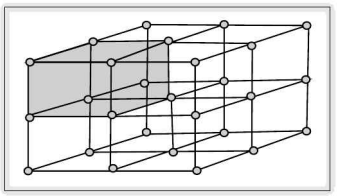


Fig. 11.5 A portion of a three dimensional cubic lattice and its unit cell

Unit Cell

Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

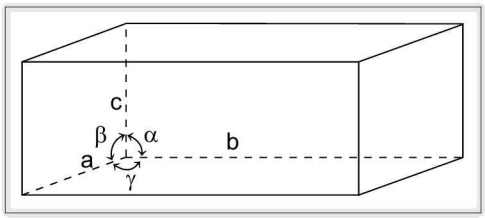


Fig. 11.6 Parameters of a unit cell

A unit cell is characterized by:

(i) its dimensions along the three edges, *a*, *b* and *c*. These edges may or may not be mutually perpendicular.

(ii) angles between the edges, α β(between *b* and *c*) β(between *a* and *c*) and γ(between *a* and *b*). Thus, a unit cell is characterised by six parameters, *a, b, c*, α, β and γ.

Types of unit cells

Unit cells can be divided into four categories depending on the manner in which they are arranged in a given shape. These are: Primitive, Body Centered, Face Centered and End Centered. For a cubic crystal system the four unit cells are shown below:

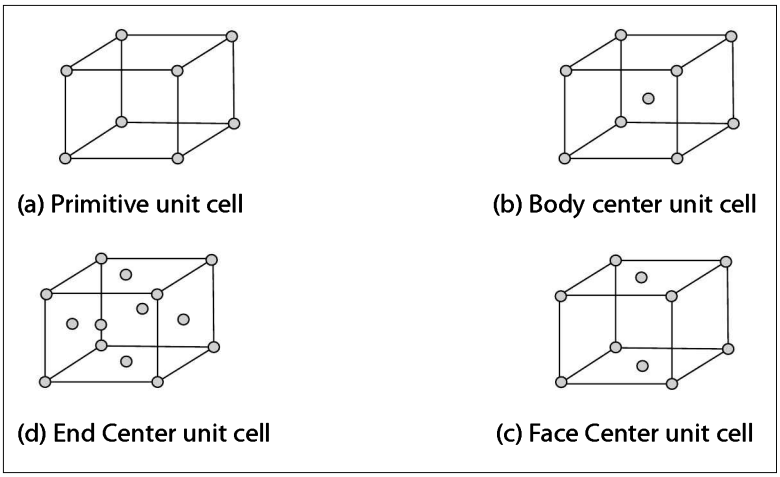


Fig. 11.7

CRYSTAL SYSTEMS

Bravais (1848) showed from geometrical considerations that there are only seven shapes in which unit cells can exist. These are:

(i) Cubic (ii) Orthorhombic (iii) Rhombohedral (v) Hexagonal
(v) Tetragonal (vi) Monoclinic and (vii) Triclinic

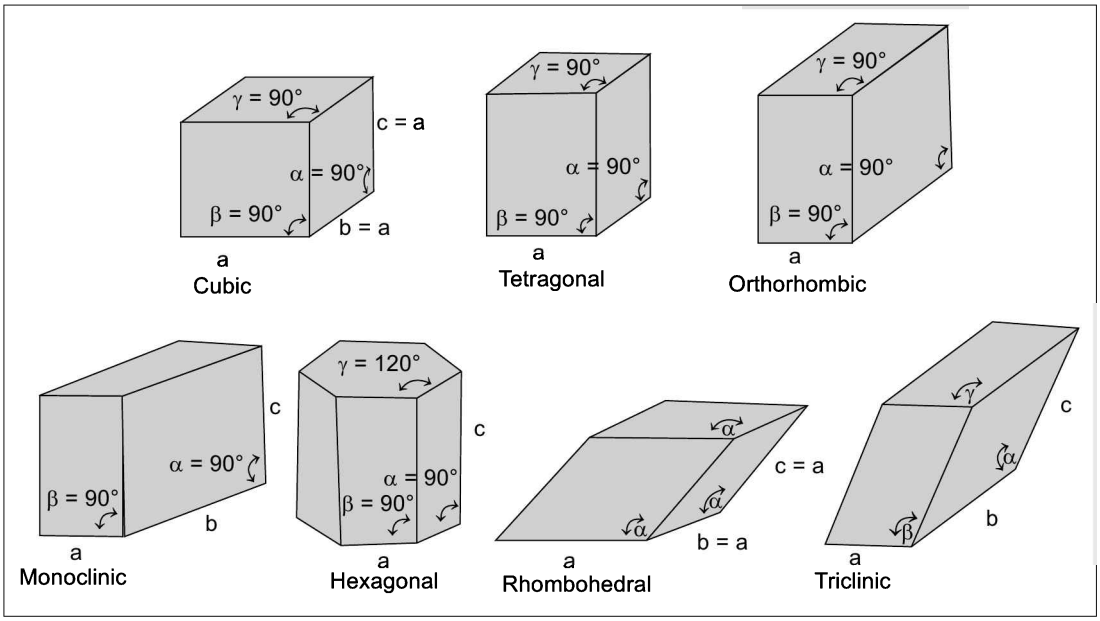


Fig. 11.8 Seven crystal systems based on shape of unit cells

Crystal System	*Bravais Lattices*	*Parameters of Unit Cell*		
		Intercepts	Crystal angle	Example
1. Cubic	Primitive, Face Centered, Body Centered = 3	a = b = c	α = β = γ = 90°	Pb,Hg,Ag,Au Diamond, NaCl, ZnS
2. Orthorhombic	Primitive, Face Centered, Body Centered, End Centered = 4	a ≠ b ≠ c	α = β = γ = 90°	KNO_2, K_2SO_4
3. Tetragonal	Primitive, Body Centered =2	a = b ≠ c	α = β = γ = 90°	TiO_2,SnO_2
4. Monoclinic	Primitive, End Centered = 2	a ≠ b ≠ c	α = γ = 90°, β ≠ 90°	$CaSO_4.2H_2O$
5. Triclinic	Primitive = 1	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90°	$K_2Cr_2O_7$, $CaSO_4.5H_2O$
6. Hexagonal	Primitive = 1	a = b ≠ c	α = β = 90°, γ = 120°	Mg, SiO_2, Zn, Cd
7. Rhombohedral	Primitive = 1	a = b = c	α = β = γ ≠ 90°	As, Sb, Bi, $CaCO_3$

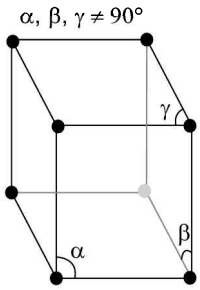
Now, there are seven crystal systems and there are four unit cells within a crystal system, hence there can be twenty eight unit cells (i.e., seven shapes × four types in each shape = 28 possible unit cells),

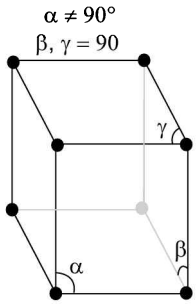
He also went on to postulate that out of the out of the twenty eight possible unit cells only fourteen actually would exist. These he postulated based only on symmetry considerations. These fourteen unit cells that actually exist are called **Bravais Lattices.**

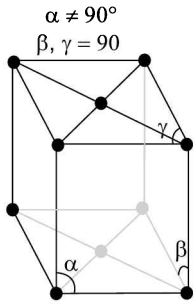
Question: Explain why an end-centered unit cell cannot be cubic. What is the highest possible symmetry for this type of unit cell?

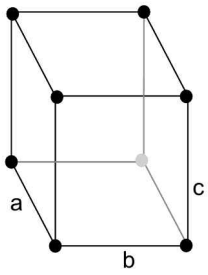
Answer: A cubic unit cell must have the six faces the same. The highest symmetry possible for an end-centered unit cell is tetragonal.

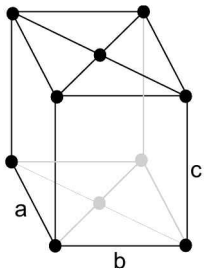
The 7 lattice systems (from least to most symmetric)	*The 14 Bravais Lattices*	*Examples*
1. Triclinic (none)	$\alpha, \beta, \gamma \neq 90°$	
2. Monoclinic (diad)	$\alpha \neq 90°$ $\beta, \gamma = 90°$	$\alpha \neq 90°$ $\beta, \gamma = 90°$
3. Orthorhombic (3 perpendicular diads)	$a \neq b \neq c$	$a \neq b \neq c$ $a \neq b \neq c$ $a \neq b \neq c$
4. Rhombohedral (1 triad)	$\alpha = \beta = \gamma \neq 90°$	

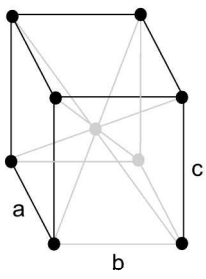


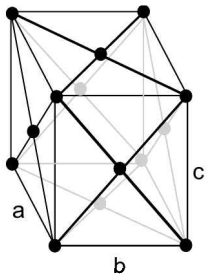


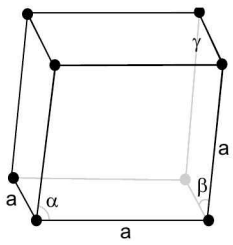












(Contd)

The 7 lattice systems (from least to most symmetric)	The 14 Bravais Lattices		Examples
	simple	body-centered	
5. Tetragonal (1 tetrad)	a ≠ c	a ≠ c	
6. Hexagonal (1 hexad)			
	simple (SC)	body-centered (BCC)	face-centered (FCC)
7. Cubic (4 triads)			

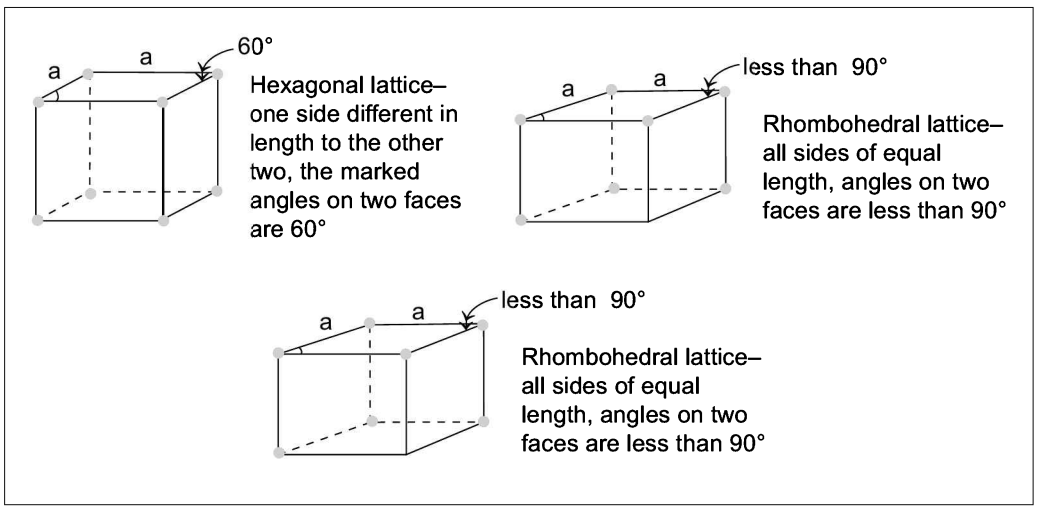


Fig. 11.9 Unit cells of 14 types of Bravais Lattices

EFFECTIVE NUMBER OF ATOMS PER CUBIC UNIT CELL

Effective number of atoms per unit cell is called rank of that unit cell consider the following points for cubic unit cell:

1. Atom at the corner of unit cell is shared by 8 unit cells. Thus, contribution of each corner atom (per unit cell) is $\frac{1}{8}$.
2. Atom present at the face of a unit cell is shared by 2 unit cells. Contribution of each face atom (per unit cell) is $\frac{1}{2}$.
3. For atom present at the centre or inside the unit cell, contribution of that atom towards one unit cell is equal to 1.
4. For atom present at the edge of unit cell is shared by 4 unit cells. Contribution of edge atom (per unit cell) is $\frac{1}{4}$.

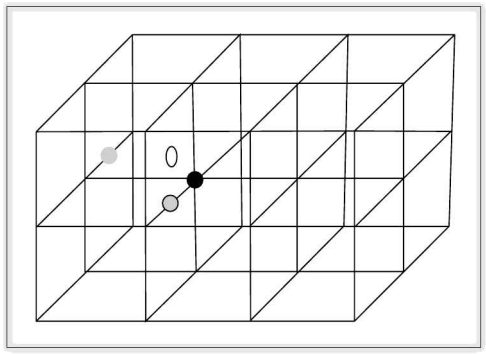


Fig. 11.10 Unit cells arranged together

● Corner atom ○ Edge center atom
Body center atom 0 Face center

If,

n_c = number of corner atoms, n_f = number of face atoms

n_b = number of body atoms (inside the cubic) n_e = number of edge atoms

$$\text{Rank} = \frac{n_C}{8} + \frac{n_f}{2} + \frac{n_e}{4} + n_b \text{ (For cubic unit cell)}$$

Consideration

(i) Atoms are considered to be solid sphere. Hence, they cannot squeeze into one another the spheres can touch each other or they can remain separated.

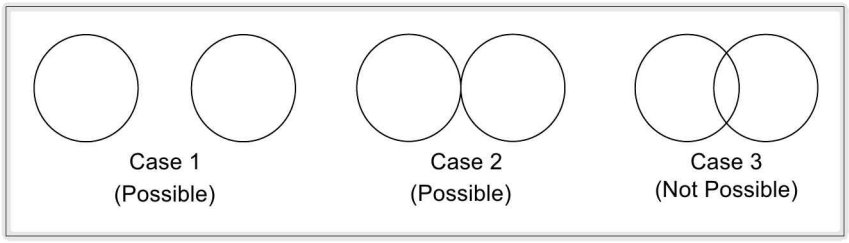


Fig. 11.11

(ii) The lattice points are the positions of the center of the spheres (nuclei of atoms).

Type of cubic unit cells

Simple or primitive cubic unit cell:

(a) All the eight corners of the cube are occupied by the same atoms.
(b) There is no such atoms present any where in the cube except corners.
(c) Contribution of each atom or sphere for one unit cell is $\frac{1}{8}$ of the volume of each sphere
(d) Therefore, number of effective atoms in a unit cell. [Rank of unit cell] is one

$$Z = \frac{n_C}{8} = \frac{8}{8} = 1$$

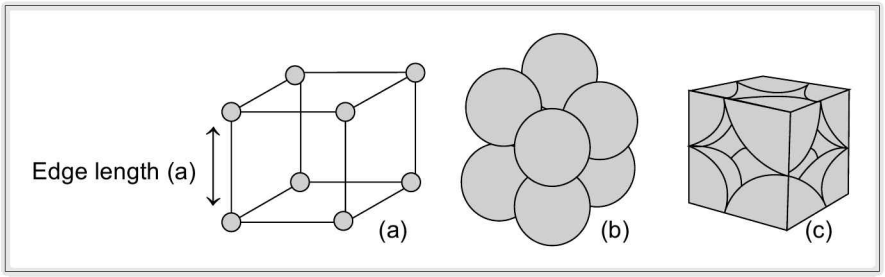


Fig. 11.12 A primitive cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

(e) The corner atoms are making contact along the edges. Hence,

$$a = 2r$$

where, r = radius of one sphere (1 atom)

So, volume of the unit cell = $a^3 = (2r)^3 = (2)^3r^3 = 8r^3$

Volume of all the atoms (spheres) in one unit cell = (rank) $\times \frac{4}{3}\pi r^3$

$$= 1 \times \frac{4}{3}\pi r^3$$

Packing fraction

It is the fraction of volume occupied by the atoms. Hence it can be numerically expressed as:

$$\frac{\text{Volume occupied by the same spheres in a unit cell}}{\text{Volume of unit cell}} = \frac{Z \times \frac{4}{3}\pi r^3}{a^3}$$

Z = rank of unit cells

For simple cubic unit cell z = 1 a = 2r

$$\text{Packing fraction} = \frac{1 \times \frac{4}{3}\pi r^3}{8r^3}$$

$$= \frac{\pi}{6} = 0.5236 = 52.36\%$$

i.e., 52.36% space is occupied and 47.64% is vacant.

Void fraction = 1–P.F = 0.48

Body diagonal and face diagonal

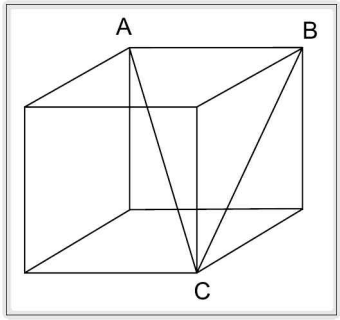


Fig. 11.13

In the above cube, $\overline{AC}$ represents the body diagonal and $\overline{BC}$ represents the face diagonal. If 'a' represents the age length of the cube, we can easily prove that body diagonal $\overline{AC} = \sqrt{3}a$ and face diagonal $\overline{BC} = \sqrt{2}a$.

A primitive unit cell is created in the manner as shown in the figure. Four atoms are present in such a way that the adjacent atoms touch each other. Therefore, if the length of the unit cell is 'a', then it is equal to 2r, where r is the radius of the sphere. Four more spheres are placed on top of these such that they eclipse these spheres. Also note that the atoms cannot make contacts along the face diagonal ($a = 2r \Rightarrow 2r < \sqrt{2}a$).

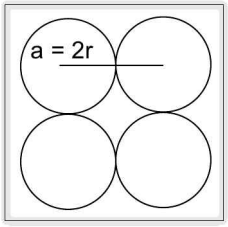


Fig. 11.14



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Body-centered cubic unit cell (bcc unit cell)

A body centred cubic unit cell is said to be ideal body centred cubic unit cell when the following conditions are satisfied:

(a) All the corner atoms are same
(b) The body center atom may be same or different to that of corner atom
(c) The atoms must make contact along the body diagonal.
(d) The rank of the unit cell

$$z = \frac{n_C}{8} + nb = \frac{8}{8} + 1 = 1+1 = 2$$

Hence, there are effectively two atoms per unit cell; effectively one corner atom and one body center atom.

Case I When all the atoms are same

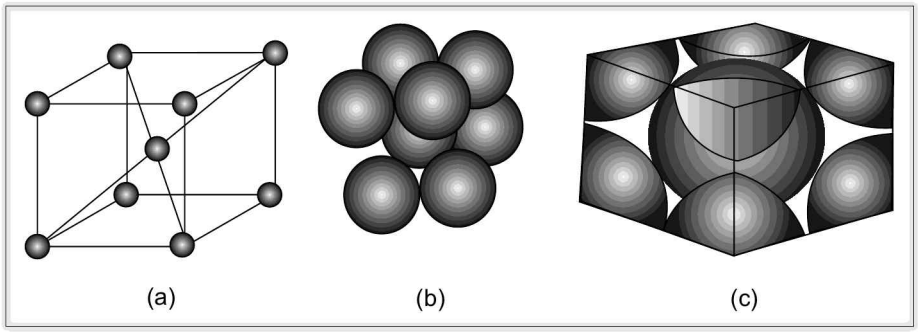


Fig. 11.15 A body-centered cubic unit cell (a) open structure (b) space-filling structure (c) actual portions of atoms belonging to one unit cell.

The atom at the body centre centre touches the spheres at the corners,

$\therefore$ Body diagonal, PS = 4r

Face diagonal $PR = \sqrt{PR^2 + QR^2} = \sqrt{2}a$

and Body diagonal $PS = \sqrt{PR^2 + RS^2} = \sqrt{2a^2 + a^2} = \sqrt{3}a$

Now, $\sqrt{3}a = 4r \Rightarrow a = \frac{4}{\sqrt{3}}r$, Volume of unit cell

$$= a^3 = \frac{64}{3\sqrt{3}}r^3$$

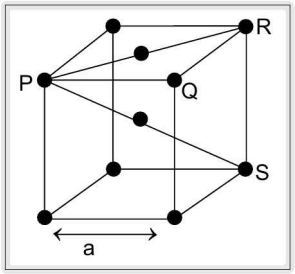


Fig. 11.16

Number of spheres per unit cell = $8 \times \frac{1}{8} + 1 \times 1 = 2$

Volume of two spheres = $2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi^3$

$\therefore$ Fraction occupied (or packing fraction) = $\frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}}r^3}$

= 0.68 or % occupied = 68%

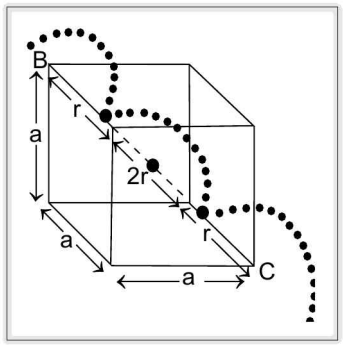


Fig. 11.17

Case II

When the body centred atom and the corner atoms are different,

$\overline{AB} = \sqrt{3a} = (2r^+ + 2r^-)$ ... (i)

Packing Fraction = $\frac{\left(\frac{4}{3}\pi r_C^3\right) + \left(\frac{4}{3}\pi r_a^3\right)}{a^3}$

r_c = radius of cation

r_a = radius of anion

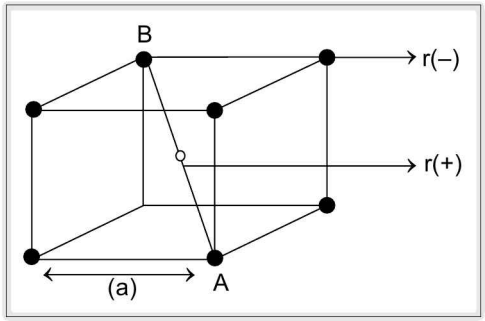


Fig. 11.18

Limiting condition or ideal condition:

$2r_{(-)} = a$ ....(ii)

i.e., Corner atoms are making a contact along the edge of a cube.
The limiting condition corresponds to the maximum stability.

So, $2r_{(-)max} = a$

Now from equation (i) we get,

$\sqrt{3a} = 2r_{(+)} + 2r_{(-)}$ Substitute value of 'a' from eq. (i)

$\sqrt{3}(2r_-) = 2r_{(+)} + 2r_{(-)}$

$2r_+ = 2r_- (\sqrt{3} - 1)$

$r_{(+)} = (\sqrt{3} - 1) r_{(-)}$

$\frac{r_+}{r_-} = 0.732$ Limiting radius ratio (min. value) in BCC

In general, $2r^- < a$ so the value of $\frac{r_\oplus}{r_-}$ in BCC will be as follows:

$$1 \geq \frac{r_+}{r_-} > 0.732$$

Packing Fraction = $\frac{\left(\frac{4}{3}\pi r_C^3\right) + \left(\frac{4}{3}\pi r_a^3\right)}{a^3} =$



For video lecture on this topic please go to http://wps.pearsoned.com/fundamentals of physical chemistry

Face centered Cubic Unit Cell (FCC Unit Cell)

A face centred cubic unit cell is said to be an ideal face centred cubic unit cell if:

(a) All the eight corners of the cube are occupied by the same atoms.
(b) All the six face of the cube are also occupied by same atoms as well as that atoms which are present at each corner of cube.
(c) Therefore, number of effective atoms in a unit cell

$$= \text{number of corner atoms } (n_c) \times \frac{1}{8} + \text{number of face centred atoms } (n_f) \times \frac{1}{2}$$

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$$

(d) Each corners atom are not in contact with each other but the face-centred atoms are in contact with the four spheres present at the four corners of a face. Each corner atom touches three spheres present at the face centre of adjoining faces.
(e) Also it is noted that all the six face centred atoms are in contact with each other.

Case I

When all atoms are same,

$$4r = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$\therefore$ Face diagonal of the cube $= 4r = \sqrt{2}a$

$$\therefore \quad r = \frac{\sqrt{2}}{4}a$$

$$\therefore \quad r = \frac{1}{2\sqrt{2}}\ a,$$

or $\quad a = 2\sqrt{2}\ r$

Therefore, volume of unit cell $= a^3 = (2\sqrt{2}r)^3$ and volume occupied by the spheres in the unit cell (If corner and face centred atoms are same)

$$= Z \times \text{volume of sphere} = 4 \times \frac{4}{3}\pi r^3$$

$$\text{Packing fraction (PF)} = \frac{\text{Volume occupied by the spheres in the unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{4 \times \frac{4}{3}\pi r^3}{\left(2\sqrt{2}r\right)^3} = 0.7406$$

$= 74.06\%$ space is occupied and 26% space is unoccupied

Case II

The face centred atoms and the corner atoms are different.

