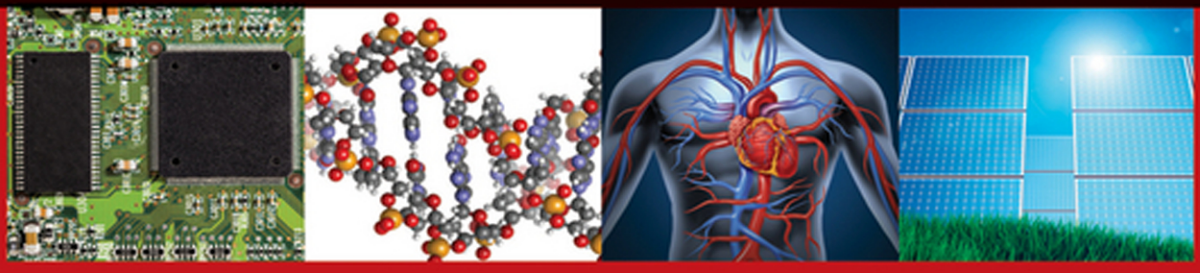
4TH EDITION

ELEMENTARY PRINCIPLES OF CHEMICAL PROCESSES



Richard M. Felder
Ronald W. Rousseau
Lisa G. Bullard

WILEY

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Elementary Principles of Chemical Processes

Richard M. Felder
Department of Chemical and Biomolecular Engineering
North Carolina State University
Raleigh, North Carolina

Ronald W. Rousseau
School of Chemical & Biomolecular Engineering
Georgia Institute of Technology
Atlanta, Georgia

Lisa G. Bullard
Department of Chemical and Biomolecular Engineering
North Carolina State University
Raleigh, North Carolina

WILEY

We dedicate this book to our first and most important teachers, our parents: Shirley and Robert Felder, Dorothy and Ivy John Rousseau, and Faye and Bobby Gardner.

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About the Authors

Richard M. Felder is Hoechst Celanese Professor Emeritus of Chemical Engineering at North Carolina State University. He received his B.Ch.E. degree from the City College of New York in 1962 and his Ph.D. in chemical engineering from Princeton University in 1966. He worked for the Atomic Energy Research Establishment (Harwell, England) and Brookhaven National Laboratory before joining the North Carolina State faculty in 1969. He is coauthor of *Teaching and Learning STEM: A Practical Guide* (Jossey-Bass, 2016), and he has authored or coauthored over 300 papers on chemical process engineering and engineering education and presented hundreds of invited talks, workshops, and short courses in both categories at conferences and to industrial and research institutions and universities throughout the United States and abroad. His honors include the International Federation of Engineering Education Societies Global Award for Excellence in Engineering Education (2010, first recipient), the ASEE Lifetime Achievement Award in Engineering Education (2012, first recipient), the ASEE Chester F. Carlson Award for innovation in engineering education, and the AIChE Warren K. Lewis Award for contributions to Chemical Engineering Education. He is a Fellow of the American Society for Engineering Education, and holds honorary doctorates from the State University of New York and the University of Illinois. Many of his education-related publications can be found at <*www.ncsu.edu/effective_teaching*>.

Ronald W. Rousseau holds the Cecil J. "Pete" Silas Chair in Chemical Engineering at the Georgia Institute of Technology, where he chaired the School of Chemical & Biomolecular Engineering from 1987 to 2014. He has B.S. and Ph.D. degrees in Chemical Engineering from Louisiana State University and a *Docteur Honoris Causa* from L'Institut National Polytechnique de Toulouse. An elected member of the LSU Engineering Hall of Distinction, he has served as executive editor of *Chemical Engineering Science*, topic editor for *Crystal Growth and Design*, consulting editor for the *AIChE Journal*, and associate editor of the *Journal of Crystal Growth* and editor of the *Handbook of Separation Process Technology*. His research in the field of separations has focused on crystal nucleation and growth, and applications of crystallization science and technology. From the American Institute of Chemical Engineers he received the AIChE Founders Award for outstanding contributions to the field of chemical engineering, the Warren K. Lewis Award for contributions to chemical engineering education, and the Clarence G. Gerhold Award for contributions to the field of chemical separations. The Chemical Engineering Division of ASEE presented him with a Lifetime Achievement Award, and the Council for Chemical Search selected him for the Mac Pruitt Award. He is a Fellow of both AIChE and the American Association for the Advancement of Science and has been a member of the AIChE Board of Directors and chair of the Council for Chemical Research.