There are 3 face centred atoms (cation) and 1 corner (anion) atom in 1 unit.

$$\text{Packing Fraction} = \frac{3\left(\frac{4}{3}\pi r_+^3\right) + 1\left(\frac{4}{8}\pi r_-^3\right)}{a^3}$$

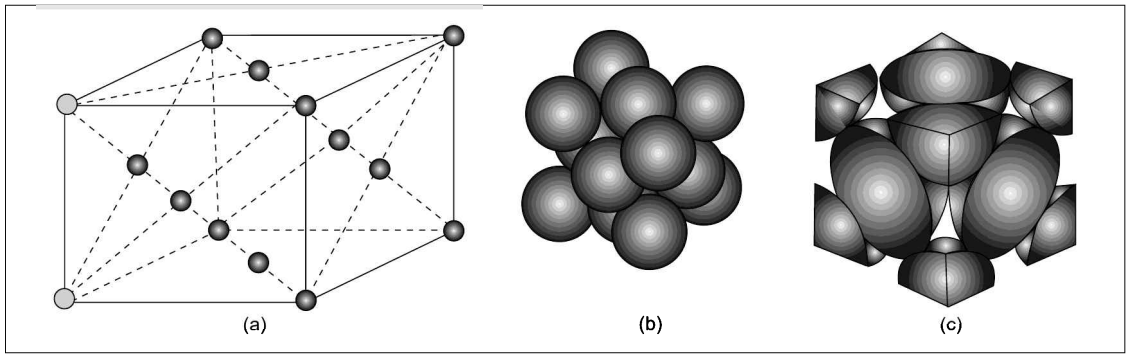


Fig. 11.19 A face-centred cubic unit cell (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell.

Limiting or Ideal Conditions

$$\overline{AB} = \sqrt{2}a = 2r_{(+)} + 2r_{(-)} \quad \text{(i)}$$

a = edge length

Corner atoms are making contact along the edge of the cubes.

$$2r_{(-)} = a \quad \text{.....(ii)}$$

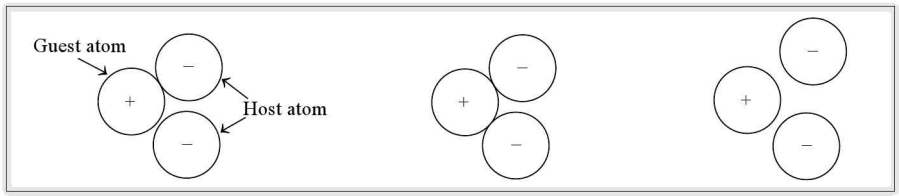
On substituting maximum radius value of anion (r^-) in (i)

Question: Explain why uncharged atoms or molecules never crystallize in simple cubic structures.

Answer: Uncharged atoms and molecules pack more efficien ly in closest-packed structures.

Voids or Interstitial Site

Vacant space in the crystal lattice is called void. It is made up of host atoms (bigger) atoms which is usually an anion. Small sized atoms are occupied in these voids. Sometimes an impurity atom can be present in a void, which is called guest atom or foreign atom. The guest atom must make a contact with host atom, but host atom may or may not make contact with each other. Example, In case II, we get the limiting radius ratio, which corresponds to the minimum value.



Host atoms are not in contact

I

Host atoms are not in contact

II

Host and guest atoms are not in contact i.e., guest atom will not be packed

III

Fig. 11.20

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Solid State: Voids

Void: It is the empty space surrounded by other atoms. We will discuss two types of voids:

1. Octahedral Voids
2. Tetrahedral Voids

These voids are not present in primitive or B.C.C. These are present in f.c.c. and h.c.p

Octahedral Voids

It is vacant position surrounded octahedrally by six other atoms.

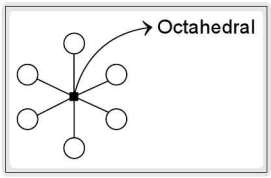


Fig .11.21

- The mid of the edges and the body centre position of f.c.c are the positions of octahedral voids. Octahedral voids in mid of the edge is created the four face centre atoms corner atoms.

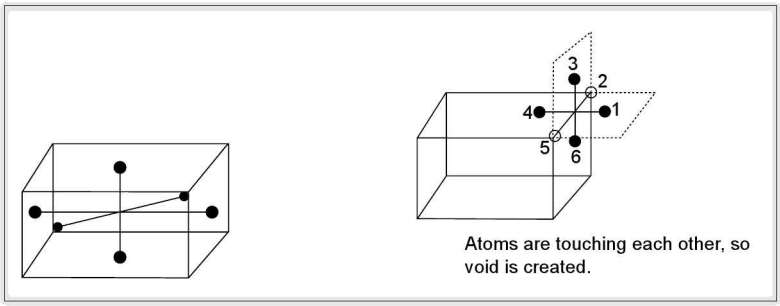


Fig .11.22

No. of octahedral void per $\text{f.c.c.} = \frac{n_e}{4} + n_b = \frac{12}{4} + 1 = 4$ HCP

No. of octahedral void per f.c.c. = Rank of unit cell edge

The above relation holds true for hcp and fcc because this is independent of geometry of unit cell. Hence body centre is the 25% of total octahedral voids

Tetrahedral Void

It is vacant space surrounded tetrahedrally by four atoms.

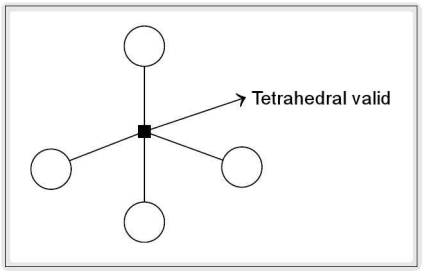


Fig .11.23

If the atoms are placed at the alternate corners on the opposite faces of a cube, the body centre of the cube becomes the position of tetrahedral void. Atoms should only be at alternate corners. No other atom should be present.

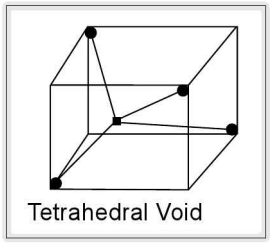


Fig .11.24

The body centre of smaller cube is tetrahedral void for larger cube. It is surrounded by three face centre atoms (of bigger cube) and one corner atom.

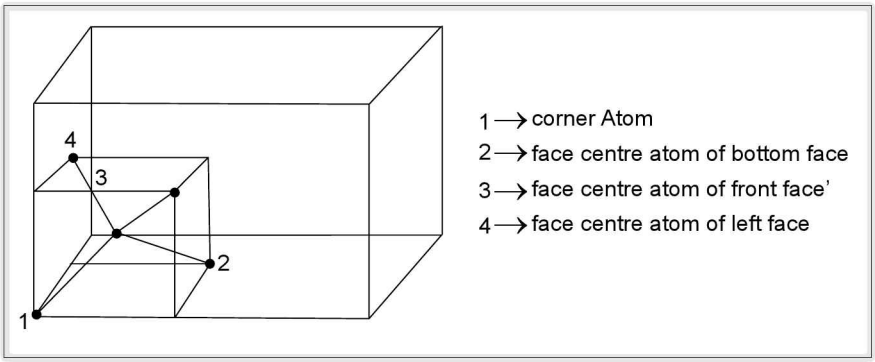


Fig .11.25

No. of smaller cube in one bigger cube = 8
∴ No. of tetrahedral voids per f.c.c. = 8

Tetrahedral = 2x octahedral Voids

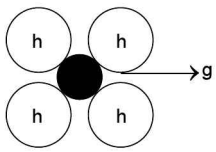
Guest Atom and Host Atom

The atoms forming the voids are called HOST atoms the atoms present in the voids are called GUEST atoms.

Radius ratio of Guest Atom Host Atom for Octahedral Void

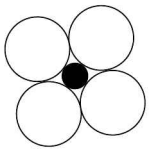
Let us consider that r_+ is the radius of guest atom and r_- is the radius of host atom.
The following criterion should be satisfied for the guest-host occupation

Case I



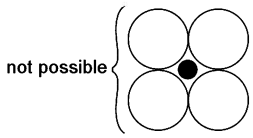
host – host contact ×
guest – host contact ✓must

Case II



host – host contact ✓
guest – host contact ✓
Limiting condition

Case III



host – host contact ✓
guest – host contact ×

The guest and host atoms must touch each other but the host atoms may or may not touch each other. Hence case I and case II are possible but case III is not possible.

Calculation of radius ratio of guest to host atoms for octahedral void

The radius ratio is calculated assuming the limiting condition

$a = 2r_+ + 2r_-$ (for g – h contact)

$\sqrt{2}a = 4r_-$ for fcc.

↓

length of face diagonal

$$2\sqrt{2}r_- = 2r_- + 2r_+$$

$$\frac{r_+}{r_-} = \sqrt{2} - 1$$

$$= 0.414$$

$$\frac{r_g}{r_h} \geq 0.414$$

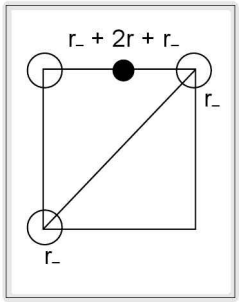


Fig .11.26

Calculation of limiting radius ratio of guest to host atoms for tetrahedral void

$r_g + r_h$ = Half of body diagonal of smaller cube

$$= \frac{1}{4} \text{ of body diagonal of larger cube}$$

$$r_h + r_g = \frac{\sqrt{3}a}{4}$$

$4r_h = \sqrt{2}a$ ... for fcc

$$r_h + r_g = \frac{\sqrt{3}}{4} \cdot \frac{4r_h}{\sqrt{2}}$$

$$\frac{r_g}{r_h} = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.732 - 1.414}{1.414}$$

$$0.414 > \frac{r_g}{r_h} \geq 0.225$$

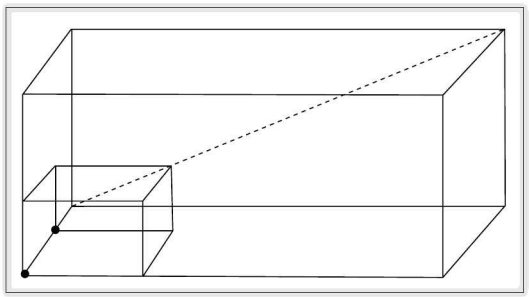


Fig .11.27

The limiting radius ratio will be independent of the geometry of unit cell or for the crystal system.

Effective number of octahedral void per unit cell = Rank of that unit cell

and

Effective number of tetrahedral voids = 2 × (effective number of octahedral voids)

Close Packing of Spheres

To begin with we shall think about crystals being built from one kind of atom only. We shall represent an atom by a ball. (In model making, polystyrene balls are very useful; marbles will do but they are not so good.) If you pack a number of balls closely together, you will find that they are most likely to line up 11.28. Here, except at the edges, there are always six balls arranged in the shape of a hexagon around a ball in the centre of the hexagon. This type of packing is called hexagonal close packing. It is impossible to squeeze a greater number of balls into the same area. We can imagine a layer like this being made as the first step when real atoms come together to make a crystal



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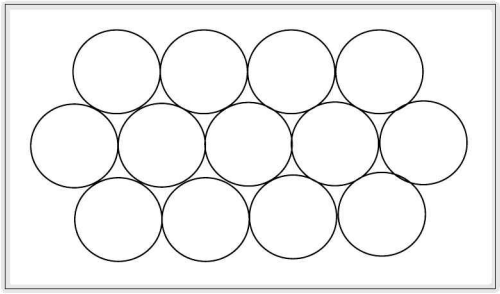


Fig. 11.28 'A' layer of spheres.

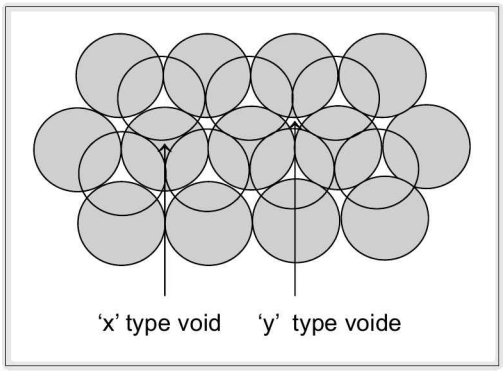


Fig. 11.29 'A' and B' layer of sphere.

If we imagine more atoms beginning to cling to the first layer they will drop into the small gaps where atoms in the first layer meet (Figure.11.29). Now we can place a third layer on top. However, there are two ways of doing this. Either the atoms in the third layer can fit so that they are directly above the first layer, or they can go on so that they are only partly above the first layer. In the first case the layers build up in pairs, usually known as the ABAB... structure (Figure 11.29). Here the third layer is directly above the first, the fourth directly above the second. The alternative structure is called ABCABC. (Figure 11.30). Here the pattern repeats every fourth layer; the fourth is above the first, the fifth above the second, the sixth above the third, and so on. The three-dimensional arrangement of the atoms is called a lattice. In both lattices, the layers are close-packed: there is the minimum amount of free space in between.

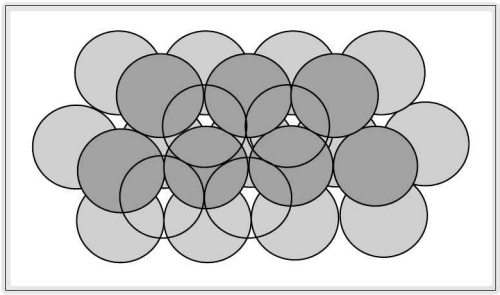


Fig. 11.30 'A' and 'B' and 'C' layer of spheres

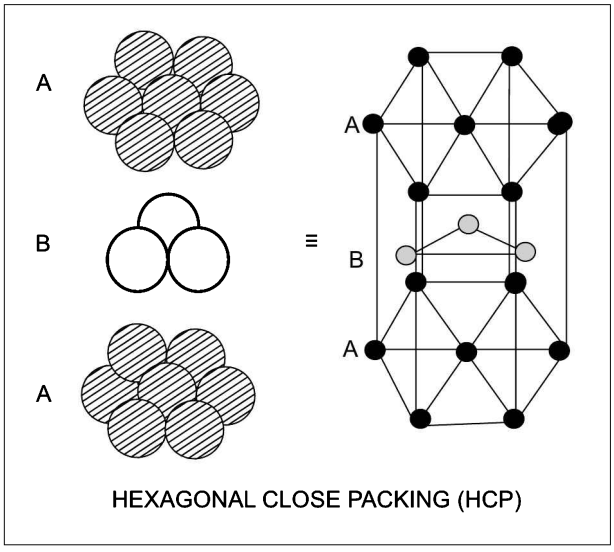


Fig. 11.31

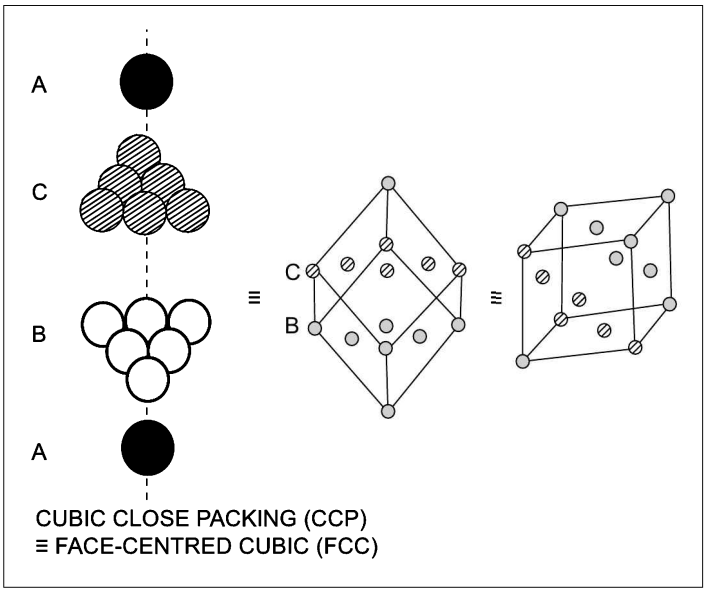


Fig. 11.32

Radius ratio rules

The structure of many ionic solids can be accounted for by considering the relative sizes of the positive and negative ions, and their relative numbers. Simple geometric calculations allow us to workout as to how many ions of a given size can be in contact with a smaller ion. Thus, we can predict the co-ordination number from the relative sizes of the ions.

Calculation of some limiting radius ratio values

(i) ***Co-ordination number 3:*** The adjacent figure shows the smaller positive ion of radius r^+ in contact with three larger negative ions of radii r^-. It can be seen that AB = BC = AC = $2r^-$, BE = $r^- + r^+$. Further, the angle ABC is 60°, and the angle DBE is 30°. By trigonometry, cos 30° = (BE/BD).

$$BD = (BE/\cos 30^\circ),\ r^+ + r^- = r^-/\cos 30^\circ$$
$$= (r^-/0.866) = r^- \times 1.55,\ r^+ = (1.155\ r^-) - r^-$$
$$= 0.155\ r^-,\ \text{Hence}\ (r^+/r^-) = 0.155.$$

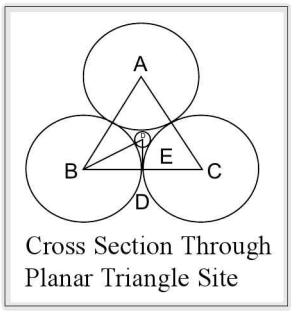


Fig. 11.33

(ii) ***Co-ordination number 4 (tetrahedron):*** Angle ABC is the tetrahedral angle of 109° 28' and hence the angle ABD is half of this, that is 54° 44'. In the triangle ABD, sin ABD = 0.8164 = AD/AB = $\frac{r^-}{r^+ + r^-}$. Taking reciprocals, $\frac{r^+ + r^-}{r^-} = \frac{1}{0.8164} = 1.225$, rearranging, we get, $\frac{r^+}{r^-} = 0.225$.

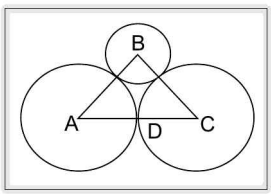


Fig. 11.34

(iii) ***Co-ordination number 6 or 4 (octahedron or square planer):***
A cross section through an octahedral site is shown in the adjacent figure and the smaller positive ion (of radius r^+) touches six larger negative ions (of radius r^-). (Note that only four negative ions are shown in this section and one is above and one below the plane of the paper). It is obvious that $AB = r^+ + r^-$ and $BD = r^-$. The angle ABC is 45° in the triangle ABD. cos ABD = 0.7071 = (BD/AB) = $\frac{r^-}{r^+ + r^-}$. Rearranging, $\frac{r^+}{r^-} = 0.414$.

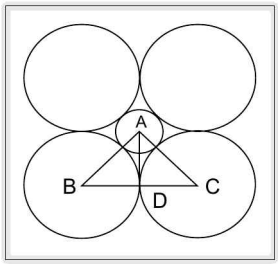


Fig. 11.35

Limiting radius ratio $\frac{r^+}{r^-}$	***Co-ordination number***	***Shape***	***Example***
< 0.155	2	Linear	BeF_2
0.155 – 0.225	3	Planar Triangle	-
0.225 – 0.414	4	Tetrahedron	ZnS
0.414 – 0.732	4	Square planar	$PtCl_4^{2-}$
0.414 – 0.732	6	Octahedron	NaCl
0.732 – 0.999	8	Body centered cubic Type	CsCl

Metal crystals

Metals usually crystallise in one of three forms: body centred cubic, hexagonal close-packed, or cubic close-packed (face centred cubic). You will find examples in Figure 1.36.

Although metals are by far the most common examples, some other substances take up the same structures. For example, the molecules in solid hydrogen and nitrogen take up hexagonal close-packed structures. Many of the noble gases exist as cubic close-packed structures when they are solidified, as does methane.

Perfect crystals, which have the same orderly arrangement of atoms throughout the lattice, are hard to make. Usually crystals contain defects. Two common defects occur when atoms are missing from their positions in the lattice, or when extra atoms become trapped, causing the symmetry of the lattice to change. The photo illustrates the types of change that can happen.

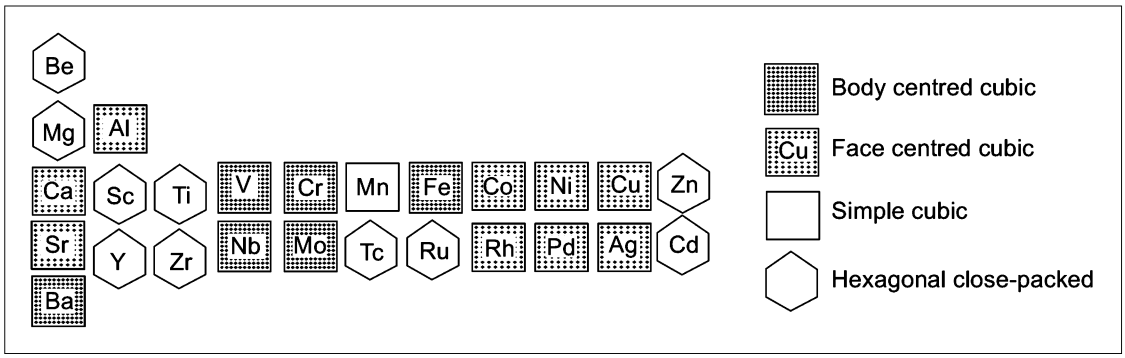


Fig. 11.36

A third defect that is often found is produced when atoms of an impurity are trapped in the lattice. it can be most useful. Indeed, in many industrial processes, impurities are added deliberately because they can change the properties of a metal. Perfect crystals often suffer from the layers sliding over one another. This can happen gradually, example in the stretching of a metal wire, or suddenly, example if cast iron is dropped and shatters. If impurity atoms find sites where they can fit into the lattice, it can become much harder for the layers to slide over one another.

Classification of ionic structures

In the following structures, a black circle would denote a cation and a white circle would denote an anion. In any solid of the type A_xB_y, the ratio of the coordination number of A to that of B would be y : x.



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Rock salt structure

Cl^- is forming a fcc unit cell in which Na^+ is in the octahedral voids. The coordination number of Na^+ is 6 and therefore that of Cl^- would also be 6. Moreover, there are 4 Na^+ ions and 4 Cl^- ions per unit cell. The formula is Na_4Cl_4 i.e., NaCl. The other substances having this kind of a structure are halides of all alkali metals except cesium halides and oxides of all alkaline earth metals except beryllium oxide.

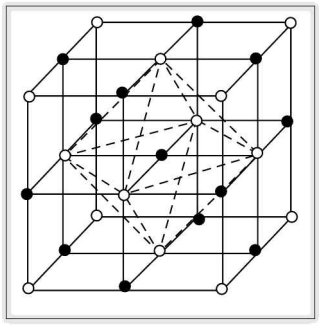


Fig. 11.37 Unit cell structure of NaCl

Zinc blende structure

Sulphide ions are face centered and Zinc is present in alternate tetrahedral voids. Formula is Zn_4S_4, i.e., ZnS. Coordination number of Zn is 4 and that of sulphide is also 4. Other substance that exists in this kind of a structure is BeO.

Fluorite structures

Calcium ions are face centered and fluoride ions are present in all the tetrahedral voids. There are four calcium ions and eight fluoride ions per unit cell. Therefore, the formula is Ca_4F_8, (i.e., CaF_2). The coordination number of fluoride ions is four (tetrahedral voids) and thus the coordination number of calcium ions is eight. Other substances which exist in this kind of structure are UO_2, and ThO_2.

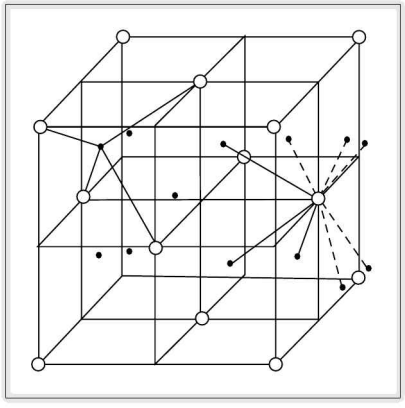


Fig. 11.38 Unit cell representation of CaF_2 structure

Anti-fluorite structure

Oxide ions are face centered and lithium ions are present in all the tetrahedral voids. There are four oxide ions and eight lithium ions per unit cell. As it can be seen, this unit cell is just the reverse of Fluorite structure, in the sense that, the positions of cations and anions is interchanged. Other substances which exist in this kind of a structure are Na_2O, K_2O and Rb_2O.

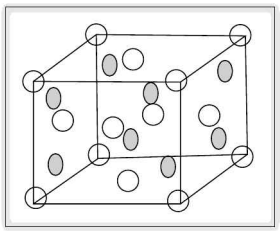


Fig. 11.39 Anti-fluorite structure

Cesium halide structure

Chloride ions are primitive cubic while the cesium ion occupies the center of the unit cell. There is one chloride ion and one cesium ion per unit cell. Therefore the formula is CsCl. The coordination number of cesium is eight and that of chloride ions is also eight. Other substances which exist in this kind of a structure are all halides of cesium.

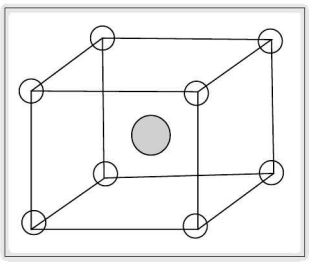


Fig. 11.40 Cesium halide structure

Corundum structure

The general formula of compounds crystallizing in corundum structure is Al_2O_3. The closest packing is that of anions (oxide) in hexagonal primitive lattice and two-third of the octahedral voids are filled with trivalent cations. Examples are: Fe_2O_3, Al_2O_3 and Cr_2O_3.

Pervoskite structure

The general formula is ABO_3. One of the cation is bivalent and the other is tetravalent. Example: $CaTiO_3$, $BaTiO_3$. The bivalent ions are present in primitive cubic lattice with oxide ions on the centers of all the six square faces. The tetravalent cation is in the center of the unit cell occupying octahedral void.

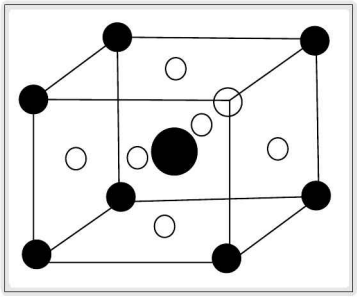


Fig. 11.41 Pervoskite structure

Example of Pervoskite Structure (Barium Titanate)

Barium ion is placed at the corner of cube and oxide ion at the face centre and Ti^{+4} at the body centre in octahedral void. FCC structure is made up of O^{-2} and Ba^{+2} ion. Its packing fraction is 63.8%. Ti^{+4} is present at the centre of body.

$$Ba^{+2} = \frac{1}{8} \times 8 = 1$$

$$O^{-2} = \frac{1}{2} \times 6 = 3$$

Ti^{+4} = one

Formula $BaTiO_3$

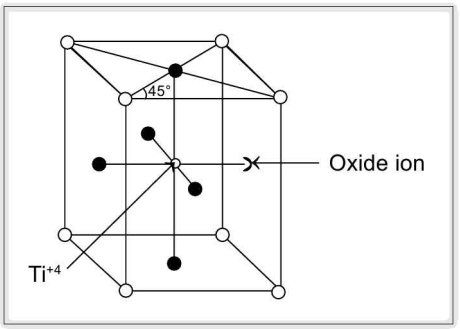


Fig. 11.42

Ti^{+4} is surrounded six O^{-2} ions arranged in octahedral form, so its co-ordination number is 6.

$$\frac{r_{Ti^{+4}}}{r_{O^{-2}}} = 0.414 \text{ (for octahedral void.)} \qquad \ldots..(1)$$

Oxide ion is surrounded by four Barium ion and two Ti^{+4} ion again in octahedral form.

$$\frac{r_{O^{-2}}}{r_{Ba^{+2}}} = 0.414$$

$$r_{O^{-2}} = 0.414 \times r_{Ba^{+2}}$$

Substitute this value in equation (1)

$$r_{Ti^{+4}} = 0.414 \times r_{O^{-2}}$$

$$r_{Ti^{+4}} = 0.414 \times 0.414 \times r_{Ba^{+2}}$$

$$\frac{r_{Ti^{+4}}}{r_{Be^{+2}}} = (0.414)^2$$

Under limiting condition when corner atoms are assumed to touch each other

$$A = 2r_{Ba^{+2}}$$

$$P.F. = \frac{4}{3}\pi \frac{(r_{Ba^{+2}})^3 + (r_{Ti^{+4}})^4 + 3 \times (r_{O^{-2}})^3}{8(r_{Ba^{+2}})^3}$$

$$= \frac{\pi}{6}\left[\left(\frac{r_{Ba^{+2}}}{r_{Ba^{+2}}}\right)^3 + \left(\frac{r_{Ti^{+4}}}{r_{Ba^{+2}}}\right)^3 + \left(\frac{r_{O^{-2}}}{r_{Ba^{+2}}}\right)^3\right]$$

$$= \frac{\pi}{6}[1+(0.414)^6 + (0.414)^3]$$

$$= 0.56 \quad \text{or} \quad 56\%$$

Diamond structure

Only those atoms which form four covalent bonds produce a repetitive three dimensional structure using only covalent bonds, e.g., diamond structure. The latter is based on a face-centred cubic lattice where four out of the eight tetrahedral holes are occupied by carbon atoms. Every atom in this structure is surrounded tetrahedrally by four others. No discrete molecule can be discerned in diamond. The entire crystal is a giant molecule, a unit cell of which is fig. 11.43. Germanium, silicon and grey tin also crystallize in the same way as diamond.

Void volume in diamond crystal

From Fig. 11.38, we observe that

$^{d}C—C$ bond $= 2r_e$, where r_e is the radius of sphere representing carbon

$\angle C - C - C = 109° 28'$

Diagonal face of the cube $= \sqrt{2}\, a$

This distance will be equal to four times the distance d_{C-C} sin (54° 44'), that is

$$4d_{C-C} \sin (54° 44') = \sqrt{2}\, a$$

$$\text{or} \quad a = \frac{4d_{C-C} \sin (54° 44')}{\sqrt{2}}$$

$$\text{Area of the cube} = a^3 = \left\{\frac{4d_{C-C} \sin(54°44')}{\sqrt{2}}\right\}^3$$

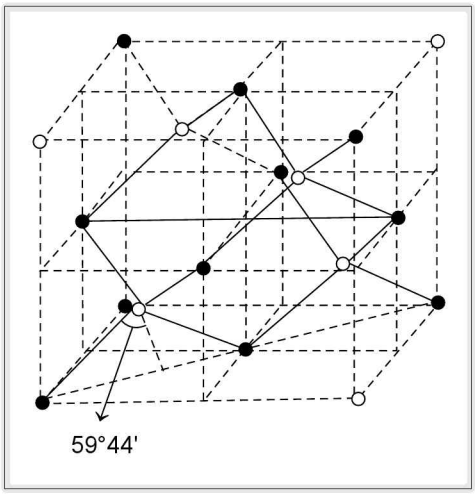


Fig. 11.43 A unit cell of diamond crystal

Total number of carbon atoms/unit cell = 8

$$\text{Volume occupied by 8 carbon} = 8\left(\frac{4}{3}\pi r_C^3\right) = \frac{4}{3}\pi(d_{C-C})^3$$

$$\text{Fraction of volume occupied} = \frac{\frac{4}{3}\pi(d_{C-C})^3}{\left\{\frac{4d_{C-C} \sin(54°44')}{\sqrt{2}}\right\}^3} = 0.34$$

Spinel structure

Spinel is a mineral $MgAl_2O_4$ having general formula MM'_2O_4, where divalent ions are occupied in tetrahedral void and trivalent ions in octahedral void and lattice is mae up of oxide ion. Only 1/8 tetrahedral and $\frac{1}{2}$ of the octahedral voids are occupied. M^{2+} is usually Mg, Fe, Co, Ni, Zn and Mn; M^{3+} is generally Al, Fe, Mn, Cr and Rh. Examples are $ZnAl_2O_4$, Fe_3O_4, $FeCr_2O_4$ etc. Many substances of the type $M^{4+}M_2^{2+}O_4$ also have this structure.

$$\frac{r_{Al^{+3}}}{r_{O^{-2}}} = 0.414 \qquad \frac{r_{Mg^{+2}}}{r_{O^{-2}}} = 0.225$$

$$\text{P.F.} = \frac{\frac{4}{3}\pi\left[2\times\left(r_{Al^{+3}}\right)^3 + \left(r_{Mg^{+2}}\right)^3 + \left(4r_{O^{-2}}\right)^3\right]}{a^3}$$

As oxide ions are arranged in FCC pattern and under limiting condition will touch to each other.

Face diagonal $\sqrt{2}\ a = 4r_{O^{-2}}$

$$a = 2\sqrt{2}\ r_{O^{-2}}$$

$$F = \frac{4}{3}\pi\left[\frac{2\times(0.414)^3 + (0.225)^3 + 4}{(2\sqrt{2})^3}\right] = 0.768 \text{ or } 76.8\%$$

Inverse spinel (Fe_3O_4 type)

In this type of structure Fe^{2+} ions are present in octahedral and Fe^{3+} are equally distributed in tetrahedral and octahedral voids. (i.e., one in each void)

Example Fe_3O_4, $MgFe_2O_2$

$4\,r_{oxide} = \sqrt{2}\ a$ (Face diagonal)

$\frac{r_{Fe^{+2}}}{r_{O^{-2}}} = 0.225$ (tetrahedral void)

$\frac{r_{Fe^{+3}}}{r_{O^{-2}}} = 0.414$ (octahedral void)

$$\text{Packing fraction} = \frac{\text{Volume occupied by all cation and anion}}{a^3}$$

i.e.,

$$= \frac{(\sqrt{2})^3}{4^3}\times\frac{4}{3}\pi\left[\left(\frac{r_{Fe^{+2}}}{r_{oxide}}\right)^3 + \left(\frac{r_{Fe^{+3}}}{r_{oxide}}\right)^3 + \left(\frac{r_{Fe^{+3}}}{r_{oxide}}\right)^3 + 4\right]$$

$$= \frac{2\sqrt{2}}{(4)^2}\times\frac{\pi}{3}[(0.414)^3 + (0.225)^3 + (0.414)^3 + 4]$$

$$= 0.185 \times 4.15$$

$$= 0.768 \qquad \text{(i.e., 76.8\% space is occupied)}$$

Hexagonal Primitive Unit Cell

Rank of unit cell:

It is the effective number of atoms present in the unit cell. It is represented by Z.

n_c = number of corner atoms

n_r = number of face atoms

n_b = number of body atoms (inside the cell)

n_e = number of edge atoms (vertical edges)

rank for hexagonal cell = $\frac{n_C}{6}+\frac{n_f}{2}+\frac{n_e}{3}+n_b$

Each corner atom would be common to 6 other unit cells, therefore their contribution to one unit cell would be 1/6. Therefore, the total number of atoms present per unit cell effectively is 6.

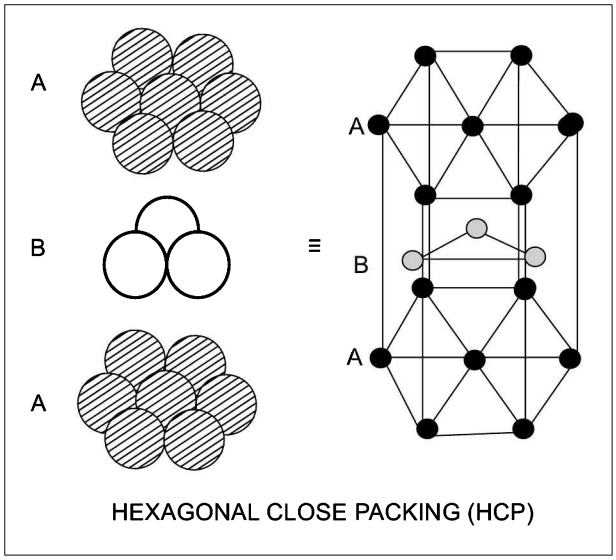


Fig. 11.44 (a)

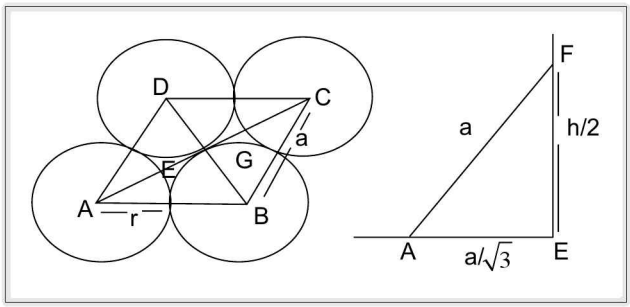


Fig. 11.44 (b)

ABCD is the base of hexagonal unit cell AD = AB = a. The sphere in the next layer has its centre F vertically above E and it touches the three spheres whose centres are A,B and D.

$\therefore \quad AE = \frac{2}{3}\times\frac{\sqrt{3}}{2}a = \frac{a}{\sqrt{3}} = \frac{2r}{\sqrt{3}}$

Hence, $\quad FE = \frac{h}{2} = \sqrt{(2r)^2-\left(\frac{2r}{\sqrt{3}}\right)^2}$

$\therefore$ The height of unit cell (h) = $4r\sqrt{\frac{2}{3}}$

The area of the base is equal to the area of six equilateral triangles, $= 6\times\frac{\sqrt{3}}{4}(2r)^2$. The volume of the unit cell $= 6\times\frac{\sqrt{3}}{4}(2r)^2\times 4r\sqrt{\frac{2}{3}}$.

$$\text{Therefore, PF} = \frac{6\times\frac{4}{3}\pi r^3}{6\times\frac{\sqrt{3}}{4}(2r)^2\times 4r\sqrt{\frac{2}{3}}}$$

$$= 0.74 \quad \therefore \text{VF} \approx 0.26$$

Density of crystal lattice

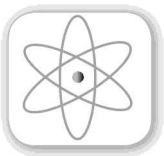
The density of crystal lattice is same as the density of the unit cell which is calculated as,

$$\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

$$= \frac{\text{number of effective atoms}}{\text{volume of unit cell}}$$

$$\rho = \frac{n\times M}{N_A\times V}$$

WHAT IS SOLID DEFECT



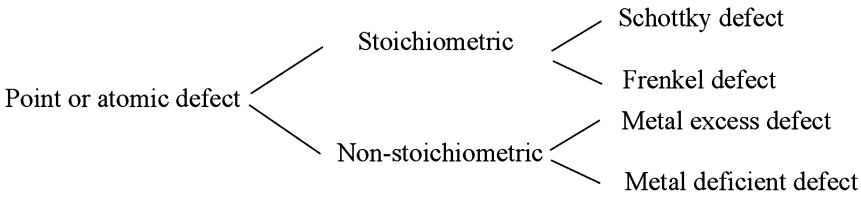
At absolute zero, crystals tend to have perfectly order arrangement. At any temperature above 0 K, the crystals have some departure from complete ordered arrangement. This constitutes a disorder or a defect in solid.

Types of Solid Defect

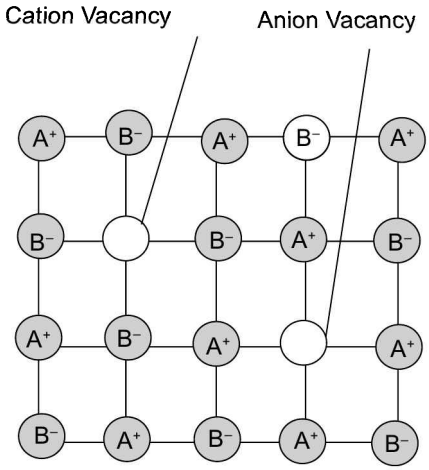
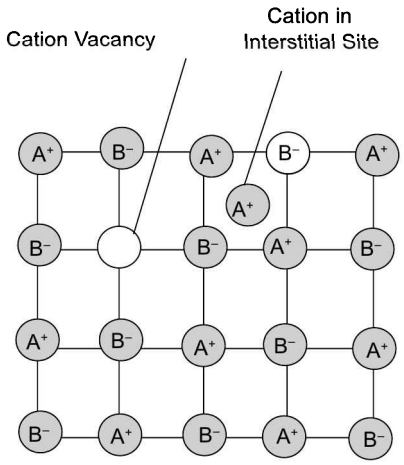
1. Electronic defect
2. Point or atomic defect
   - Stoichiometric
     - Schottky defect
     - Frenkel defect
   - Non-stoichiometric
     - metal excess defect
     - metal deficient defect

1. **Electronic imperfection:** At 0 K, perfectly ionic or covalent crystal have electron in the fully occupied lowest energy state, But at higher temperature some of the e^- may occupy higher energy state. As a result of this free e^- and holes are created in the crystal and causes to electronic imperfection and also responsible for electrical conductance.
2. **Point or Atomic defect:** The defect which arise due to the irregularity in the arrangement of atoms or ions are called point or atomic defect.
   Cause of point defect: As the temperature increases, the amount of thermal vibration of ions in their lattice sites increases, and if the vibration of a particular ion becomes large enough, it may jump out of its lattice site. This constitutes vacancies. The higher the temperature, the greater the chance that lattice sites may be unoccupied. Since the number of defects depends on the temperature, they are sometimes called thermodynamic defects.

Type of point defect



Stoichiometric Defects: Stoichiometric compounds are those where the numbers of the different types of atoms or ions present are exactly in the ratios indicated by their chemical formulae. They obey the law of constant composition.

Schotty Defect	***Frenkel Defect***
1. It consists of a pair of 'holes' in the crystal lattice. One positive and one negative ion are absent from there normal lattic sites.	1. It arises when an ion (cation) is missing from its normal position (creating a hole) and occupies an interstitial site between the lattice points.
 **Fig. 11.45**	 **Fig. 11.46**
2. It is generally shown by ionic solids having high co-ordination number (usually 8 or 6) and in which cations and anions are of equal sizes. Example, NaCl, CsCl.	2. It is generally exhibited by ionic solids having low co-ordination number (4 or 6) and in which anions are larger in size than cations. Example AgCl, ZnS. **Note:** Since small positive ions are highly polarizing and large negative ions are readily polarized, these compounds have some covalent character.
3. This defect lowers the density of crystal.	3. It does not affect the density of the crystal.
4. Number of Schottky defects formed per cm^3(n_s) is given by $$n_s = N \exp\left(-\frac{W_s}{2kT}\right)$$ where N → number of sites per cm^3 that could be left vacant. W_s → work necessary to form a Schottky defect. k → gas constant T → absolute temperature	4. Number of Frenkel defects formed per cm^3(n_s) is given by $$n_s = \sqrt{NN'} \exp\left(-\frac{W_f}{2kT}\right)$$ where N → number of sites per cm^3 that could be left vacant. N′ → number of alternative interstitial positions per cm^3 W_f → work necessary to form a Frenkel defect. k → gas constant T → absolute temperature

NONSTOICHIOMETRIC DEFECTS

Non-stoichiometric or Berthollide compounds — The ratio of the number of atoms of one kind to the number of atoms of the other kind does not correspond exactly to the ideal whole number ratio implied by the formula. Such compounds do not obey the law of constant composition.

FeO, FeS or CuS the ratio of Fe : O, Fe : S or Cu : S differs from that indicated by the ideal chemical formula. If the ratio of atoms is not exactly 1 : 1 in the above cases, there must be either an excess of metal ions, or a deficiency of metal ions (example $Fe_{0.84}O$ – $Fe_{0.94}O$, $Fe_{0.9}S$). Electrical neutrality is maintained either by having extra electrons in the structure, or changing the charge on some of the metal ions.

Meal Excess

This may occur in two different ways:

F-centres

A negative ion may be absent from its lattice site, leaving a 'hole' which is occupied by an electron, thereby maintaining the electrical balance (see fig.). When compounds such as NaCl, KCl, LiH or δ-TiO are heated with excess of their constituent metal vapours, or treated with high energy radiation, they become deficient in the negative ions, and their formulae may be represented by $AX_{1-\delta}$, where δ is a small fraction. The nonstoichiometric form of NaCl is yellow, and the nonstoichiometric form of KCl is blue-lilac in colour.

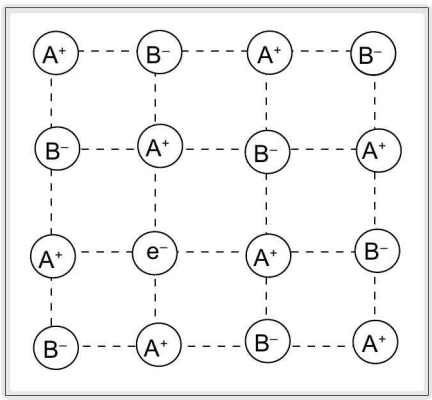


Fig. 11.47

Note the similarity with the flame colorations for Na and K.

Anion sites occupied by electrons in this way are called F-centres. F-centres are associated with the colour of the compound and the more F-centres present, the greater the intensity of the coloration. Solids containing F-centres are paramagnetic, because the electrons occupying the vacant sites are unpaired. When electrons in the F-centres absorb sufficient light (or heat) energy, the electron is promoted into a conduction band, rather similar to the conduction bands present in metals. Since conduction is by electrons it is n-type semiconduction.

Interstitial ions and electrons

Metal excess defects also occur when an extra positive ion occupies an interstitial position in the lattice, and electrical neutrality is maintained by the inclusion of an interstitial electron (see Fig.). Their composition may be represented by the general formula $A_{1+\delta}X$.

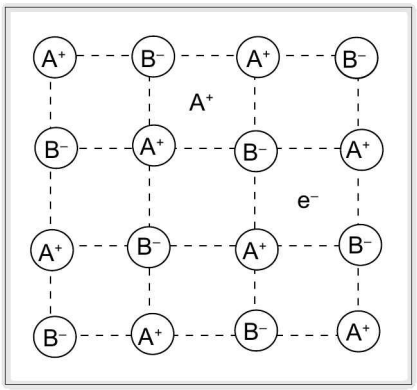


Fig. 11.48

Examples include ZnO, CdO, Fe_2O_3 and Cr_2O_3.

Crystals with either type of metal excess defect contain free electrons called semi-conductors and these are called n-type semiconductors.

Metal deficiency

Metal-deficient compounds may be represented by the general formula $A_{1-\delta}X$. In principal, metal deficiency can occur in two ways. Both require variable valency of the metal, and might therefore be expected with the transition metals.

Suppose the lattice contains A^+ and A^{2+} metal ions. If an electron 'hops' from an A^+ ion to the positive centre (an A^{2+} ion), the original A^+ becomes a new positive centre. There has been an apparent movement of A^{2+}. With a series of similar 'hops', an electron may be transferred in one direction across the structure, and at the same time the positive hole migrates in the opposite direction across the structure. This is called positive hole, or p-type semiconduction.

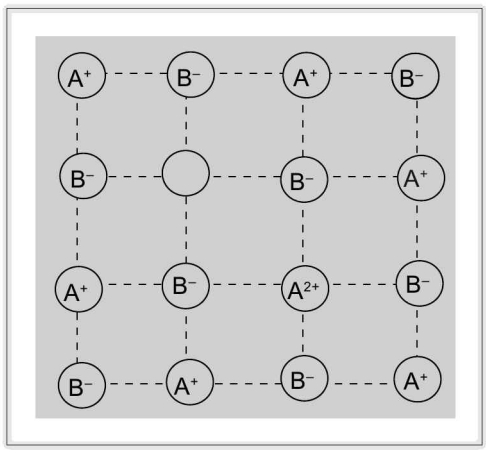


Fig. 11.49

Extra interstitial negative ions

In principal, it might be possible to have an extra negative ion in an interstitial position and to balance the charges by means of an extra charge on an adjacent metal ion. However, since negative ions are usually large, it would be difficult to fit them into interstitial positions. No examples of crystals containing such negative interstitial ions are known at present.

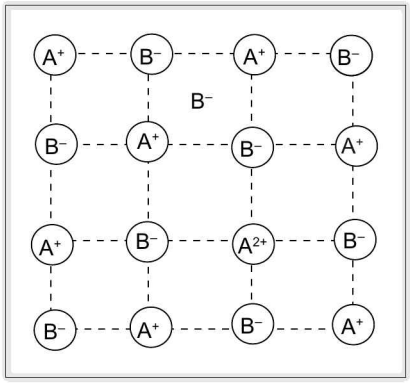


Fig. 11.50

Magnetic fields and forces

The phenomenon of magnetism is "mediated" by the magnetic field. An electric current or magnetic dipole creates a magnetic field, and that field, in turn, imparts magnetic forces on other particles that are in the fields.

Maxwell's equations (which simplify to the Biot-Savart law in the case of steady currents) describe the origin and behaviour of the fields that govern these forces. Therefore, magnetism is seen whenever electrically charged particles are in motion—for example, from movement of electrons in an electric current, or in certain cases from the orbital motion of electrons around an atom's nucleus. They also arise from "intrinsic" magnetic dipoles arising from quantum-mechanical spin.

The same situations that create magnetic fields (charge moving in a current or in an atom, and intrinsic magnetic dipoles) are also the situations in which a magnetic field has an effect, creating a force. Following is the formula for moving charge; for the forces on an intrinsic dipole.

When a charged particle moves through a magnetic field **B**, it feels a force **F** given by the cross product: where,

$$F = qv \times B,$$

q is the electric charge of the particle,

v is the velocity vector of the particle, and

B is the magnetic field.

Because this is a cross product, the force is perpendicular to both the motion of the particle and the magnetic field. It follows that the magnetic force does no work on the particle; it may change the direction of the particle's movement, but it cannot cause it to speed up or slow down. The magnitude of the force is where θ is the angle between **v** and **B**.

One tool for determining the direction of the velocity vector of a moving charge, the magnetic field, and the force exerted is labeling the index finge "V", the middle finge "B", and the thumb "F" with your right hand. When making a gun-like configuration (with the middle finger crossing under the index finger), the finger represent the velocity vector, magnetic field vecto , and force vector, respectively. See also right hand rule.

Magnetic dipoles

A very common source of magnetic field shown in nature is a dipole, with a "South pole" and a "North pole," terms dating back to the use of magnets as compasses, interacting with the Earth's magnetic fiel to indicate North and South on the globe. Since opposite ends of magnets are attracted, the north pole of a magnet is attracted to the south pole of another magnet. The Earth's North Magnetic Pole (currently in the Arctic Ocean, north of Canada) is physically a south pole, as it attracts the north pole of a compass.

A magnetic field contains energy, and physical systems move toward configurations with lower energy. When diamagnetic material is placed in a magnetic field, a **magnetic dipole** tends to align itself

in opposed polarity to that field, thereby lowering the net field strength. When ferromagnetic material is placed within a magnetic field, the magnetic dipoles align to the applied field, thus expanding the domain walls of the magnetic domains. For instance, two identical bar magnets placed side-to-side normally line up North to South (because the magnetic field lines are aligned), resulting in a much smaller net magnetic field (external to the magnet), and resist any attempts to reorient them to point in the same direction. The energy required to reorient them in that configuration is then stored in the resulting magnetic field, which is double the strength of the field of each individual magnet. (This is, of course, why a magnet used as a compass interacts with the Earth's magnetic field to indicate North and South).

An alternative, equivalent formulation, which is often easier to apply but perhaps offers less insight, is that a magnetic dipole in a magnetic field experiences a torque and a force that can be expressed in terms of the field and the strength of the dipole (i.e., its magnetic dipole moment). For these equations, see magnetic dipole and magnetic monopoles.

Since a bar magnet gets its ferromagnetism from electrons distributed evenly throughout the bar, when a bar magnet is cut in half, each of the resulting pieces is a smaller bar magnet. Even though a magnet is said to have a north pole and a south pole, these two poles cannot be separated from each other. A monopole—if such a thing exists—would be a new and fundamentally different kind of magnetic object. It would act as an isolated north pole, not attached to a south pole, or vice versa. Monopoles would carry "magnetic charge" analogous to electric charge. Despite systematic searches since 1931, as of 2006, they have never been observed, and could very well not exist.

Nevertheless, some theoretical physics models predict the existence of these magnetic monopoles. Paul Dirac observed in 1931 that, because electricity and magnetism show a certain symmetry, just as quantum theory predicts that individual positive or negative electric charges can be observed without the opposing charge, isolated South or North magnetic poles should be observable. Using quantum theory Dirac showed that if magnetic monopoles exist, then one could explain the quantization of electric charge—that is why, the observed elementary particles carry charges that are multiples of the charge of the electron.

Certain grand unified theories predict the existence of monopoles which, unlike elementary particles, are solitons (localized energy packets). The initial results of using these models to estimate the number of monopoles created in the big bang contradicted cosmological observations—the monopoles would have been so plentiful and massive that they would have long since halted the expansion of the universe. However, the idea of inflation (for which this problem served as a partial motivation) was successful in solving this problem, creating models in which monopoles existed but were rare enough to be consistent with current observations.

The term **magnetism** is used to describe how materials respond on the microscopic level to an applied magnetic field; to categorize the magnetic phase of a material. For example, the most well-known form of magnetism is ferromagnetism such that some ferromagnetic materials produce their own persistent magnetic field(such as iron). However, all materials are influenced to greater or lesser degree by the presence of a magnetic field. Some are attracted to a magnetic field (paramagnetism); others are repulsed by a magnetic field (diamagnetism); others have a much more complex relationship with an applied magnetic field. Substances that are negligibly affected by magnetic fields are known as **non-magnetic** substances. They include copper, aluminium, water, and gases.

The magnetic state (or phase) of a material depends on temperature (and other variables such as pressure and applied magnetic field) so that a material may exhibit more than one form of magnetism depending on its temperature, etc.

The magnetic properties of materials are a consequences of magnetic moments associated will individual electrons. The magnetic moment of an electron is due to its orbital motion and also due to its spin around its own axis.

A moving electron may be considered to be a small current loop, generating a small magnetic field, which has a magnetic moment along the axis and the magnetic moment due to electron spin is directed along the spin axis.

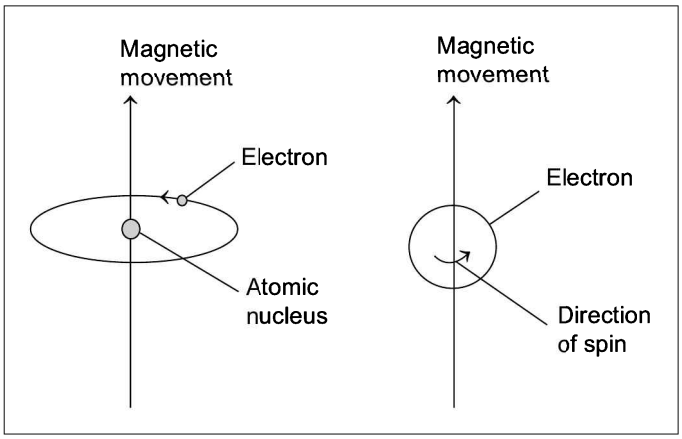


Fig. 11.51

The fundamental magnetic movement is the Bohr Magneton (m_B), which is equal to 9.27×10^{-24} Am^2.

For each electron in an atom, the spin magnetic moment is $\pm\mu B$ (depending on the two possibilities of the spin). The contribution of the orbital magnetic movement is equal to $m_l\, m_B$, where m_l is the magnetic quantum number of the electron.

Materials can be classified depending on their response to external magnetic field

Diamagnetism

Diamagnetism appears in all materials, and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. However, in a material with paramagnetic properties (that is, with a tendency to enhance an external magnetic field), the paramagnetic behaviour dominates. Thus, despite its universal occurrence, diamagnetic behaviour is observed only in a purely diamagnetic material. In a diamagnetic material, there are no unpaired electrons, so the intrinsic electron magnetic moments cannot produce any bulk effect. In these cases, the magnetization arises from the electrons' orbital motions, which can be understood classically as follows:

> *When a material is put in a magnetic field, the electrons circling the nucleus will experience, in addition to their Coulomb attraction to the nucleus, a Lorentz force from the magnetic field. Depending on which direction the electron is orbiting, this force may increase the centripetal force on the electrons, pulling them in towards the nucleus, or it may decrease the force, pulling them away from the nucleus. This effect systematically increases the orbital magnetic moments that were aligned opposite the field, and decreases the ones aligned parallel to the field (in accordance with Lenz's law). This results in a small bulk magnetic moment, with an opposite direction to the applied field.*

Note that this description is meant only as an heuristic; a proper understanding requires a quantum-mechanical description.

Note that all materials undergo this orbital response. However, in paramagnetic and ferromagnetic substances, the diamagnetic effect is overwhelmed by the much stronger effects caused by the unpaired electrons.

(Example TiO_2, NaCl, C_6H_6) are weakly repelled by external magnetic fields. This property is shown only by those substances which contain fully-filled orbitals i.e., no unpaired electrons is present

Paramagnetism

In a paramagnetic material there are *unpaired electrons*, i.e., atomic or molecular orbitals with exactly one electron in them. While paired electrons are required by the Pauli exclusion principle to have their intrinsic ('spin') magnetic moments pointing in opposite directions, causing their magnetic fields to cancel out, an

unpaired electron is free to align its magnetic moment in any direction. When an external magnetic field is applied, these magnetic moments will tend to align themselves in the same direction as the applied field, thus reinforcing it.

(example O_2, Cu^{2+}, Fe^{3+}) are attracted by a magnetic field but lose their magnetism in the absence of the magnetic field. This property is shown by those substances whose atoms, ions or molecules contain unpaired electrons.

Ferromagnetism

A ferromagnet, like a paramagnetic substance, has unpaired electrons. However, in *addition* to the electrons' intrinsic magnetic movements tendency to be parallel to *an applied field*, there is also in these materials a tendency for these magnetic moments to orient parallel to *each other* to maintain a lowered energy state. Thus, even when the applied field is removed, the electrons in the material maintain a parallel orientation.

Every ferromagnetic substance has its own individual temperature, called the Curie temperature, or Curie point, above which it loses its ferromagnetic properties. This is because the thermal tendency to disorder overwhelms the energy-lowering due to ferromagnetic order.

Some well-known ferromagnetic materials that exhibit easily detectable magnetic properties (to form magnets) are nickel, iron, cobalt, gadolinium and their alloys.

Examples: FeO and CrO_2

Fe, Co, Ni show ferromagnetism even at room temperature.

CrO_2 is used to make magnetic tapes for use in cassette recorders.

The spontaneous alignment of magnetic moments due to unpaired electrons in the same direction gives rise to ferromagnetism.

↑ ↑ ↑ ↑ ↑ ↑

Magnetic domains

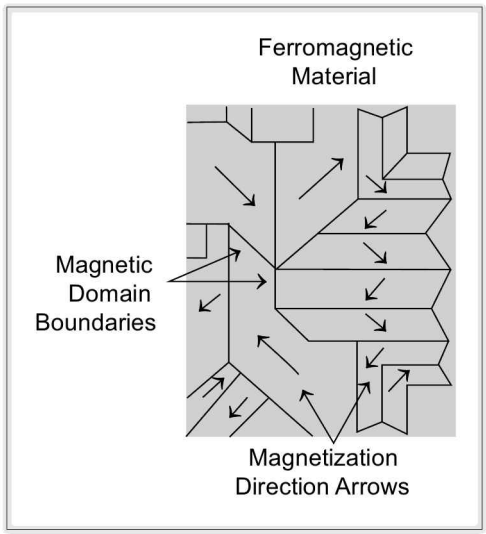


Fig. 11.52

The magnetic moment of atoms in a ferromagnetic material cause them to behave something like tiny permanent magnets. They stick together and align themselves into small regions of more or less uniform alignment called magnetic domains or Weiss domains. Magnetic domains can be observed with a magnetic force microscope to reveal magnetic domain boundaries that resemble white lines in the sketch. There are many scientific experiments that can physically show magnetic field

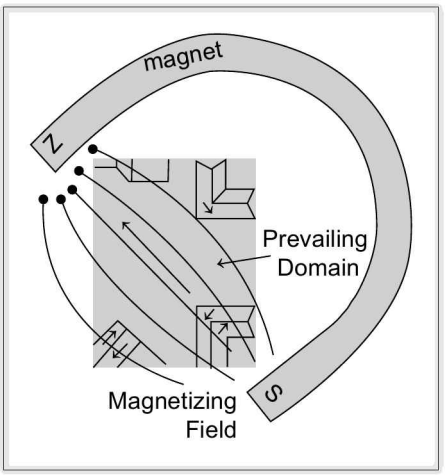


Fig. 11.53 Effect of a magnet on the domains.

When a domain contains too many molecules, it becomes unstable and divides into two domains aligned in opposite directions so that they stick together more stably as shown at the right.

When exposed to a magnetic field, the domain boundaries move so that the domains aligned with the magnetic field grow and dominate the structure as shown at the left. When the magnetizing field is removed, the domains may not return to an unmagnetized state. This results in the ferromagnetic material's being magnetized, forming a permanent magnet.

When magnetized strongly enough that the prevailing domain overruns all others to result in only one single domain, the material is magnetically saturated. When a magnetized ferromagnetic material is heated to the Curie point temperature, the molecules are agitated to the point that the magnetic domains lose the organization and the magnetic properties they cause cease. When the material is cooled, this domain alignment structure spontaneously returns, in a manner roughly analogous to how a liquid can freeze into a crystalline solid.

Antiferromagnetism

Anti-ferromagnetic substances are expected to possess paramagnetism or ferromagnetism on the basis of unpaired electrons present in them but actually they possess zero net magnetic moment.

This is because of the alignment of dipoles is in a compensatory way so as to give a net zero dipole moment, then we get anti-ferromagnetic substances (MnO).

↑ ↓ ↑ ↓ ↑ ↓

In an anti-ferromagnet, unlike a ferromagnet, there is a tendency for the intrinsic magnetic moments of neighboring valence electrons to point in *opposite* directions. When all atoms are arranged in a substance so that each neighbor is 'anti-aligned', the substance is **anti-ferromagnetic**. Anti-ferromagnets have a zero net magnetic moment, meaning no field is produced by them. Anti-ferromagnets are less common compared to the other types of behaviors, and are mostly observed at low temperatures. In varying temperatures, anti-ferromagnets can be seen to exhibit diamagnetic and ferrimagnetic properties.

In some materials, neighboring electrons want to point in opposite directions, but there is no geometrical arrangement in which *each* pair of neighbors is anti-aligned. This is called a spin glass, and is an example of geometrical frustration.

Ferrimagnetism

Ferrimagnetic substances are expected to possess large magnetism on the basis of the number of unpaired electrons present in them, but actually have small net magnetic moment.

This is because the moments are aligned in parallel and anti-parallel directions in unequal numbers resulting in a net dipole moment.

Example: Fe_3O_4, ferrites of formula $M^{2+}Fe_2O_4$ where, M = Mg, Cu, Zn etc.

↑ ↑ ↓ ↑ ↑ ↓

Like ferromagnetism, ferrimagnets retain their magnetization in the absence of a field. However, like antiferromagnets, neighboring pairs of electron spins like to point in opposite directions. These two properties are not contradictory, because in the optimal geometrical arrangement, there is more magnetic moment from the sublattice of electrons that point in one direction, than from the sublattice that points in the opposite direction.

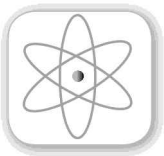
The first discovered magnetic substance, magnetite, was originally believed to be a ferromagnet; Louis Néel disproved this, however, with the discovery of ferrimagnetism.

Effect of temperature

Ferromagnetic, Antiferromagnetic and Ferrimagnetic solids transform to the paramagnetic state at some temperature due to randomisation of spins. Ferrimagnetic Fe_3O_4 becomes paramagnetic at 850 K.

It is also observed that Ferromagnetic substances have a characteristic temperature above which no ferromagnetism is observed. This is known as Curie temperature.

ELECTRICAL PROPERTIES OF SOLIDS



A conductor is a material which contains movable elecric charges. In metallic conductors, such as copper or aluminium, the movable charged particles are electrons. Positive charges may also be mobile in the form of atoms in a lattice that are missing electrons (known as holes), or in the form of ions, such as in the electrolyte of a battery.

An insulator, also called a *dielectric*, is a material that resists the flow of electric current. An insulating material has atoms with tightly bonded valence electrons. These materials are used in parts of electrical equipment, also called *insulators* or *insulation*, intended to support or separate electrical conductors without passing current through themselves. The term is also used more specifically to refer to insulating supports that attach electric power transmission wires to utility poles or pylons.

Some materials such as glass, paper or Teflo are very good electrical insulators. A much larger class of materials, for example rubber-like polymers and most plastics are still "good enough" to insulate electrical wiring and cables even though they may have lower bulk resistivity. These materials can serve as practical and safe insulators for low to moderate voltages (hundreds, or even thousands, of volts).

A **semiconductor** is a material that has an electrical conductivity between that of a conductor and an insulator, that is, generally in the range 10^3 Siemens/cm to 10^{-8} S/cm. Devices made from semiconductor materials are the foundation of modern electronics, including radio, computers, telephones, and many other devices. Semiconductor devices include the various types of transistor, solar cells, many kinds of diodes including the light-emitting diode, the silicon controlled rectifie , and digital and analog integrated circuits. Solar photovoltaic panels are large semiconductor devices that directly convert light energy into electrical energy. An external electrical field may change a semiconductor's resistivity. In a metallic conductor, current is carried by the flow of electrons. In semiconductors, current can be carried either by the flow of electrons or by the flow of positively-ch ged "holes" in the electron structure of the material.

Common semiconducting materials are crystalline solids but amorphous and liquid semiconductors are known, such as mixtures of arsenic, selenium and tellurium in a variety of proportions. They share with better known semiconductors intermediate conductivity and a rapid variation of conductivity with temperature but lack the rigid crystalline structure of conventional semiconductors such as silicon and so are relatively insensitive to impurities and radiation damage.

Silicon is used to create most semiconductors commercially. Dozens of other materials are used, including germanium, gallium arsenide, and silicon carbide. A pure semiconductor is often called an "intrinsic" semiconductor. The conductivity, or ability to conduct, of common semiconductor materials can be drastically changed by adding other elements, called "impurities" to the melted intrinsic material and then allowing the melt to solidify into a new and different crystal. This process is called "doping".

Semi-Insulators

Some materials are classified as semi-insulators. These have electrical conductivity nearer to that of electrical insulators. Semi-insulators find applications in micro-electronics. An example of a common semi-insulator is gallium arsenide.

Energy bands and electrical conduction

Like in other solids, the electrons in semiconductors can have energies only within certain bands (i.e., ranges of levels of energy) between the energy of the ground state, corresponding to electrons tightly bound to the atomic nuclei of the material, and the free electron energy, which is the energy required for an electron to escape entirely from the material. The energy bands each correspond to a large number of discrete quantum states of the electrons, and most of the states with low energy (closer to the nucleus) are full, up to a particular band called the *valence band*. Semiconductors and insulators are distinguished from metals because the valence band in the semiconductor materials is nearly filled under usual operating conditions, thus causing more electrons to be available in the "conduction band," which is the band immediately above the valence band.

The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the band gap between the bands, and it is the size of this energy bandgap that serves as an arbitrary dividing line (roughly 4 eV) between semiconductors and insulators.

In the picture of covalent bonds, an electron moves by hopping to a neighboring bond. Because of the Pauli exclusion principle it has to be lifted into the higher anti-bonding state of that bond. In the picture of delocalized states, for example in one dimension-that is in a nanowire, for every energy there is a state with electrons flowing in one direction and one state for the electrons flowing in the other. For a net current to flow some more states for one direction than for the other direction have to be occupied and for this energy is needed. For a metal this can be a very small energy while in the semiconductor the next higher states lie above the band gap. Often this is stated as: full bands do not contribute to the electrical conductivity. However, as the temperature of a semiconductor rises above absolute zero, there is more energy in the semiconductor to spend on lattice vibration and—more importantly for us—on lifting some electrons into an energy states of the conduction band. The current-carrying electrons in the conduction band are known as "free electrons", although they are often simply called "electrons" if context allows this usage to be clear.

Electrons excited to the conduction band also leave behind electron holes, or unoccupied states in the valence band. Both the conduction band electrons and the valence band holes contribute to electrical conductivity. The holes themselves do not actually move, but a neighboring electron can move to fill the hole, leaving a hole at the place it has just come from, and in this way the holes appear to move, and the holes behave as if they were actual positively charged particles.

One covalent bond between neighboring atoms in the solid is ten times stronger than the binding of the single electron to the atom, so freeing the electron does not imply destruction of the crystal structure.

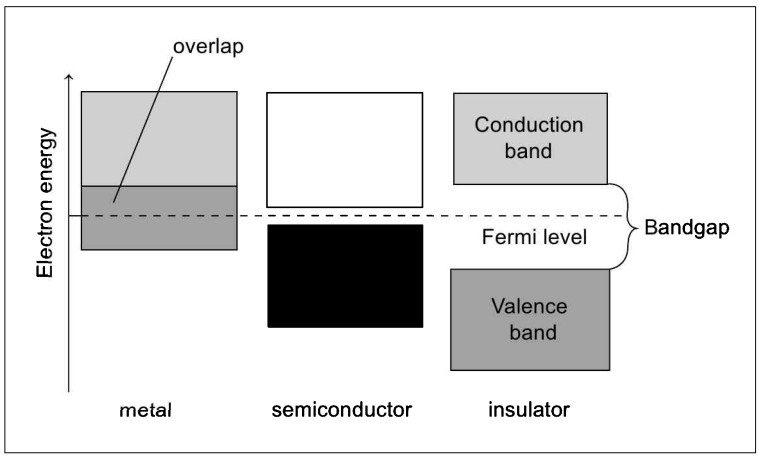


Fig. 11.54

Any solid has a large number of bands. In theory, it can be said to have infinitely many bands (just as an atom has infinitely many energy levels). However, all but a few lie at energies so high that any electron that reaches those energies escapes from the solid. These bands are usually disregarded.

Bands have different widths, based upon the properties of the atomic orbitals from which they arise. Also, allowed bands may overlap, producing (for practical purposes) a single large band.

Figure 11.54 shows a simplified picture of the bands in a solid that allows the three major types of materials to be identified: metals, semiconductors and insulators

Metals contain a band that is partly empty and partly filled regardless of temperature. Therefore, they have very high conductivity.

The lowermost, almost fully occupied band in an *insulator* or *semiconductor*, is called the *valence band* by analogy with the valence electrons of individual atoms. The uppermost, almost unoccupied band is called the *conduction band* because only when electrons are excited to the conduction band can current flow in these materials. The difference between insulators and semiconductors is only that the forbidden band gap between the valence band and conduction band is larger in an insulator, so that fewer electrons are found there and the electrical conductivity is lower. Because one of the main mechanisms for electrons to be excited to the conduction band is due to thermal energy, the conductivity of semiconductors is strongly dependent on the temperature of the material.

This band gap is one of the most useful aspects of the band structure, as it strongly influences the electrical and optical properties of the material. Electrons can transfer from one band to the other by means of carrier generation and recombination processes. The band gap and defect states created in the band gap by doping can be used to create semiconductor devices such as solar cells, diodes, transistors, laser diodes, and others.

Doping

The property of semiconductors that makes them most useful for constructing electronic devices is that their conductivity may easily be modified by introducing impurities into their crystal lattice. The process of adding controlled impurities to a semiconductor is known as *doping*. The amount of impurity, or dopant, added to an *intrinsic* (pure) semiconductor varies its level of conductivity. Doped semiconductors are often referred to as *extrinsic*. By adding impurity to pure semiconductors, the electrical conductivity may be varied not only by the number of impurity atoms but also, by the type of impurity atom and the changes may be thousand folds and million folds. For example, 1 cm^3 of a metal or semiconductor specimen has a number of atoms on the order of 10^{22}. Since every atom in metal donates at least one free electron for conduction in metal, 1 cm^3 of metal contains free electrons on the order of 10^{22}. At the temperature close to 20 °C, 1 cm^3 of pure germanium contains about 4.2×10^{22} atoms and 2.5×10^{13} free electrons and 2.5×10^{13} holes (empty spaces in crystal lattice having positive charge) The addition of 0.001% of arsenic (an impurity) donates an extra 10^{17} free electrons in the same volume and the electrical conductivity increases about 10,000 times."

Dopants

The materials chosen as suitable dopants depend on the atomic properties of both the dopant and the material to be doped. In general, dopants that produce the desired controlled changes are classified as either electron acceptors or donors. A donor atom that activates (that is, becomes incorporated into the crystal lattice) donates weakly-bound valence electrons to the material, creating excess negative charge carriers. These weakly-bound electrons can move about in the crystal lattice relatively freely and can facilitate conduction in the presence of an electric field. (The donor atoms introduce some states under, but very close to the conduction band edge. Electrons at these states can be easily excited to the conduction band, becoming free electrons, at room temperature.) Conversely, an activated acceptor produces a hole. Semiconductors doped with **donor** impurities are called *n-type*, while those doped with acceptor impurities are known as *p-type*. The n and p type designations indicate which charge carrier acts as the material's majority carrier. The opposite carrier is called the minority carrier, which exists due to thermal excitation at a much lower concentration compared to the majority carrier.

For example, the pure semiconductor silicon has four valence electrons. In silicon, the most common dopants are IUPAC group 13 (commonly known as *group III*) and group 15 (commonly known as *group V*) elements. Group 13 elements all contain three valence electrons, causing them to function as acceptors when used to dope silicon. Group 15 elements have five valence electrons, which allows them to act as a donor. Therefore, a silicon crystal doped with boron creates a p-type semiconductor whereas one doped with phosphorus results in an n-type material.

Carrier concentration

The concentration of dopant introduced to an intrinsic semiconductor determines its concentration and indirectly affects many of its electrical properties. The most important factor that doping directly affects is the material's carrier concentration. In an intrinsic semiconductor under thermal equilibrium, the concentration of electrons and holes is equivalent. That is,

$$n = p = n_i$$

If we have a non-intrinsic semiconductor in thermal equilibrium the relation becomes:

$$n_0 p_0 = (n_i)^2$$

Where n_0 is the concentration of conducting electrons, p_0 is the electron hole concentration, and n_i is the material's intrinsic carrier concentration. Intrinsic carrier concentration varies between materials and is dependent on temperature. Silicon's n_i, for example, is roughly 1.0×10^{10} cm^{-3} at 300 kelvin (room temperature).

In general, an increase in doping concentration affords an increase in conductivity due to the higher concentration of carriers available for conduction. Degenerately (very highly) doped semiconductors have conductivity levels comparable to metals and are often used in modern integrated circuits as a replacement for metal. Often superscript plus and minus symbols are used to denote relative doping concentration in semiconductors. For example, n^+ denotes an n-type semiconductor with a high, often degenerate, doping concentration. Similarly, p^- would indicate a very lightly doped p-type material. It is useful to note that even degenerate levels of doping imply low concentrations of impurities with respect to the base semiconductor. In crystalline intrinsic silicon, there are approximately 5×10^{22} atoms/cm^3. Doping concentration for silicon semiconductors may range anywhere from 10^{13} cm^{-3} to 10^{18} cm^{-3}. Doping concentration above about 10^{18} cm^{-3} is considered degenerate at room temperature. Degenerately doped silicon contains a proportion of impurity to silicon in the order of parts per thousand. This proportion may be reduced to parts per billion in very lightly doped silicon. Typical concentration values fall somewhere in this range and are tailored to produce the desired properties in the device that the semiconductor is intended for.

Effect on band structure

Band diagram of a p^+n junction. The band bending is a result of the positioning of the Fermi levels in the p^+ and n sides.

Doping a semiconductor crystal introduces allowed energy states within the band gap but very close to the energy band that corresponds to the dopant type. In other words, donor impurities create states near the conduction band while acceptors create states near the valence band. The gap between these energy states and the nearest energy band is usually referred to as dopant-site bonding energy or E_B and is relatively small. For example, the E_B for boron in silicon bulk is 0.045 eV, compared with silicon's band gap of about 1.12 eV. Because E_B is so small, it takes little energy to ionize the dopant atoms and create free carriers in the conduction or valence bands. Usually, the thermal energy available at room temperature is sufficient to ionize most of the dopant.

Dopants also have the important effect of shifting the material's Fermi level towards the energy band that corresponds with the dopant with the greatest concentration. Since the Fermi level must remain constant in a system in thermodynamic equilibrium, stacking layers of materials with different properties leads to many useful electrical properties. For example, the p-n junction's properties are due to the energy band bending that happens as a result of lining up the Fermi levels in contacting regions of p-type and n-type material.

This effect is shown in a *band diagram*. The band diagram typically indicates the variation in the valence band and conduction band edges versus some spatial dimension, often denoted x. The Fermi energy is also usually indicated in the diagram. Sometimes the *intrinsic Fermi energy*, E_i, which is the Fermi level in the absence of doping, is shown. These diagrams are useful in explaining the operation of many kinds of semiconductor devices.

Basic science of n-type semiconductors

Piezoelectricity is the ability of some materials (notably crystals and certain ceramics, including bone) to generate an electric fiel or electric potential in response to applied mechanical stress. The effect is closely related to a change of polarization density within the material's volume. If the material is not short-circuited, the applied stress induces a voltage across the material. The word is derived from the Greek *piezo* or *piezein*, which means to squeeze or press.

The piezoelectric effect is reversible in that materials exhibiting the *direct piezoelectric effect* (the production of an electric potential when stress is applied) also exhibit the *reverse piezoelectric effect* (the production of stress and/or strain when an electric field is applied). For example, lead zirconate titanate crystals will exhibit a maximum shape change of about 0.1% of the original dimension.

The effect finds useful applications such as the production and detection of sound, generation of high voltages, electronic frequency generation, microbalances, and ultra fine focusing of optical assemblies. It is also the basis of a number of scientific instrumental techniques with atomic resolution, the scanning probe microscopies such as STM, AFM, MTA, SNOM etc, and everyday uses such as acting as the ignition source for cigarette lighters and push-start propane barbecues.

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field.

The term is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment. Ferromagnetism was already known when ferroelectricity was discovered in 1920 in Rochelle salt by Valasek. Thus, the prefix *ferro*, meaning iron, was used to describe the property despite the fact that most ferroelectric materials do not have iron in their lattice.

When these crystals are subjected to mechanical stress, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity. But if an electric field is applied to these crystal there will be atomic displacement causing mechanical strain.

These crystals act as mechanical-electrical transducers.

Uses

As pick-ups in record players.

Pyroelectricity

Some polar crystals when heated produce a small current or pyroelectricity.

Ferroelectricity

In some piezoelectric crystals the dipoles are permanently lined up even in the absence of an electric field. However, on applying electric field the direction of polarization changes

Example: Barium titanate ($BaTiO_3$), Sodium potassium tartrate (Rochelle Salt) and Potassium dihydrogen phosphate (KH_2PO_4).

Anti-ferroelectric

If there is no net dipole moment it is said to be an anti-ferroelectric crystal. This is because the dipoles are alternately arranged.

Example: ($PbZrO_3$) Lead zirconate.

When the electrical resistance of materials becomes almost zero, the material becomes superconductor. The temperature at which the material shows superconductivity is called transition temperature.

Example: $YBa_2\ Cu_3\ O_7$ at 90K.

Uses

- Electronic
- Power transmission
- Levitation
- Transportation.

Crystal planes and miller indices

In a real crystal, the lattice points are occupied by atoms. One can think of a very large number of lattice planes and one set of parallel planes can be distinguished from another set by their orientation. Miller indices are the labels used to distinguish one set of parallel planes from another. It is a set of three numbers *h k l* that defines a set of parallel planes in a crystal

The following proceedure is generally followed to determine the Miller indices.

1. Choose an origin;
2. Find out the intercept that the first such plane makes with the three crystallographic axes
3. Obtain their reciprocals;
4. Eliminate fractions.

The set of numbers thus generated in relation with the axes *a, b* and *c* are *h, k* acid *l* respectively. A set of parallel planes are labelled by a set of hkl numbers, Different set of parallel planes have different hkl or Miller indices. This is illustrated in fig. 11.55. Here, the plane nearest to the origin and cutting the *b* axis at $\frac{1}{2b}$, the a axis at $\frac{1}{3a}$ and the *c* axis at $\frac{1}{2c}$ is shown. This makes $\frac{1}{3}$ intercept along *a* axis, $\frac{1}{2}$ intercept along and axis and \ along c axis.

	a	b	c
Intercept	1/3	1/2	1/2
Reciprocal	3	2	2

Hence, this plane and a set of parallel planes separated by a distance d have the Miller indices (322).

It should be noted that a point on a paper actually represents line of points when one considers the three dimensional lattice. Hence, on the plane of paper a line of points actually represents a plane.

The major advantage of the Miller indices is that it permits to express interplanar distance of a set of *hkl* planes in terms of lattice parameters. For a cubic crystal,

$$d_{hkl} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}}$$

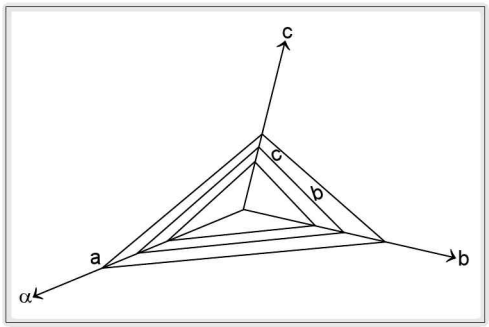


Fig. 11.55 The (322) Miller planes

Lattice Planes in a Cubic Systems

Some of the lattice planes in the cubic crystals are shown in fig. 1.56.

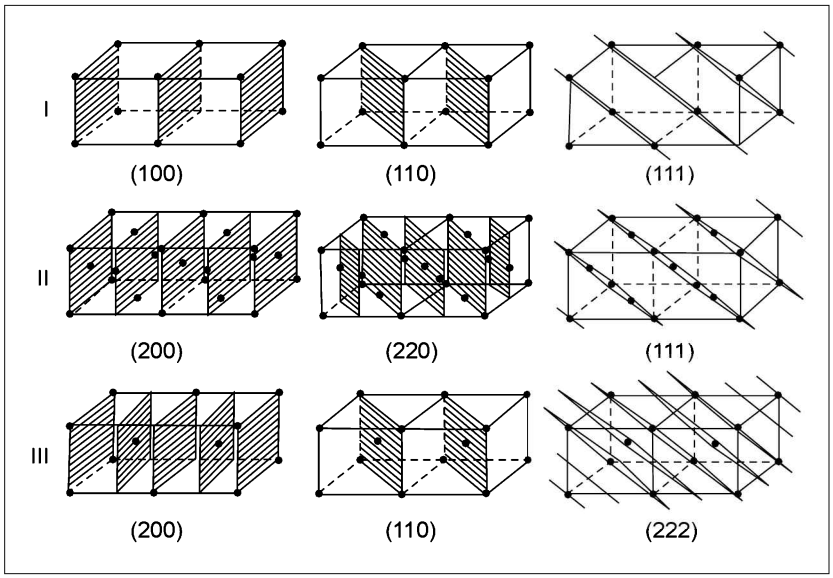


Fig. 11.56 Some of the lattice planes of cubic lattice: (I) Primitive cubic lattice, (II) Face-centred cubic lattice, (III) Body-centred cubic lattice

X-RAY DIFFRACTION AND BRAGG'S EQUATION



What causes X-ray diffraction?

X-rays are a variety of electromagnetic radiation with fairly high energies. The wavelength of X-rays is of the order 100pm (10^{-10} m). They show the normal properties of waves; especially, they can be *diffracted.* Diffraction occurs whenever a wave meets a barrier with one or more openings that are about the same size as the wavelength. It so happens that the layers of atoms or ions in crystals are separated by distances around 100 or 200 pm. This is just the right range to cause X-rays to be diffracted. Thus, we can say that:

The layers of atoms in a crystals act as a diffraction for X-ray

The reason why atoms are able to produce diffraction patterns has much to do with the number of electrons they contain. The electric field of the X-rays interacts with the cloud of electrons around an atom. The result of many thousands of the interactions produces the diffraction pattern. Large atoms have many electrons. These atoms produce the strongest patterns. Small atoms, like hydrogen, may have so few electrons that they have little effect on X-rays.

More about diffraction

Before we go into more detail about X-ray diffraction, it is important that you understand some basic ideas about diffraction in general (Figure 11.58)

If light is passed through a row of slits (known as a diffraction grating), the diffraction pattern can be captured on a photograph. By using sophisticated equipment it is possible to measure the amount of blackening of the film. This tells us the intensity of the light falling on various parts of the film. Alternatively the intensity can be measured electronically, without photographs.

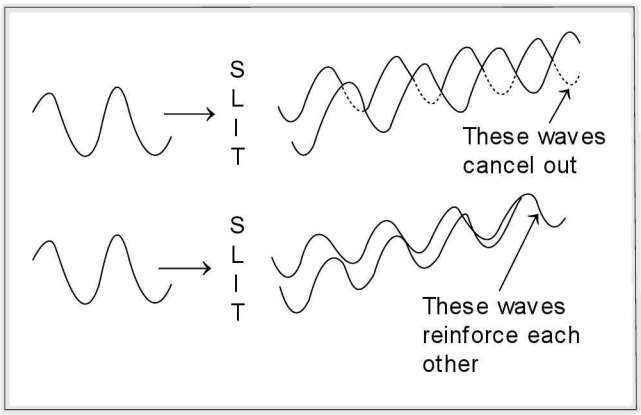


Fig. 11.57 After waves pass through a narrow slit there are places where they reinforce and places where they cancel out. The overall pattern is a diffraction pattern

As with water waves, the diffracted light waves reinforce one another provided the difference in the distances they travel is a whole number of wavelengths. If their paths are different by more or less than a wavelength, then the waves will tend to cancel out, as shown in figure 11.59. With this background, you should be able to understand the diagram in figure 1.60.

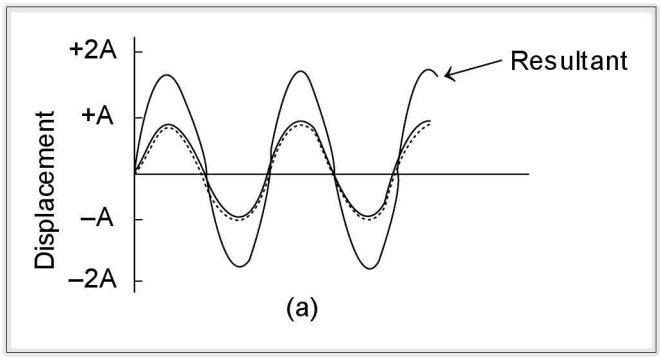
In the diagrams X-rays are shown encountering atoms in a layer of a crystal. The waves have their crests and troughs matching; they will reinforce constructively and give a patch of high intensity on a photographic film. We have already said that this happens if the distances that the waves travel differ by a whole number of wavelengths, λ. We shall call this whole number n. Thus, constructive interference occurs when,

path difference = nλ

Now, if you look at Figure 11.59 you will find that path di ference in crystal = x sin A
Thus we find

nλ = x sin A

However, crystals contain many planes of atoms, which criss-cross in three dimensions, and we have only dealt with diffraction in one of these dimensions. In a real diffraction experiment not just one but three equations must be satisfied before a spot would be seen on a photographic fil



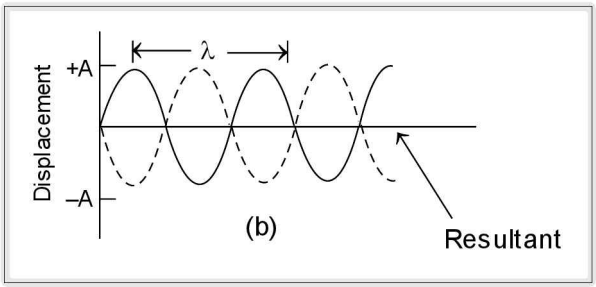


Fig. 11.58 Two ways in wihch waves can overlap with one another. (a) Two waves that have equal amplitude, A, and are completely in phase interfere completely construcitvely. (b) Two waves that have the same amplitude, A, and are completely out of phase give a resultant of zero amplitude. There is completely destructive interference

Bragg's Equation

An alternative theory of X-ray diffraction was published in 1912 by Sir (William) Lawrence Bragg. He worked closely with his father, Sir William Henry Bragg, and both received the Noble Prize for their work in using X-rays to discover the structures of crystals.

Bragg (the younger) proposed that the formation of diffraction patterns could be explained by assuming that the X-rays were reflect d from the various planes of atoms in a crystals. (It is possible to show that the diffraction and reflecti n explanations are equivalent to one another. Most people find Bragg's explanation easier to work with.)

If you look at figure 11.60 you will se that the difference in the distance travelled by rays bouncing off two different planes is 2d sin θ. For constructive interference then we must have,

$$n\lambda = 2d \sin \theta \qquad \text{Bragg's equation}$$

If n = 1 we say that a first-order reflection occurs; if n = 2 then we have a second-order reflection; and so on. Normally, it is only necessary to bother with first-order reflection

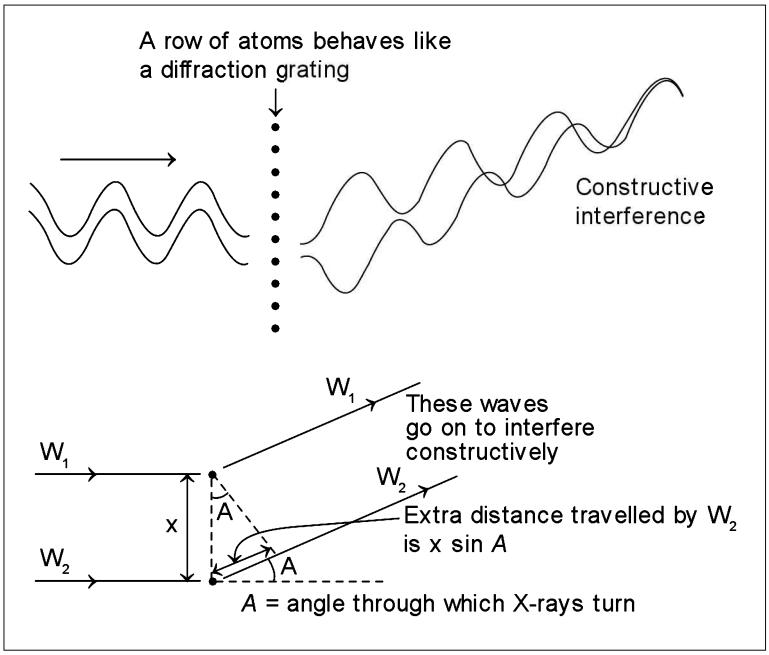


Fig. 1159 The lower diagram is an expanded view of the upper diagram. For constructive interference, the extra distance travelled bty wave W_2 must by a whole number of wavelength, i.e., $n\lambda = x \sin A$

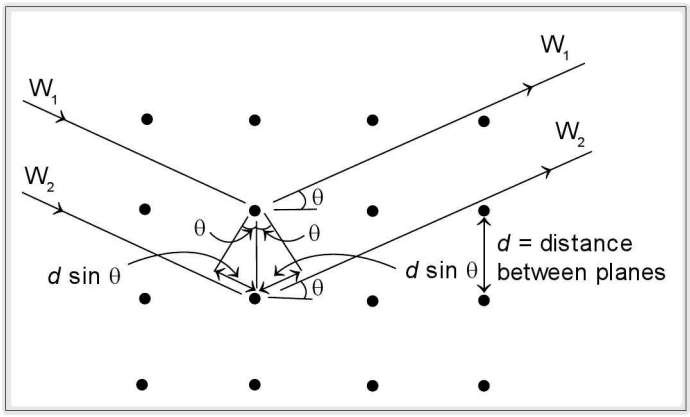


Fig. 11.60 The extra distance travelled by wave W_2 is $2 \times d \sin \theta$, i.e., $2d \sin \theta$. For constructive interference, $n\lambda = 2d \sin \theta$

Geometric method

The general formula for the interplanar spacing in a system of orthogonal axes can be derived geometrically. As stated earlier, the Miller indices define the set of parallel planes, one of which passes through the origin. Thus, if a perpendicular is drawn from the origin to the nearest plane of Miller indices *(hkl)*, then this perpendicular distance, represented as d_{hkl}, will be equal to the interplanar spacing between planes of Miller indices *(hkl)* as shown in fig. 1.61.

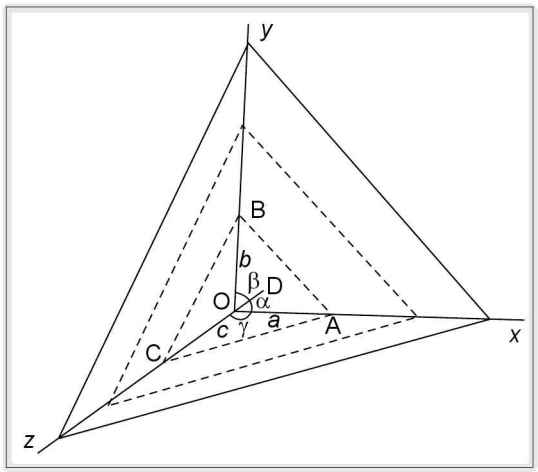


Fig. 11.61 Interplanar distance of the planes

If α, β and γ are the angles which this perpendicular makes with the three axes, then

$$d_{hkl} = OA \cos \alpha = \left(\frac{a}{h}\right) \cos \alpha, \quad d_{hkl} = OB \cos \beta = \left(\frac{b}{k}\right) \cos \beta$$

$$\text{and } d_{hkl} = OC \cos \gamma = \left(\frac{c}{l}\right) \cos \gamma$$

$$\text{or } \cos \alpha = \left(\frac{h}{a}\right) d_{hkl}, \ \cos \beta = \left(\frac{k}{b}\right) d_{hkl}, \text{ and } \cos \gamma = \left(\frac{l}{c}\right) d_{hkl}$$

Now, since $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ are the direction cosines of the perpendicular line, therefore

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

* See Annexure II at the end of this chapter for the more general expression of interplanar distances.

Substituting their value in terms of d_{hkl}, we have

$$\left(\frac{h}{a}\right)^2 d_{hkl}^2 + \left(\frac{k}{b}\right)^2 d_{hkl}^2 + \left(\frac{l}{c}\right)^2 d_{hkl}^2 = 1$$

$$\text{or} \quad \frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$$

For a cubic system a = b = c, we have

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad \text{or} \qquad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For a tetragonal system, a = b ≠ c, we have

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

For an orthorhombic system a ≠ b ≠ c, we have

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

d-Spacing

The distance between two parallel planes in a cubic crystal (d-spacing) is given by,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad \ldots(3)$$

where a is the length of the side of cybe and h, k and l are Miller indices of the parallel planes.
For the planes of (1 0 0), (1 1 0) and (1 1 1) in a cube unit cell,

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a \qquad d_{100} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}} \qquad d_{101} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

One of the consequences of this ordered internal arrangement of atoms is that all crystals of the same mineral look similar. This was discovered by Nicolas Steno in 1669 and is expressed as Steno's Law of constancy of interfacial angles-angles between corresponding crystal faces of the same mineral have the same angle. This is true even if the crystals are distorted as illustrated by the cross-sections through 3 quartz crystals shown below.

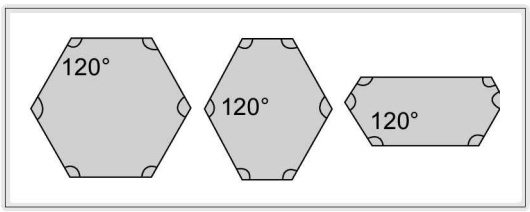


Fig. 11.62

Intercepts of Crystal Faces (Weiss Parameters)

Crystal faces can be defined by their intercepts on the crystallographic axes. For non-hexagonal crystals, there are three cases.

1. A crystal face intersects only one of the crystallographic axes.
   As an example the top crystal face shown here intersects the c axis but does not intersect the a or b axes. If we assume that the face intercepts the c axis at a distance of 1 unit length, then the intercepts, sometimes called Weiss Parameters, are: ∞ **a,** ∞ **b, 1c**

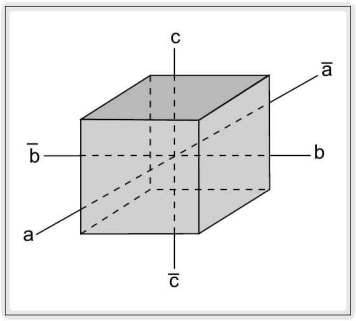


Fig. 11.63

2. A crystal face intersects two of the crystallographic axes.
   As an example, the darker crystal face shown here intersects the a and b axes, but not the c axis. Assuming the face intercepts the a and c axes at 1 unit cell length on each, the parameters for this face are: **1 a, 1 b, ∞c**

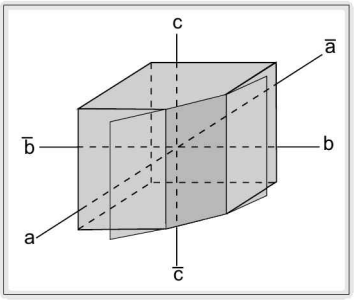


Fig. 11.64

3. A crystal face that intersects all 3 axes.
   In this example the darker face is assumed to intersect the a, b, and c crystallographic axes at one unit length on each. Thus, the parameters in this example would be: **1a, 1b, 1c**

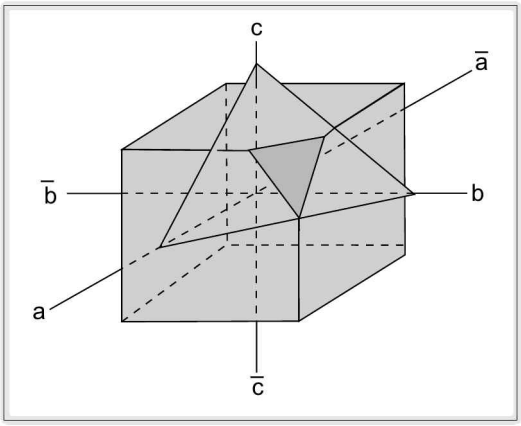


Fig. 11.65

Symmetry

Crystals, have an ordered internal arrangement of atoms. This ordered arrangement shows symmetry, i.e., the atoms are arranged in a symmetrical fashion on a three dimensional network referred to as a ***lattice***.

When a crystal forms in an environment where there are no impediments to its growth, crystal faces form as smooth planar boundaries that make up the surface of the crystal. These crystal faces reflect the ordered internal arrangement of atoms and thus reflect the symmetry of the crystal lattice. To see this, let's first imagine a small 2 dimensional crystal composed of atoms in an ordered internal arrangement as shown below. Although, all of the atoms in this lattice are the same, I have coloured one of them gray, so we can keep track of its position.

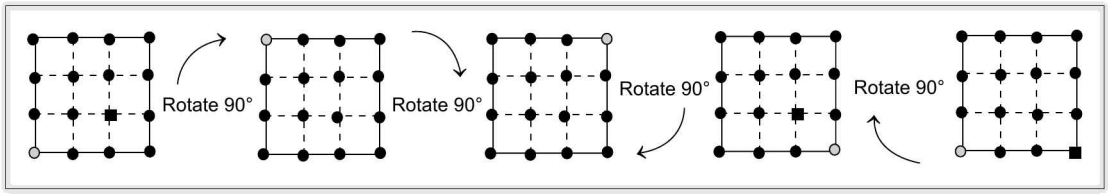


Fig. 11.66

If we rotate the simple crystals by 90° notice that the lattice and crystal look exactly the same as what we started with. Rotate it another 90° and again its the same. Another 90° rotation again results in an identical crystal, and another 90° rotation returns the crystal to its original orientation. Thus, in 1 360° rotation, the crystal has repeated itself, or looks identical 4 times. We thus say that this object has 4-fold rotational symmetry.

Symmetry Operations and Elements

A Symmetry operation is an operation that can be performed either physically or imaginatively that results in no change in the appearance of an object. Again it is emphasized that in crystals, the symmetry is internal, that is it is an ordered geometrical arrangement of atoms and molecules on the crystal lattice. But, since the internal symmetry is reflected in the external form of perfect crystals, we are going to concentrate on external symmetry, because this is what we can observe.

There are 3 types of symmetry operations: rotation, reflection, and inversion. We will look at each of these in turn.

Rotational Symmetry

As illustrated above, if an object can be rotated about an axis and repeats itself every 90° of rotation then it is said to have an axis of 4-fold rotational symmetry. The axis along which the rotation is performed is an element of symmetry referred to as a rotation axis. The following types of rotational symmetry axes are possible in crystals.

- ***1-Fold Rotation Axis***-An object that requires rotation of a full 360° in order to restore it to its original appearance has no rotational symmetry. Since, it repeats itself 1 time every 360°, it is said to have a 1-fold axis of rotational symmetry.

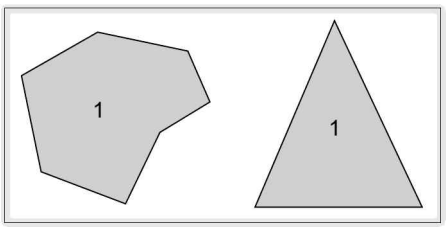


Fig. 11.67

- ***2-fold Rotation Axis***-If an object appears identical after a rotation of 180°, that is twice in a 360° rotation, then it is said to have a 2-fold rotation axis (360/180 = 2). Note that in these examples, the axes

we are referring to are imaginary lines that extend toward you perpendicular to the page or blackboard. A filled oval shape represents the point where the 2-fold rotation axis intersects the page

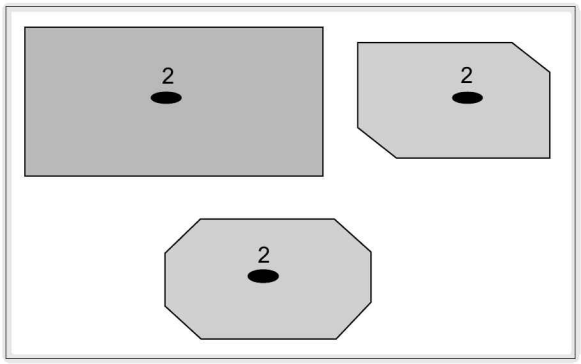


Fig. 11.68

This symbolism will be used for a 2-fold rotation axis throughout the lectures and in your text.

- ***3-Fold Rotation Axis***-Objects that repeat themselves upon rotation of 120° are said to have a 3-fold axis of rotational symmetry (360/120 =3), and they will repeat 3 times in a 360° rotation. A filled triangle is used to symbolize the location of 3-fold rotation axis.

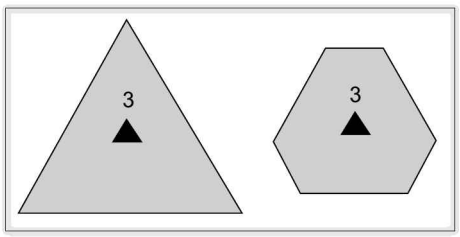


Fig. 11.69

- ***4-Fold Rotation Axis***-If an object repeats itself after 90° of rotation, it will repeat 4 times in a 360° rotation, as illustrated previously. A filled square is used to symbolize the location of 4-fold axis of rotational symmetry.

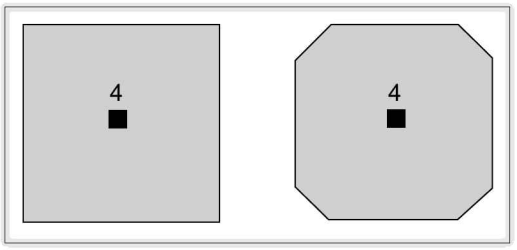


Fig. 11.70

- ***6-Fold Rotation Axis***-If rotation of 60° about an axis causes the object to repeat itself, then it has 6-fold axis of rotational symmetry (360/60=6). A filled hexagon is used as the symbol for a 6-fold rotation axis.

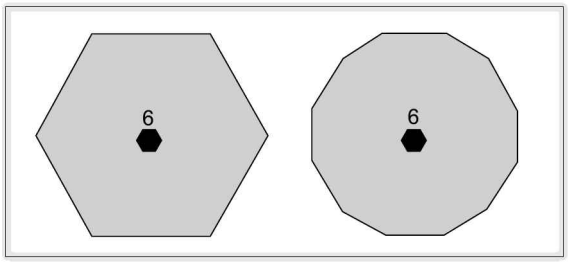


Fig. 11.71

Although, objects themselves may appear to have 5-fold, 7-fold, 8-fold, or higher-fold rotation axes, these are not possible in crystals. The reason is that the external shape of a crystal is based on a geometric arrangement of atoms. Note that if we try to combine objects with 5-fold and 8-fold apparent symmetry, that we cannot combine them in such a way that they completely fill space, as illustrated below.

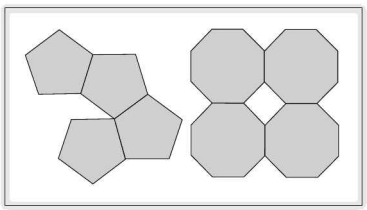


Fig. 11.72

Mirror Symmetry

A mirror symmetry operation is an imaginary operation that can be performed to reproduce an object. The operation is done by imagining that you cut the object in half, then place a mirror next to one of the halves of the object along the cut. If the reflection in the mirror reproduces the other half of the object, then the object is said to have mirror symmetry. The plane of the mirror is an element of symmetry referred to as a ***mirror plane***, and is symbolized with the letter m. As an example, the human body is an object that approximates mirror symmetry, with the mirror plane cutting through the center of the head, the center of nose and down to the groin.

The rectangles shown below have two planes of mirror symmetry.

The rectangle on the left has a mirror plane that runs vertically on the page and is perpendicular to the page. The rectangle on the right has a mirror plane that runs horizontally and is perpendicular to the page. The dashed parts of the rectangles below show the part of the rectangles that would be seen as a reflection in the mirror.

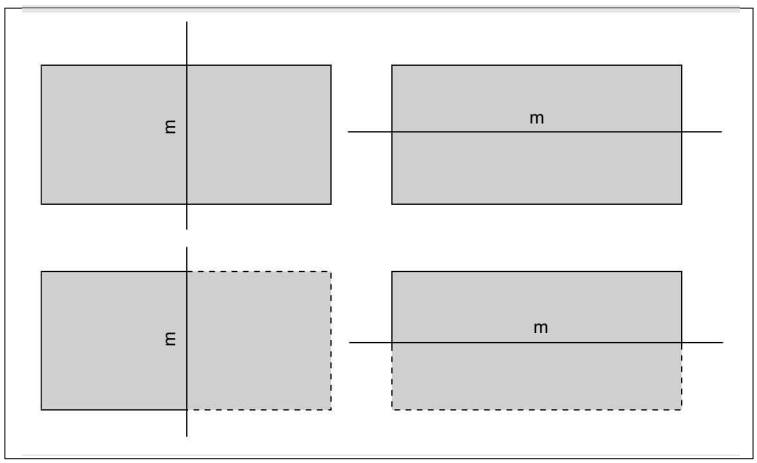


Fig. 11.73

The rectangles shown above have two planes of mirror symmetry. Three dimensional and more complex objects could have more. For example, the hexagon shown above, not only has a 6-fold rotation axis, but has 6 mirror planes.

Note that a rectangle does not have mirror symmetry along the diagonal lines. If we cut the rectangle along a diagonal such as that labeled "m", as shown in the upper diagram, reflected the lower half in the mirror, then we would see what is shown by the dashed lines in lower diagram. Since this does not reproduce the original rectangle, the line "m" does not represent a mirror plane.

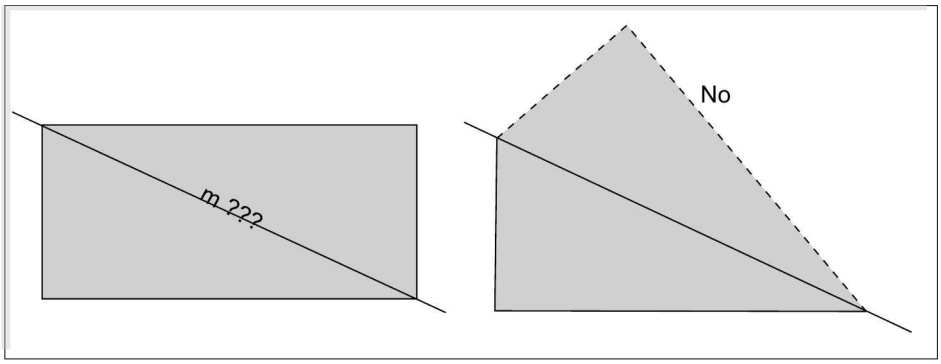


Fig. 11.74

Center of Symmetry

Another operation that can be performed is inversion through a point. In this operation lines are drawn from all points on the object through a point in the center of the object, called a symmetry center (symbolized with the letter "i"). The lines each have lengths that are equidistant from the original points. When the ends of the lines are connected, the original object is reproduced inverted from its original appearance. In the diagram shown here, only a few such lines are drawn for the small triangular face. The right hand diagram shows the object without the imaginary lines that reproduced the object.

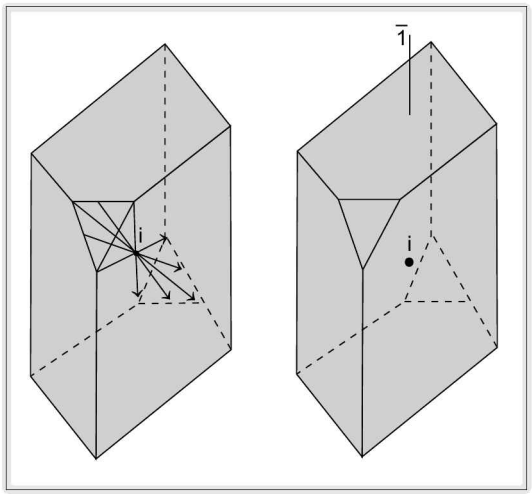


Fig. 11.75

If an object has only a center of symmetry, we say that it has a 1 fold rotoinversion axis. Such an axis has the symbol $\bar{6}$, as shown in the right hand diagram above. Note that crystals that have a center of symmetry will exhibit the property that if you place it on a table there will be a face on the top of the crystal that will be parallel to the surface of the table and identical to the face resting on the table.

Rotoinversion

Combinations of rotation with a center of symmetry perform the symmetry operation of rotoinversion. Objects that have rotoinversion symmetry have an element of symmetry called a rotoinversion axis. A 1-fold rotoinversion axis is the same as a center of symmetry, as discussed above. Other possible rotoinversion are as follows:

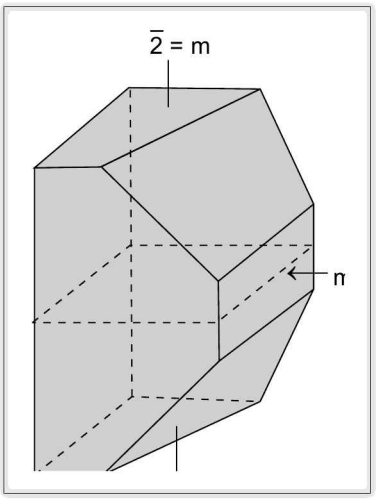


Fig. 11.76

- ***2-fold Rotoinversion***-The operation of 2-fold rotoinversion involves first rotating the object by 180° then inverting it through an inversion center. This operation is equivalent to having a mirror plane perpendicular to the 2-fold rotoinversion axis. A 2-fold rotoinversion axis is symbolized as a 2 with a bar over the top, and would be pronounced as "bar 2". But, since this the equivalent of a mirror plane, m, the bar 2 is rarely used.
- ***3-fold Rotoinversion***-This involves rotating the object by 120° (360/3 = 120), and inverting through a center. A cube is good example of an object that possesses 3-fold rotoinversion axes. A 3-fold rotoinversion axis is denoted as $\bar{6}$ (pronounced "bar 3"). Note that there are actually four $\bar{6}$ axes in a cube, one running through each of the corners of the cube. If one holds one of the $\bar{6}$ axes vertical, then note that there are 3 faces on top, and 3 identical faces upside down on the bottom that are offset from the top faces by 120°.

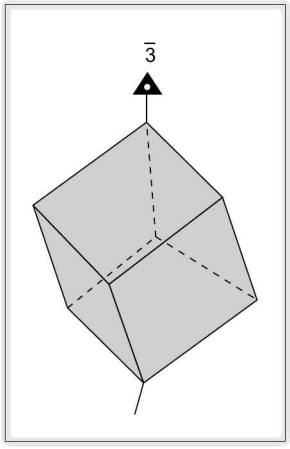


Fig. 11.77

- ***4-fold Rotoinversion***-This involves rotation of the object by 90° then inverting through a center. A four fold rotoinversion axis is symbolized as $\bar{6}$. Note that an object possessing a 4-fold rotoinversion axis will have two faces on top and two identical faces upside down on the bottom, if the $\bar{6}$ axis is held in the vertical position.

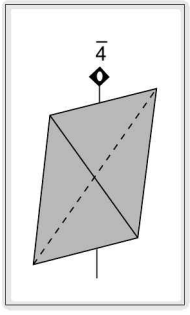


Fig. 11.78

- ***6-fold Rotoinversion***-A 6-fold rotoinversion axis ($\bar{6}$) involves rotating the object by 60° and inverting through a center. Note that this operation is identical to having the combination of a 3-fold rotation axis perpendicular to a mirror plane.

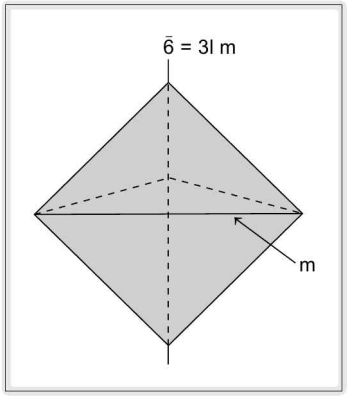


Fig. 11.79

Combinations of symmetry operations

As should be evident by now, in three dimensional objects, such as crystals, symmetry elements may be present in several different combinations. In fact, in crystals there are 32 possible combinations of symmetry elements. These 32 combinations define the ***32 Crystal Classes***. Every crystal must belong to one of these 32 crystal classes. In the next lecture we will start to go over each of these crystal classes in detail, but the best way to be able to identify each crystal class is not by listening to my lecture, not necessarily by reading about each class, but actually looking at models of perfect crystals in the lab. In fact, it is my opinion that it is next to impossible to identify symmetry elements and crystal classes without spending a lot of time examining and studying the 3-dimensional models in lab.

Here, I will just give one example of how the various symmetry elements are combined in a somewhat completed crystal. One point that I want to emphasize in this discussion is that if 2 kinds of symmetry elements are present in the same crystal, then they will operate on each other to produce other symmetrical symmetry elements. This should become clear as we go over the example below.

In this example, we will start out with the crystal shown here. Note that this crystal has rectangular-shaped sides with a square-shaped top and bottom. The square-shaped top indicates that there must be a 4-fold rotation axis perpendicular to the square shaped face. This is shown in the diagram.

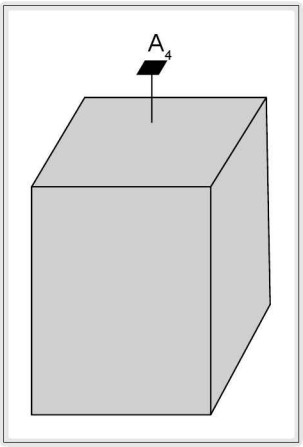


Fig. 11.80

Also note that the rectangular shaped face on the left side of the crystal must have a 2-fold rotation axis that intersects it. Note that the two fold axis runs through the crystal and exits on the left-hand side (not seen in this view), so that both the left and right-hand sides of the crystal are perpendicular to a 2-fold rotation axis.

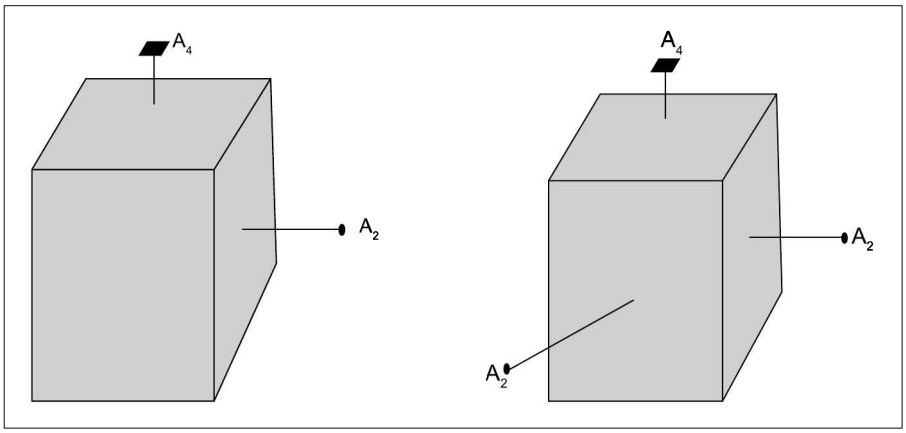


Fig. 11.81

Since the top face of the crystal has a 4-fold rotation axis, operation of this 4-fold rotation must reproduce the face with the perpendicular 2-fold axis on a 90° rotation. Thus, the front and back faces of the crystal will also have perpendicular 2-fold rotation axes, since these are required by the 4-fold axis.

The square-shaped top of the crystal also suggests that there must be a 2-fold axis that cuts diagonally through the crystal. This 2-fold axis is shown here in the left-hand diagram. But, again operation of the 4-fold axis requires that the other diagonals also have 2-fold axis, as shown in the right-hand diagram.

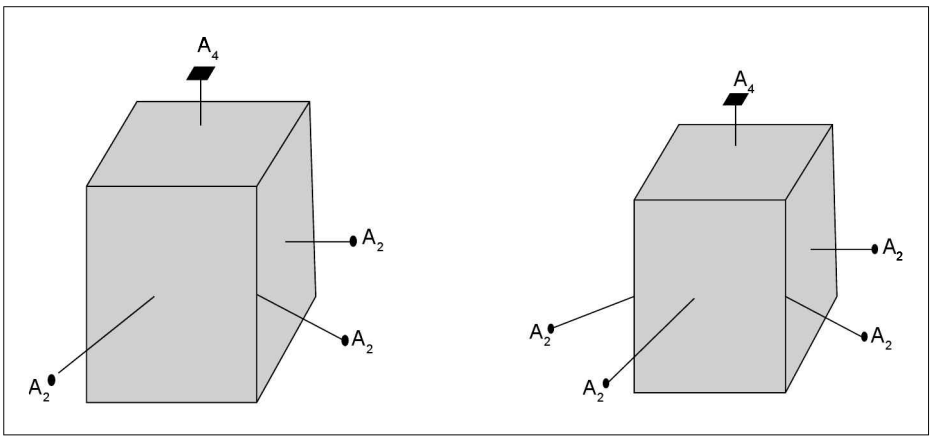


Fig. 11.82

Furthermore, the square-shaped top and rectangular-shaped front of the crystal suggest that a plane of symmetry is present as shown by the left-hand diagram here. But, again, operation of the 4-fold axis requires that a mirror plane is also present that cuts through the side faces, as shown by the diagram on the right.

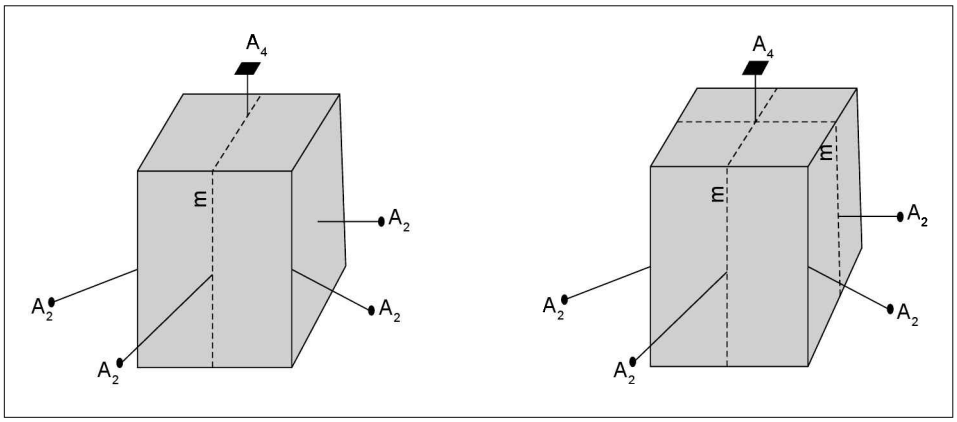


Fig. 11.83

The square top further suggests that there must be a mirror plane cutting the diagonal through the crystal. This mirror plane will be reflected by the other mirror planes cutting the sides of the crystal, or will be reproduced by the 4-fold rotation axis, and thus the crystal will have another mirror plane cutting through the other diagonal, as shown by the diagram on the right.

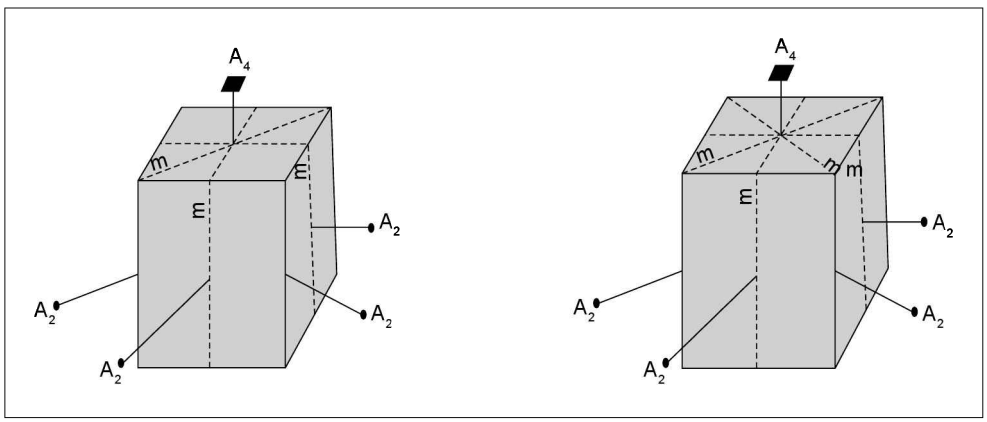


Fig. 11.84

Finally, there is another mirror plane that cuts through the center of the crystal parallel to the top and bottom faces.

Thus, this crystal has the following symmetry elements:

- 1– 4-fold rotation axis (A_4)
- 4–2-fold rotation axes (A_2), 2 cutting the faces and 2 cutting the edges.
- 5 mirror planes (m), 2 cutting across the faces, 2 cutting through the edges, and one cutting horizontally through the center.
- Note also that there is a center of symmetry (i).

The symmetry content of this crystal is thus: i, $1A_4$, $4A_2$, 5m

List of symmetry elements of the cube

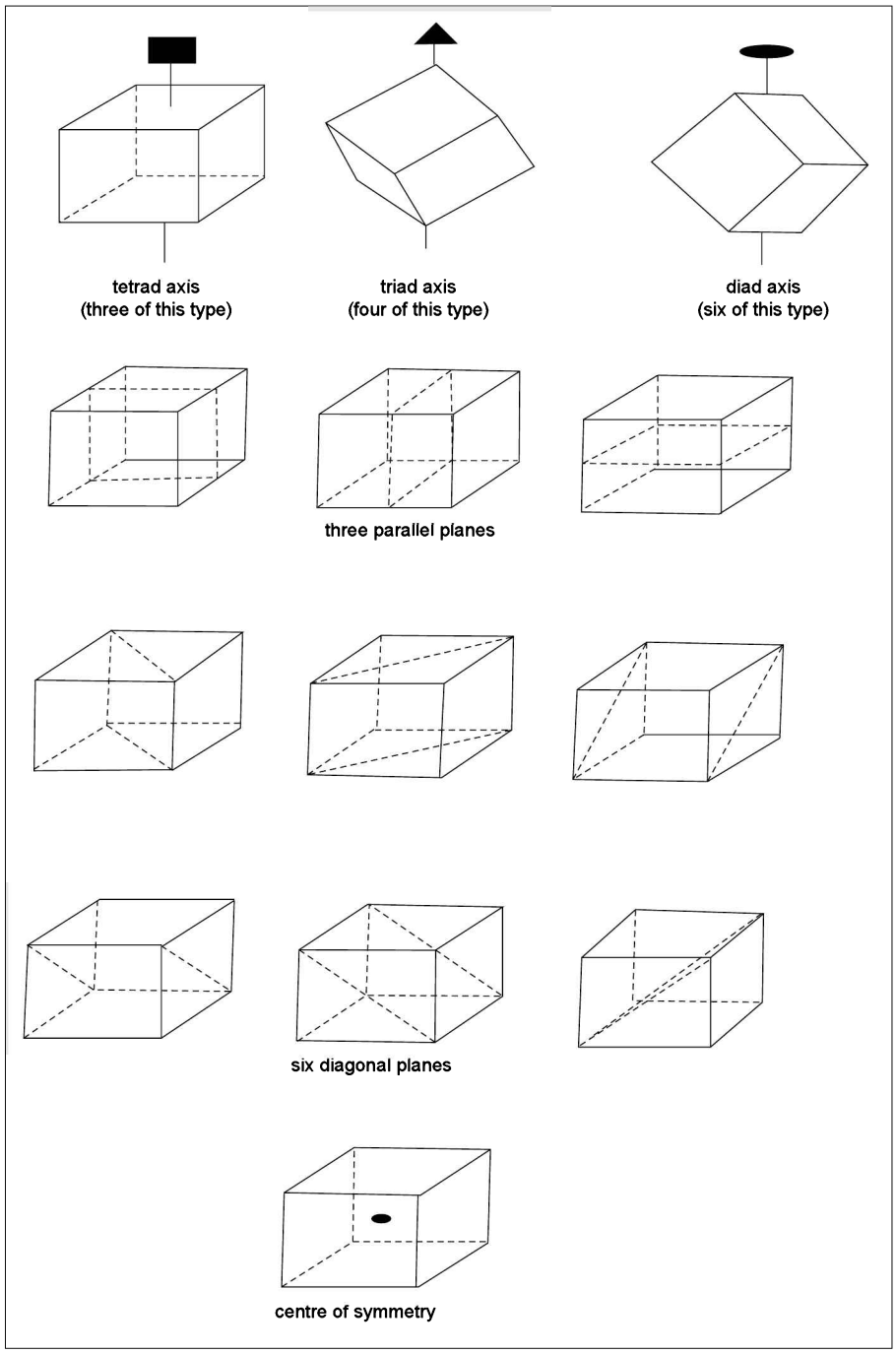


Fig. 11.85 Symmetry elements of a cube

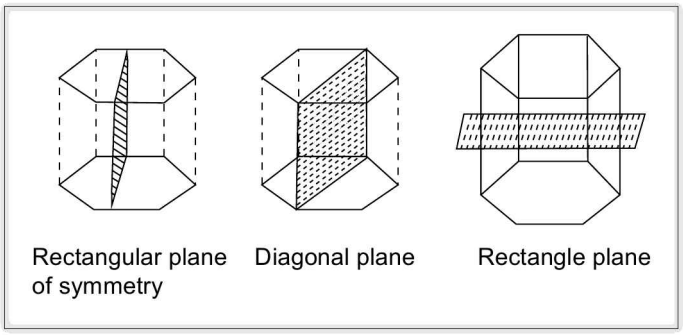


Fig. 11.86

There are 3 vertical rectangular planes of symmetry
There is 1 horizontal rectangular planes of symmetry
There are 3 vertical diagonal planes of symmetry
Hence there are total of 7 planes of symmetry.

Worked-out Example

1. The number of planes of symmetry which an HCP can have are

(a) 2 (b) 6
(c) 3 (d) 7

Solution (d)

ONE CORRECT OPTION TYPE QUESTIONS

1. In a fcc arrangement of A and B atoms, where A atoms are at the Corners of the unit cell, B atoms at the face centers, two atoms are missing from two corners in each unit cell, then the simplest formula of the compound is
(a) A_7B_6 (b) A_6B_7
(c) A_7B_{24} (d) AB_4

2. A solid is made of two elements P and Q. Atoms P are in ccp arrangement and atoms Q occupy all the octahedral voids and half of the tetrahedral voids, then the simplest formula of the compound is
(a) PQ_2 (b) P_2Q
(c) PQ (d) P_2Q_2

3. The limiting radius ratio of the complex$[Ni(CN)_4]^{2-}$ is
(a) 0.225 – 0.414 (b) 0.414 – 0.732
(c) 0.155 – 0.225 (d) None

4. If the ratio of co-ordination number P to that of Q be Y:Z, then the formula of the solid is
(a) P_yQ_z (b) P_zQ_y
(c) $P_{1/y}Q_{1/z}$ (d) None

5. In the body centered cubic unit cell and simple cubic unit cell, the radius of atom in terms of edge length (a) of the unit cell is respectively:
(a) $\frac{a}{2}, \frac{a}{2\sqrt{2}}$ (b) $\frac{a}{\sqrt{2}}, \frac{a}{2}$
(c) $\frac{a}{2\sqrt{2}}, \frac{a}{2}$ (d) $\frac{\sqrt{3}a}{4}, \frac{a}{2}$

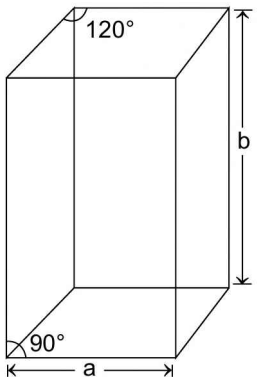
6. Which of the following statements for crystals having Schottky defect is not correct?
(a) Schottky defect arises due to the absence of a cation or anion from the position which it is expected to occupy.
(b) Schottky defect are more common in ionic compounds with high co-ordination numbers.
(c) The density of the crystals having Schottky defect is larger than that of the perfect crystal.
(d) The crystal having Schottky defect is electrical neutral as a whole.

7. When heated above 916°C, iron changes its bcc crystalline form to fcc without the change in the radius of atom. The ratio of density of the crystal before heating and after heating is:
(a) 1.069 (b) 0.918
(c) 0.725 (d) 1.231

8. The density of solid argon (Ar = 40 g/mol) is 1.68 g/mL at 40 K. If the argon atom is assumed to be a sphere of radius 1.50×10^{-8} cm, what % of solid Ar is apparently empty space? (use $N_A = 6 \times 10^{23}$)
(a) 35.64 (b) 64.36
(c) 74% (d) None of these

9. If an element (at. wt. = 50) crystallises in fcc lattice, with a = 0.50 nm. What is the density of unit cell if it contains 0.25% Schottky defects (use $N_A = 6 \times 10^{23}$)?
(a) 2.0 g/cc (b) 2.66 g/cc
(c) 3.06 g/cc (d) None of these

10. A_2B molecules (molar mass = 259.8 g/mol) crystallizes in a hexagonal lattice as shown in figure. The lattice constants were a = 5 Å and b = 8 Å. If density of crystal is 5 g/cm³ then how many molecules are contained in given unit cell? (use $N_A = 6 \times 10^{23}$)



(a) 6 (b) 4
(c) 3 (d) 2

11. Select right expression for determining Packing fraction (P.F.) of NaCl unit cell (assume ideal), if ions along an edge diagonal are absent:
(a) $\text{P.F.} = \frac{\frac{4}{3}\pi(r_+^3 + r_-^3)}{16\sqrt{2}r_-^3}$
(b) $\text{P.F.} = \frac{\frac{4}{3}\pi\left(\frac{5}{2}r_+^3 + 4r_-^3\right)}{16\sqrt{2}r_-^3}$

(c) P.F. $= \dfrac{\frac{4}{3}\pi\left(\frac{5}{2}r_+^3 + r_-^3\right)}{16\sqrt{2}r_-^3}$

(d) P.F. $= \dfrac{\frac{4}{3}\pi\left(\frac{7}{2}r_+^3 + r_-^3\right)}{16\sqrt{2}r_-^3}$

12. A body centered cubic lattice is made up of hollow spheres of B. Spheres of solid A are present in hollow spheres of B. Radius A is half of radius of B. What is the ratio of total volume of spheres of B unoccupied by A in a unit cell and volume of unit cell?

(a) $\dfrac{7\sqrt{3\pi}}{64}$ (b) $\dfrac{7\sqrt{3}}{128}$

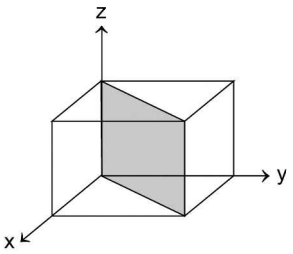
(c) $\dfrac{7.\pi}{24}$ (d) None of these

13. Which of the following compounds represent an inverse 2 : 3 spinel structure?

(a) Fe_3O_4 (b) PbO_2

(c) Al_2O_3 (d) Mn_3O_4

14. The Miller indices of the shaded plane shown in the figure below are

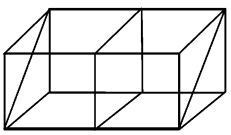


(a) (1 0 0) (b) $(1\ \bar{1}\ 0)$

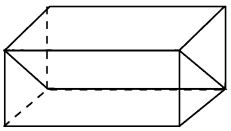
(c) (1 1 1) (d) (0 0 1)

15. Which of the following figures represents the (101) plane?

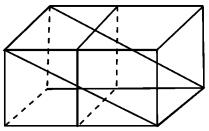
(a)



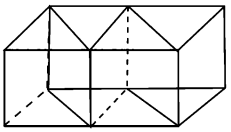
(b)



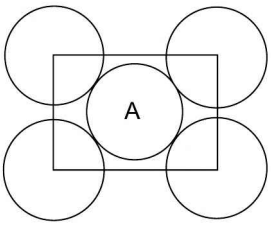
(c)



(d)



16. A solid having unit cell made up of planes as shown in Fig.

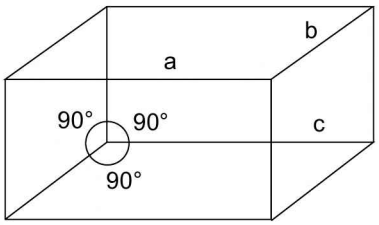


Co-ordination number of 'A' is

(a) 4 (b) 8

(c) 6 (d) 12

17. The unit cell with the structure below refers to ____ crystal system.



(a) cubic (b) orthorhombic

(c) tetragonal (d) trigonal

18. In second order Bragg diffraction of x-rays with λ = 1.00 Å from a set of parallel planes in a metal occurs at an angle of 60°. The distance between the scattering planes in the crystal is

(a) 0.575 Å (b) 1.00 Å

(c) 2.00 Å (d) 1.15 Å

19. The lattice energy of solid NaCl is 180 k cal/mole. The dissolution of the solid in water is the form of ions is endothermic to the extent of 1 kcal/mole. If the solution energies of Na^+ and Cl^- are in the ratio of 6 : 5, what is the enthalpy of hydration of Na^+ ion.

(a) –85.6 k cal/mol (b) –97.5 k cal/mol

(c) 82.6 k cal/mol (d) 100 k cal/mol

20. The composition of a sample of Wustite is $Fe_{0.93}O$. What is the percentage of iron present as Fe^{+3}?

(a) 15% (b) 25%

(c) 35% (d) 45%

21. In fluorite structure (CaF_2)

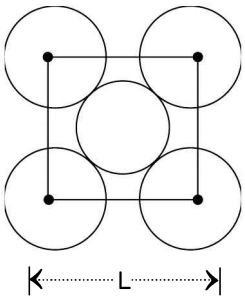
(a) Ca^{++} ions are ccp and F^- ions are present in all the tetrahedral voids

(b) Ca^{++} ions are ccp and F^- ions are present in all the octahedral voids

(c) Ca^{++} ions are ccp and F^- ions are present in all the octahedral voids and half of ions are

(d) None

22. The packing efficiency of the two-dimensional square unit cell shown below is



(a) 39.27% (b) 68.02%

(c) 74.05% (d) 78.54%

23. If the ratio of co-ordination number P to that of Q be Y:Z, then the formula of the solid is

(a) P_yQ_z (b) P_zQ_y

(c) $P_{1/y}Q_{1/z}$ (d) None

24. The number of unit cells in 58.8 g of NaCl approximately is

(a) 6×10^{20} (b) 3×10^{22}

(c) 1.5×10^{23} (d) 0.5×10^{24}

25. The number of atoms in 100 g of a FCC crystal with density 'd' = 10 g cm^{-3} and cell edge 200 pm are

(a) 3×10^{25} (b) 0.5×10^{25}

(c) 1.0×10^{25} (d) 2.0×10^{25}

26. In a fcc arrangement of A and B atoms, where A atoms are at the Corners of the unit cell, B atoms at the face centers, two atoms are missing from two corners in each unit cell, then the simplest formula of the compound is

(a) A_7B_6 (b) A_6B_7

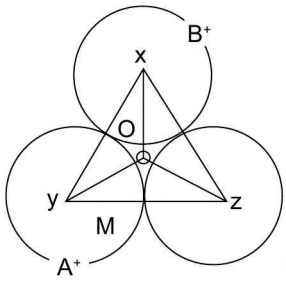
(c) A_7B_{24} (d) AB_4

27. A face-centered cubic arrangement has 'A' and 'B' atoms. 'A' atoms are at the corners of the unit cell and 'B' atoms are at the face centers. One of the 'A' atom is missing from one corner in the unit cell. The formula of the compound is

(a) A_7B_3 (b) AB_3

(c) A_7B_{24} (d) $A_{7/8}B_3$

28. In the following diagram, A^- ions of radius R are in contact with B^+ ions of radius r. Hence,



(a) $\frac{YM}{YO} = \cos 60^\circ = \frac{R}{R+r}$

(b) $\frac{YM}{YO} = \cos 30^\circ = \frac{R}{r}$

(c) $\frac{YM}{YO} = \cos 45^\circ = \frac{R}{R+r}$

(d) $\frac{YM}{YO} = \cos 30^\circ = \frac{R}{R+r}$

29. The percentage vacant space in one layer of square packing of spheres touching each other having 4 spheres is

(a) $\frac{3}{8}\pi \times 100$ (b) $100 - \frac{\pi}{6}$

(c) $\frac{3}{8}\pi$ (d) $100 - \frac{\pi}{6} \times 100$

30. The number of planes of symmetry which an HCP can have are

(a) 2 (b) 6

(c) 3 (d) 7

31. Analysis shows that an oxide ore of nickel has formula $Ni_{0.98}O_{1.00}$. The percentage of nickel as Ni^{3+} ions is nearly

(a) 2 (b) 96

(c) 4 (d) 98

32. The composition of a sample of wrustite is $Fe_{0.93}O_{1.00}$. Percentage of iron present in the form of iorn (III) is nearly

(a) 85 (b) 15

(c) 7.00 (d) 93.00

33. In an atomic bcc, what fraction of edge is not covered by atoms?

(a) 0.32 (b) 0.16
(c) 0.134 (d) 0.268

34. The packing efficiency of a simple cubic crystal with an interstitial atom exactly fitting at the body center is:
(a) 0.48 (b) 0.52
(c) 0.73 (d) 0.91

35. An atomic solid crystallizes in a body centre cubic lattice and the inner surface of the atoms at the adjacent corner are separated by 60.3 pm. If the atomic weight of A is 48, then density of the solid, is nearly.
(a) 2.7 g/cc (b) 5.07 g/cc
(c) 3.5 g/cc (d) 1.75 g/cc

36. Sodium (Na = 23) crystallizes in bcc arrangement with the interfacial separation between the atoms at the edge 53.6 pm. The density of sodium crystal is:
(a) 2.07 g/cc
(b) 2.46 g/cc
(c) 1.19 g/cc
(d) None of these

37. The density of solid argon (Ar = 40 g/mol) is 1.68 g/mL at 40 K. If the argon atom is assumed to be a sphere of radius 1.50×10^{-8} cm, what % of solid Ar is apparently empty space?
(use $N_A = 6 \times 10^{23}$)
(a) 35.64 (b) 64.36
(c) 74% (d) None of these

$= \frac{14}{93} \times 100 = 15.05$

38. First three nearest neighbour distances for body centered cubic lattice are respectively:
(a) $\sqrt{2}a$, a, $\sqrt{3}$ a
(b) $\frac{a}{\sqrt{2}}$, a, $\sqrt{3}a$
(c) $\frac{\sqrt{3}a}{2}$, a, $\sqrt{2}a$
(d) $\frac{\sqrt{3}a}{2}$, a, $\sqrt{3}a$

39. How many unit cells are present in 5.0 g of crystal AB (formula mass of AB = 40) having rock salt type structure? (N_A = Avogadro's number)
(a) N_A (b) $\frac{N_A}{10}$
(c) $4N_A$ (d) None of these

40. CdO has NaCl structures with density 8.27 g/cc. If the ionic radius of O^{2-} is 1.24 Å, determine ionic radius of Cd^{2+}:
(a) 1.5 Å (b) 1.1 Å
(c) 1.9 Å (d) 1.5 Å

41. KC1 crystallizes in the same type of lattice as does NaCl. Given that $r_{Na^+}/r_{Cl^-} = 0.50$ and $r_{Na^+}/r_{K^+} = 0.70$ calculate the ratio of the side of the unit cell for KC1 to that for NaCl:
(a) 1.143 (b) 1.224
(c) 1.414 (d) 0.875

42. Ferrous oxide has a cubic structure and edge length of the unit cell is 5.0 Å. Assuming the density of ferrous oxide to be 3.84 g/cm³, the number of Fe^{2+} andO^{2}" ions present in each unit cell be: (use $N_A = 6 \times 10^{23}$):
(a) $4Fe^{2+}$ and $4O^{2-}$
(b) $2Fe^{2+}$ and $2O^{2-}$
(c) 1 Fe^{2+} and $1O^{2-}$
(d) 3 Fe^{2+} and $4O^{2-}$

43. If an element (at. wt. = 50) crystallises in fee lattice, with a = 0.50 nm. What is the density of unit cell if it contains 0.25% Schottky defects (use $N_A = 6 \times 10^{23}$)?
(a) 2.0 g/cc (b) 2.66 g/cc
(c) 3.06 g/cc (d) None of these

44. The distance between an octahedral and tetrahedral void in fcc lattice would be:
(a) $\sqrt{3}$ a (b) $\frac{\sqrt{3}a}{2}$
(c) $\frac{\sqrt{3}a}{3}$ (d) $\frac{\sqrt{3}a}{4}$

45. KCl crystallizes in the same type of lattice as does NaCl. Given that $r_{Na^+}/r_{Cl^-} = 0.55$ and $r_{K^+}/r_{Cl^-} = 0.74$. Calculate the ratio of the side of the unit cell for KCl to that of NaCl
(a) 1.123 (b) 0.891
(c) 1.414 (d) 0.414

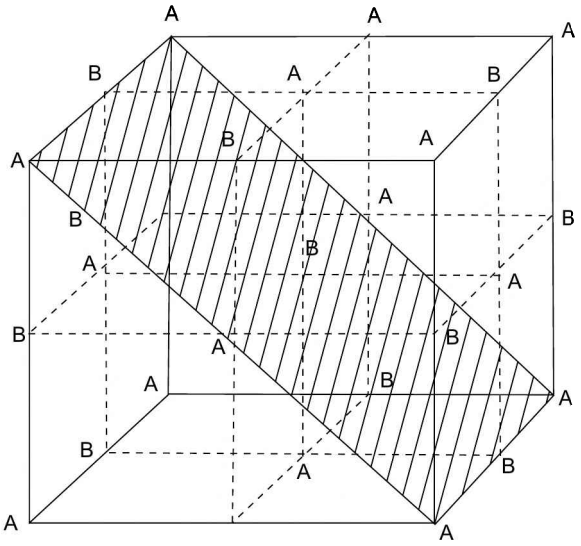
46. Graphite has h.c.p. arrangements of carbon atoms and the parallel planes are 3.35 $\mathring{A}$ apart. Determine density of graphite:

(a) 2.46 g/cc (b) 0.41 g/cc
(c) 1 g/cc (d) 1.41 g/cc

47. A crystal is made of particles X and Y. X forms fcc packing and Y occupies all the octahedral voids. If all the particles along one body diagonal are removed then the formula of the crystal would be:

(a) X_4Y_3
(b) X_5Y_4
(c) X_4Y_5
(d) None of these

48. A crystal is made of particles X, Y and Z. X forms fcc packing. Y occupies all the octahedral voids of X and Z occupies all the tetrahedral voids of X. If all the particles along the plane as shown in figure are removed, then, the formula of the crystal would be:



(a) $X_5Y_5Z_8$ (b) $X_5Y_7Z_8$
(c) $X_7Y_5Z_4$ (d) None of these

ANSWER KEYS

1. (d)	**2.** (a)	**3.** (b)	**4.** (b)	**5.** (d)	**6.** (c)	**7.** (b)	**8.** (b)	**9.** (b)	**10.** (d)
11. (b)	**12.** (d)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (d)	**17.** (b)	**18.** (d)	**19.** (a)	**20.** (a)
21. (a)	**22.** (d)	**23.** (b)	**24.** (c)	**25.** (b)	**26.** (d)	**27.** (c)	**28.** (d)	**29.** (d)	**30.** (d)
31. (c)	**32.** (b)	**33.** (c)	**34.** (c)	**35.** (d)	**36.** (c)	**37.** (b)	**38.** (c)	**39.** (d)	**40.** (b)
41. (a)	**42.** (a)	**43.** (b)	**44.** (d)	**45.** (a)	**46.** (a)	**47.** (b)	**48.** (a)		

HINTS AND EXPLANATIONS

1. (d) Since there are six atoms (A) in the corner of the unit cell. So, contribution of atoms in 1 unit cell is $\frac{6}{8}$.

Since 3 face-centered atoms (b) contributes to one unit cell,

So, formula is $A_{6/8}B_3$
or A_6B_{24}, or AB_4

2. (a) Four atoms (p) contributes to one unit cell from ccp arrangement and 4-atoms (Q) from the all octahedral voids and 4-atoms (Q) from the half of the tetrahedral void contributes one unit cell.

So, formula of solid is P_4Q_8 so, the simplest formula of the solid is PQ_2

3. (b) The complex $[Ni(CN)_4]^{-2}$ is square planar. So, it has limiting radius ratio as octahedral structure i.e., 0.414 – 0.732

4. (b) Since the ratio of the co-ordination number P to that of Q is Y : Z

i.e., P is surrounded by Y atoms of Q and Q is surrounded by Z atoms of P

i.e., number of atoms of P is Z

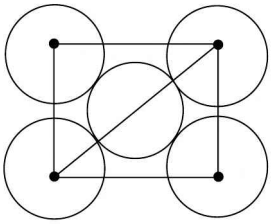
and number of atoms of Q is Y

So, the formula is P_ZQ_Y

21. (a) Ca^{2+} ions are ccp and F^- ions are present in the tetrahedral voids. So, the number of Ca^{2+} ions is 4 and number of F^- ions is 8.

So, the formula of the Calcium fluoride Ca_4F_8 or, the simplest formula of calcium fluoride is CaF_2

22. (d)



$a = (2\sqrt{2}r)$

$$P.F. = \frac{2 \times \pi r^2}{(2\sqrt{2}r)^2} = \frac{2\pi r^2}{8r^2} = \frac{\pi}{4}$$

The complex $[Ni(CN)_4]^{-2}$ is square planar. So, it has limiting radius ratio as octahedral structure i.e., 0.414 – 0.732

23. (b) Since the ratio of the co-ordination number P to that of Q is Y : Z
i.e., P is surrounded by Y atoms of Q and Q is surrounded by Z atoms of P
i.e., number of atoms of P is Z
and number of atoms of Q is Y
So, the formula is P_ZQ_Y.

24. (c) 58.5 g NaCl = 1.0 mole = 6.023×10^{23} Na^+ and 6.023×10^{23} Cl^-.
Each unit cell contains 4 Na^+ and 4 Cl^-
Number of unit cell = $6.023 \times 10^{23}/4$.

25. (b) $$M = \frac{\rho \times a^3 \times N_a \times 10^{-3}}{Z}$$

Where, Z = Number of atoms per unit cell
M = Atomic mass of the element
a = Edge of the unit cell (in pm)
N_a = Avogadro Number

$$\rho = \frac{10 \times (200)^3 \times 6.023 \times 10^{23} \times 10^{-30}}{4}$$

density in gm/cm^3

$$M = \frac{6.02 \times 10^{23} \times 100}{12.04} = 0.5 \times 10^{25}$$

$M = 12.04$

12.04 g of crystal contain 6.02×10^{23} atoms
100 g of crystal contain atoms

26. (d) There are six atoms (A) in the corner of the unit cell. So, contribution of atoms in 1 unit cell is $\frac{6}{8}$.
Since 3 face-centered atoms (B) contributes to one unit cell
So, formula is $A_{6/8}B_3$
or A_6B_{24}, or AB_4

27. (c) Since one 'A' atom is missing from one corner, the number of 'A' atoms per unit cell = atoms.
Number of atoms 'B' present at the face centres =
Therefore, A : B = 7/8 : 3. The formula is A_7B_{24}.

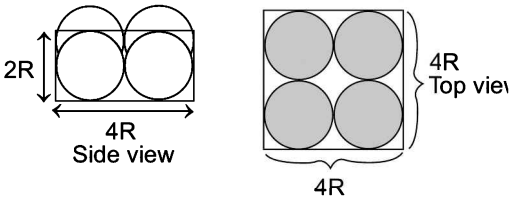
28. (d) In the figure x, y, z is an equilateral triangle.
YO bisects angle x y x.
$\Rightarrow \angle OYM = 30^\circ$

$$\cos\theta = \frac{\text{Base}}{\text{Hypotenuse}} = \frac{YM}{YO} = \cos 30^\circ$$

$$= \frac{R}{R+r} = \cos 30^\circ$$

Hence, choice (d) is correct while (a), (b) and (c) are incorrect.

29. (d)



Volume of cuboid box = $l \times b \times h = 4R \times 4R \times 2R = 32\,R^3$

Volume of one sphere = $\frac{4}{3}\pi R^3$

There are 4 spheres in the cuboid.

Volume of 4 sphere = $\frac{16}{3}\pi R^3$

% vacant space = 100 – % volume occupied = 100 – 100 × Packing fraction

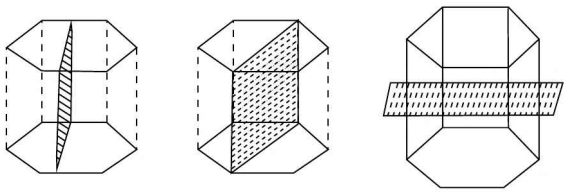
$$PF = \frac{\text{volume occupied by spheres}}{\text{Total volume}}$$

$$= \frac{16}{3}\pi R^3/32R^3 = \frac{\pi}{6}$$

$$\Rightarrow \%\text{ vacant space} = 100 - \frac{\pi}{6} \times 100 = 100\left(1 - \frac{\pi}{6}\right)$$

Hence, choice (d) is correct while (a), (b) and (c) are incorrect.

30. (d)



Rectangular plane of symmetry | Diagonal plane | Rectangle plane

There are 3 vertical rectangular planes of symmetry
There is 1 horizontal rectangular planes of symmetry
There are 3 vertical diagonal planes of symmetry
Hence, there are total of 7 planes of symmetry.

31. Let number of nickel ions = 98

$\therefore$ Number of oxide ions = 100

Total negative charge on O^{2-} ions

$= 2 \times 100 = 200$

Let number of Ni^{3+} ions = x

$\therefore$ Number of Ni^{2+} ions = 98–x

$x \times 3 + (98-x) \times 2 = 200$

$3x - 2x = 200 - 196$

$x = 4$

Percentage of nickel as Ni^{3+}

$$= \frac{4}{98} \times 100 = 4.08$$

32. Let the sample contains 93 iron ions and 100 oxide ions

Total negative charge on oxide ions

$= 2 \times 100 = 200$

Let number of ions as Fe^{3+} = x

$\therefore$ Number of Fe^{2+} ions = 93–x

$x \times 3 + (93-x)2 = 200$

$3x - 186 - 2x = 200$

$x = 200 - 186$

$x = 14$

Percentage of iron as Fe^{3+}.

45. (a) $\frac{r_{Na^+}}{r_{Cl^-}} = 0.55, \frac{5_{K^+}}{r_{Cl^-}} = 0.74$

$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 1.55 \quad \text{.... (1)}$$

$$\frac{r_{K^+}}{r_{Cl^-}} + 1 = 1.74 \quad \text{.... (2)}$$

Dividing (2) by (1)

$$\frac{1.74}{1.55} = \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}}$$

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.122$$

ONE OR MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

1. In α-WCl_6,

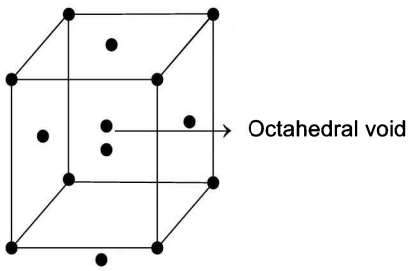
(a) all Cl^- ions are present in cubic close packing.
(b) W occupies, 1/6th of the octahedral holes.
(c) W occupies 1/3rd of the tetrahedral holes.
(d) All Cl^- ions are present in all octahedral.

2. Select the correct statement(s):

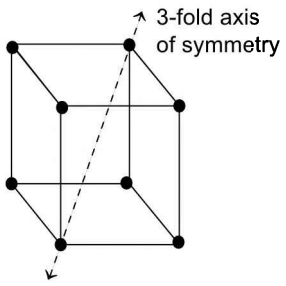
(a) The co-ordination number of each type of ion in a CsCl crystal is twelve
(b) A metal that crystallizes in a bcc structure has a co-ordination number of twelve
(c) A unit cell of an ionic crystal shares some of its ions with other unit cells
(d) The length of the unit cell in NaCl in 532 pm (given that r_{Na^+} = 85 pm and r_{Cl^-} = 181 pm)

3. Which of the following statements are correct?

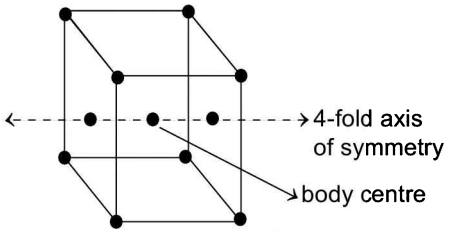
(a)



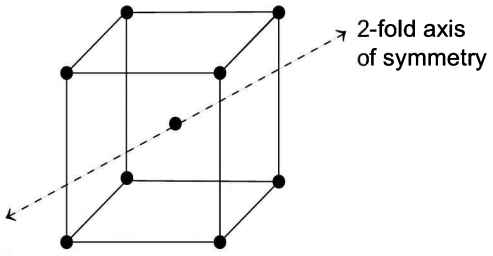
(b)



(c)



(d)



4. Which of the following statements are correct?

(a) A NaCl type AB crystal lattice can be interpreted to be made up of two individual FCC type unit lattice of A^+ and B^- fused together in such a manner that the corner of one unit lattice becomes the edge centre of the other.

(b) In a face centred unit lattice, the body centre is an octahedral void.

(c) In an SCC lattice, there can be no octahedral void.

(d) In an SCC lattice, the body centre is the octahedral void.

5. Which of the following exhibit Frenkel defects?

(a) AgBr (b) AgCl

(c) KBr (d) ZnS

ANSWER KEYS

1. (a, b) **2.** (c, d) **3.** (a, b, c) **4.** (a, b, c) **5.** (a, b, d)

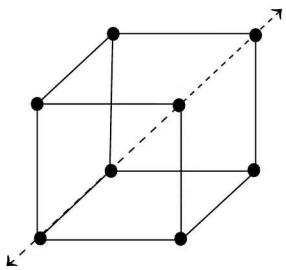
HINTS AND EXPLANATIONS

1. (a, b) In $\alpha - |x|Cl_6$, Cl^- ions are arranged in cubic close packing, so, there is only one Cl^- ion in 1-unitcell. So, the formula can be written $W_{1/6}Cl$, i.e., $\frac{1}{6}$ of the octahedral hole is filled by W.

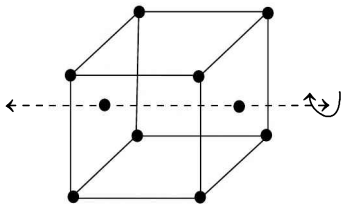
3. (a, b, c) (a) is correct. The body centre of simple cubic closed pack is equal to a octahedral void

(b) is correct. The line joining the diagonally opposite coners of a cube is called the 3-fold axis of symmetry.

(c) is correct. The joining the centers of 2-opposite faces of a cube is called the 4-fold axis of symmetry.

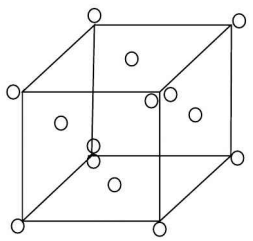


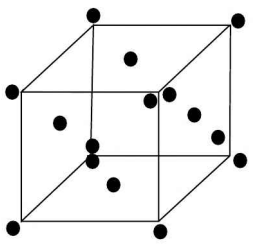
4-fold axis of symmetry

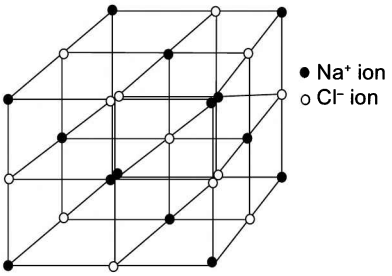


4-fold axis of symmetry

4. (a, b, c): (a) is correct

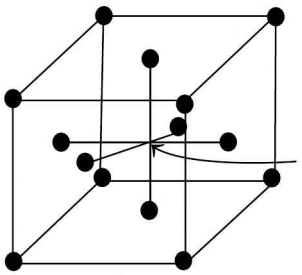






One NaCl is said to be made of one Na^+ FCC and one Cl^- FCC both fused together.

Choice (*b*) is correct This is the body centred and this is also an octahedral void. Hence, choice (b) is correct.



5. (a, b, d) show Frenkel because cation and anion differ in size appreciably whereas (c) does not.

COMPREHENSION BASED QUESTIONS

COMPREHENSION-I

PASSAGE-2

A spinel is an important class of oxides consisting of two types of metal ions with the oxide ions arranged in ccp layers. The normal spinel has one eighth of the tetrahedral holes occupied by one type of metal ion and one-half of the octahedral holes occupied by another type of metal ion. Such a spinel is formed by Zn^{+2}, Al^{3+} and O^{2-}. The neutrality of the crystal is being maintained.

1. The formula of the spinel is
(a) $ZnAl_2O_4$
(b) Zn_2AlO_4
(c) both A and B
(d) None

2. Types of hole occupied by Zn^{+2} ion is
(a) octahedral (d) tetrahedral
(c) both a and b (d) None

3. If all the species touch each other, the fraction of volume occupied in the unit cell
(a) 0.74 (b) 0.52
(c) 0.68 (d) None of these

4. If oxide ion is replaced by $X^{-8/3}$, the number of anionic vacancy per unit cell is
(a) 1 (b) 2
(c) 3 (d) none

5. Types of hole occupied by Al^{+3} ion is
(a) tetrahedral (b) octahedral
(c) both A and B (d) None

ANSWER KEYS

1. (a) **2.** (b) **3.** (d) **4.** (a) **5.** (b)

ASSERTION/REASON TYPE QUESTIONS

Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 **is** a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 **is NOT** a correct explanation for Statement-1.
(c) Statement-1 is True, Statement-2 is False.
(d) Statement-1 is False, Statement-2 is True.

1. **Statement-1**
   Due to Frenkel effect, there is no effect on the density of crystalline solid.
   Statement-2
   In Frenkel defect, no cation or anion leaves the crystal.
2. **Statement-1**
   In metals width of forbidden zone is zero. In semiconductor width of forbidden zone is very low.
   Statement-2
   As soon as potential difference is applied the electron jumps to conduction band from valence band and conduct electric current.
3. **Statement-1**
   The presence of a large number of Schottky defect in NaCl lowers its density.
   Statement-2
   In NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature.
4. **Statement-1**
   All the alkaline-earth oxides except BeO have NaCl structure.
   Statement-2
   Be atom is so small that it involve strong oxygen-oxygen repulsion and to avoid this actual structure of BeO is Wurtzite.
5. **Statement-1**
   Large number of Frenkel defect is lead to lowering in density of crystal lattice.
   Statement-2
   The defect is due to missing of ions at lattice and found in some where in inter stitial site.

ANSWER KEYS

1. (a) **2.** (b) **3.** (b) **4.** (a) **5.** (a)

TRUE/FALSE TYPE QUESTIONS

1. Initially the term pseudo solid was given for solids which were easily distorted by bending and compressing forces. The even tend to flow slowly under its own weight and lose shape.
2. The close packing of atoms in cubic structure is in the order fcc > bcc > sc.
3. Bragg's equation has no solution if $n = 2$ and $\lambda > d$
4. 6 : 6 co-ordination at normal temperature and pressure changes to 8 : 8 co-ordination at high pressure.
5. Solids containing F-centres are diamagnetic.

ANSWER KEYS

1. T **2.** T **3.** T **4.** T **5.** F

Question Bank

COMPREHENSION BASED QUESTIONS

COMPREHENSION-1

When an atom or an ion is missing from its normal lattice site, a lattice vacancy (Schottky defect) is created. In stoichionetric ionic crystals, a vacancy of one on has to be accompanied by the vacancy of the oppositely charged ion in order to maintain electrical neutrality.

In a Frenkel defect, an ion leaves its position in the lattice and occupies an interstitial void. This is the Frenkel defect commonly found along with the Schottky defects and interstitial. In pure alkali halides, Frenkel defects are not found since the ions cannot get into the interstitial sites. Frenkel defects are found in silver halides because of the small size of the Age ion. Unlike Schottky defects, Frenket defects do not change the density of the solids. In certain ionic solids (e.g. AgBr) both Schottky and Frenkel defects occur.

The defects discussed above do not disturb the stoichiometry of the crystalline material. There is large variety of Non-stoichiometric inorganic solids which contain an excess or deficiency of one of the elements. Such solids showing deviations from the ideal stoichiometric composition form an important group of solid. For example, in the vanadium oxide, VO_x, x can be anywhere between 0.6 and 1.3. There are solids which are difficult to prepare in the stoichiometric composition. Thus, the ideal composition in compounds such as Fe0 is difficult to obtain (normally we get a composition of $Fe_{.96}O$, but it may range from FeO_{93} 0 to $Fe_{.96}O$). Non-stoichiometric behaviour is mostcominonly found for transition metal compounds though is also known for some Ianthanoids and actinoids.

Zinc oxide loses oxygen reversibly at high temperatures and turns yellow in colour. The excess metal is accommodated interstitially, giving rise to electrons trapped in the neighbourhood. the enhanced electrical conductivity of the non-stoichiometric ZnO arises from these electrons.

Anion vacancies in alkali halides are produced by heating the alkali halide crystals in an atmosphere of the alkali metal vapour. When the metal atoms deposit on the surface they diffuse into the crystal and after ionisation the alkali metal ion occupies cationic vacancy whereas electron occupies anionic vacancy. Electrons trapped in anion vacancies are referred to as F-centres (from Farbe the German word for colour) that gives rise to interesting colour in alkali halides. Thus, the excess of potassium in KCI makes the crystal appear violet and the excess of lithium in LiCI makes it pink.

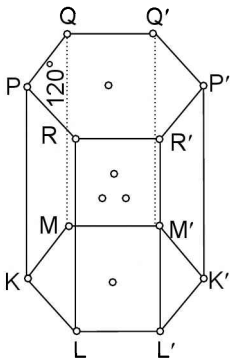
1. The type of semicondution shown by crystal capable of showing Schottky defect, will be.

(a) p - type (b) n - type
(c) both (d) None

2. Which of the following is most appropriate crystal to show Freckle defect.

(a) CsCI (b) NaCI
(c) AgBr (d) $CaCl_2$

3. In the crystal of $Fe_{0.93}O$, the percentage of Fe(III) will be



(a) 15% (b) 85%
(c) 30% (d) 78%

COMPREHENSION-2

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-

filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible.

There spheres are then placed cver the first layer, so that, they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with third layer that is identical to the bottom layer in relative position.

Total number of atoms per unit = $\frac{1}{6}$ (corners atoms) + $\frac{1}{2}$ (face-atoms) + 3 (body centered atoms).

$$= \frac{1}{6}\times 12 + \frac{1}{2}\times 2 + 3 = 2 + 1 + 3 = 6.$$

4. If in place of above HCP, close packing of sphere is changed such that 4 body centered atoms are arranged in middle layer, 4 atoms above the middle layer and 4 below the middle layer, what will be the co-ordination number of new closed packed arrangement?

(a) 12 (b) 13

(c) 14 (d) cannot be predicted.

5. If the angles $\angle$Q'QP be changed to 150°, then what will be the contribution of atom at this position per unit cell?

(a) $\frac{1}{24}$ (b) $\frac{1}{12}$

(c) $\frac{1}{6}$ (d) $\frac{5}{24}$

6. If only the angles of position P, P′, K and K′ is changed from 120° to 60°, and the angle of positions Q, Q′, R, R′, M, M′, L and L′ is changed from 120° to 150° shown in figure, then what will be effect in density of the crystal?

(a) will decrease

(b) will increase

(c) no effect

(d) cannot be predicted.

COMPREHENSION-3

Only those atoms which form four covalent bonds produce a repetitive three dimesional structure using only covalent bonds, e.g., diamond structure. The latter is based on a FCC lattice, where lattice points are occupied by carbon atoms. Every atom in this structure is surrounded tetrahedrally by four others. Germanium, silicon and grey tin also crystallize in the same way as diamond. (Given : $N_A = 6 \times 10^{23}$, sin 54°44′ = 0.8164).

7. If edge length of the cube is 3.60A, then radius of carbon atom is

(a) 0.78 A (b) 0.92 A

(c) 0.64 A (d) 0.35 A.

8. If the edge length is 3.60A, density of diamond crystal is

(a) 3.92 gm/cc (b) 2.40 gm/cc

(c) 3.37 gm/cc (d) 2.58 gm/cc.

9. Total number of diamond unit cells in 1.2 gm of diamond sample is

(a) 6.0×10^{21} (b) 6.0×10^{22}

(c) 7.5×10^{21} (d) 5.0×10^{22}.

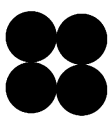
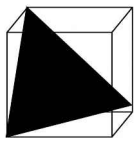
MATCH THE COLUMN TYPE QUESTIONS

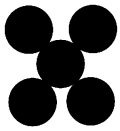
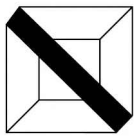
10. Match the column:

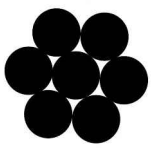
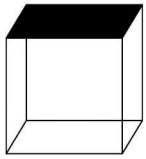
Column-I	**Column-II**
(a) Cubic	(p) Have 2-fold axis of symmetry.
(b) Orthorhombic	(q) Have all axial angles identical.
(c) Tetragonal	(r) Have all edge lengths identical.
(d) Rhombohedral	(s) More than one types of Bravias lattices are found.

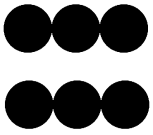
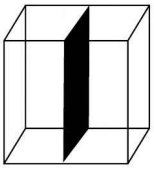
11. Match the followings

Column 1 (Arrangement of the atoms/ions) Column II (Planes in fcc lattice)

(a)  (p) 

(b)  (q) 

(c)  (r) 

(d)  (s) 

12. Match the column

Column-1	Column-II
(a) AB (Zinc blended)	(p) $d(gm/cm^3) = \frac{4 \times \text{molar mass}}{\text{Avogardo's number} \times \text{Volume of unit cell}}$
(b) AB (Rock salt)	(q) All the voids along one of the body diagonal are not occupied
(c) AB_2 (Fluorite)	(r) Voids along one face plane are not occupied.
(d) AB_2(Anti-Fluorite)	(s) Anion & cation have similar surroundings.

SUBJECTIVE

13. Ionic solid BMA^- crystallizes in rock salt type of structure. 1.296 gm ionic solid salt B^+A^- is dissolved in water to make one litre solution. The pH of the solution is measured to be 6.0. If the value of face diagonal in the unit cell of B^+A^- be 600. $\sqrt{2}$ pm. Calculate the density of ionic solid in gm/cc. [T = 298 K, K_b for BOH is 10^{-5}, (Avogadro Number = 6.0×10^{23})]

LONG SUBJECTIVE

14. A group 3A metal has a density of 2.7 g/cm³ and a cubic unit cell with an edge length of 405.5 pm. Reaction of a 1 cm³ chunk of the metal with an excess of hydrochloric acid gives a colourless gas that occupies 4 L at 27°C and a pressure of 701.1 mm Hg. (R = 0.082 It-atm/mol-K, $\mathbf{N_A} = 6 \times 10^{23}$, $\sqrt[3]{66.67} = 405.5$ pm),

(a) Identify the metal?

(b) Is the unit cell primitive, body-centered, or face-centered?

What is the atomic radius of the metal atom in picometers?

15. A solid cube of edge length = 25.32 mm of an ionic compound which has NaCItype lattice is added to 1kg of water. The boiling point of this solution is found to be 100.52°C (assume 100% ionisation of ionic compound). If radius of anion of ionic solid is 200 pm, then calculate radius of cation of solid in pm′ (picometer).

(K_b of water = 0.52 K kg mole¹, Avogadro's number, $N_A = 6 \times 10^{23}$, $(\sqrt[3]{75}) = 4.22$)

16. 5.35 g of a salt ACI (of weak base AOH) is dissolved in 250 ml of solution. The pH of the resultant solution was found to be 4.85. Find the ionic radius of A^+ & Cl^- if ACI forms CsCI type crystals having density 2 2g/cc .Given $K_b(AOH) = 2 \times 10^{-5}$ $\frac{r^+}{r^-} = 0.731$ for this unit cell.

ANSWER KEYS

1. (a) **2.** (c) **3.** (a) **4.** (a) **5.** (d) **6.** (a) **7.** (a) **8.** (c) **9.** (c)
10. (a – p, q, r, s), (b – p, q, s), (c – p, q, s), (d – p, q, r)
11. (a – r, s), (b – r, s), (c – p), (d – q)
12. (a – p, q, r, s), (b – p, q, r, s), (c – p, q, r), (d – p, q, r)
13. (4 g/cc) **14.** (a)

HINTS AND EXPLANATIONS

3. (a) $3x + (0.93 - x) \times 2 = 2$

$x = 0.14$

$\%$ of Fe as Fe (III) $= \frac{0.14}{0.93} \times 100 = 15\%$

6. (a) Any arrangement formed are less packed then closest packed arrangement.

7. (a) $4dc - c \sin(54°44') = \sqrt{2}$

$\Rightarrow r = \frac{d_{c-c}}{2} = 0.78$

8. (c) $d = \frac{8 \times 12}{N_A \times a^3} = 3.37$ gm/cc.

9. (c) Total number of unit cells $= \frac{1.2 \times N_A}{12 \times 8} = 7.5 \times 10^{21}$.

10. (a – p, q, r s), (b – p, q, s), (c – p, q, s), (d – p, q, r)

11. (a – r, s), (b – r, s), (c – p), (d – q)

12. (a – p, q, r, s), (b – p, q, r, s), (c – p, q, r), (d – p, q, r).

13. $pH = \frac{1}{2}\{pK_w - pK_b - \log C\}$

$\Rightarrow ,6 = 7.0 - \frac{5}{2} - \frac{1}{2}\log C$

$\Rightarrow C = 0.01M$

$\therefore \quad C = \dfrac{1.296}{\text{Molar mass}} = \dfrac{1}{100}$

$\Rightarrow$ molar mass of salt = 129.6

For rock salt $600\sqrt{2} = \sqrt{2}\ a$

$\therefore$ a = 600 pm = 600 × 10^{-10} cm.

Now density

$$= \frac{Z}{N_A}\left(\frac{M}{a^3}\right) = \frac{4}{6.0\times10^{23}}\left[\frac{129.6}{(600)^3\times10^{30}}\right] = 4\text{gm/cc.}$$

14. (a) Moles of H_2 gas $= \dfrac{701.1\times4}{760\times0.082\times300} = 0.15.$

$$M + 3H^+ \rightarrow M3+ + \frac{3}{2}H_2$$

$\therefore$ moles of M used = 0.1 $= \dfrac{2.7\times1}{\text{atomic weight}}$

$\Rightarrow$ atomic weight of metal = 27 gm/mol.

$\therefore$ metal is Al.

(b) Density $= \dfrac{Z}{N_A}\left(\dfrac{M}{a^3}\right)$

$$\Rightarrow 2.7 = \frac{Z}{6\times10^{23}}\left(\frac{27}{(405.5\times10^{-10})^3}\right)$$

$\Rightarrow$ Z = 4.

(c) For FCC unit cell, $4r = \sqrt{2}\ a$

$\Rightarrow$ r = 143.4 pm.

15. Effective molality of solution = 1

Hence, number of moles of ionic solid in given cube = 0.5

So, number of formula units in given cube = 0.5 × 6 × 10^{23}

Number of unit cells $= \dfrac{1}{4}\times0.5\times10^{23} = 7.5\times10^{22}$

Number of unit cells along one edge of cube = $\sqrt[3]{75}$ × 10^7 = 4.22 × 10^7

edge length of unit cell = a $= \dfrac{25.32\times10^{-3}}{4.22\times10^7}$

m = 600 × 10^{-12} m = 600 pm

for NaCl type unit cell, $a = 2(r_+ + r_-) \Rightarrow r_+ = 100$ pm.

16. **$r_+ = 126$ pm, $r_- = 171$ pm.**

$$pH = \frac{1}{2} \times [pK_w - pK_b - \log C]$$

$$\Rightarrow 4.85 = \frac{1}{2} \times [14 - 4.7 - \log C]$$

$\Rightarrow$ a = 3.43 × 10^{-8} cm.

$\therefore \quad C = 0.4 = \dfrac{5.35}{\text{molar mass}} \times 4$

$\Rightarrow$ molar mass of the salt = 53.5 gm/mole

Now, density $= \dfrac{1\times53.5}{6.022\times10^{23}\times a^3} = 2.2$

$\Rightarrow$ a = 3.43 × 10^{-8} cm.

and for CsCl type of crystals, $\sqrt{3}\ a = 2(r_+ + r_-)$

$\Rightarrow$ $r_+ = 1.26 \times 10^{-8}$ cm and $r_- = 1.71 \times 10^{-8}$ cm.

SUBJECTIVE ANSWER TYPE QUESTIONS

22. In a compound AB, the ionic radii of A^+ and B^- are 88 pm and 200 respectively. What is the co-ordination number of A^+?

Sol. Radius ratio $= \dfrac{r^+}{r^-} = \dfrac{88}{220} = 0.44$

The radius ratio lying in between 0.414 and 0.732 and thus, represents for octahedral voids. Also B^- is larger than A^+ and thus B^- forms closed packed structure and A^+ occupies the void space. Thus, co-ordination number of cation A^+ in AB is six.

23. A compound AB has rock type structure with A : B = 1 : 1. The formula weight of AB is 6.023y amu and the closest A – B distance is $y^{1/3}$ nm.
Calculate the density of lattice.

Sol. AB has rock salt (A : B :: 1: 1) structure, i.e., f.c.c. structure (n = 4) and formula weight of BB is 6.023 y g having closest distance A – B $y^{1/3}$ nm. Therefore edge length of unit cell

(a) = $2(A^+ + B^-) = 2 \times y^{1/3} \times 10^{-9}$m

$\therefore$ Density of AB $= \dfrac{n\times\text{mol.wt.}}{\text{Av. no.}\times V} = \dfrac{n\times\text{mol.wt.}}{6.023\times10^{23}\times a^3}$

$$= \frac{4\times6.023\times y\times10^{-3}}{6.023\times10^{23}(2y^{1/3}\times10^{-9})^3}\ (\text{mol. Wt. in kg})$$

$= 5.0\ \text{kg m}^{-3}$