Lisa G. Bullard is an Alumni Distinguished Undergraduate Professor and Director of Undergraduate Studies in the Department of Chemical and Biomolecular Engineering at North Carolina State University. After obtaining her BS in Chemical Engineering at NC State in 1986 and her Ph.D. in Chemical Engineering from Carnegie Mellon University in 1991, she served in engineering and management positions within Eastman Chemical Company in Kingsport, TN from 1991–2000. A faculty member at NC State since 2000, Dr. Bullard has won numerous awards for both teaching and advising, including the ASEE Raymond W. Fahien Award, the John Wiley Premier Award for Engineering Education Courseware, NC State Faculty Advising Award, National Effective Teaching Institute Fellow, NC State Alumni Outstanding Teacher Award, George H. Blessis Outstanding Undergraduate Advisor Award, the ASEE Martin Award, and the ASEE Southeastern Section Mid-Career Teacher Award. She is a past Chair of the Chemical Engineering Division of ASEE, editor of the "Lifelong Learning" column for *Chemical Engineering Education*, and a member of the 2017 ASEE Chemical Engineering Summer School planning team. Her research interests lie in the area of educational scholarship, including teaching and advising effectiveness, academic integrity, process design instruction, organizational culture, and the integration of writing, speaking, and computing within the curriculum.

Preface to the Fourth Edition

An introductory material and energy balance course traditionally plays several important roles in the chemical engineering curriculum. On the most obvious level, it prepares the student to formulate and solve material and energy balances on chemical process systems and lays the foundation for subsequent courses in thermodynamics, transport phenomena, separation processes, kinetics and reactor design, and process dynamics and control. More fundamentally, it introduces the engineering approach to solving process-related problems: breaking a process into its components, establishing the relations between known and unknown process variables, assembling the information needed to solve for the unknowns using a combination of experimentation, empiricism, and the application of natural laws, and, finally, putting the pieces together to obtain the desired problem solution.

We have tried in this book to fulfill each of these functions. Moreover, recognizing that the material and energy balance course is often the students' first real encounter with what they think may be their chosen profession, we have attempted to provide in the text a realistic, informative, and positive introduction to the practice of chemical engineering. In the first chapter we survey fields that recent chemical engineering graduates have entered and describe the variety of research, design, and production problems they might confront. In the rest of the book we systematically develop the structure of elementary process analysis: definitions, measurement and calculation of process variables, conservation laws and thermodynamic relations that govern the performance of processes, and physical properties of process materials that must be determined in order to design a new process or analyze and improve an existing one.

The chemical process constitutes the framework for the presentation of all of the text material. When we bring in concepts from physical chemistry such as vapor pressure, solubility, and heat capacity, we introduce them as quantities whose values are required to determine process variables or to perform material and energy balance calculations on a process. When we discuss spreadsheets and computational techniques, we present them on the same need-to-know basis in the context of process analysis.

Not much has happened to the laws of conservation of mass and energy or the basic principles of physical chemistry since the most recent edition of *Elementary Principles* appeared a decade ago, so instructors who used the third edition of the book will see some changes in the chapter texts, but they won't be dramatic. The biggest difference is in the problems, which reflect the broadening of the scope of chemical engineering during the lifetime of this book from almost exclusively industrial chemistry and petrochemicals to biomedical, biochemical, biomolecular, environmental, energy, materials, and safety applications. There are around 350 new and revised chapter-end problems in this edition, many of which address those diverse areas. In addition, an entirely new suite of resources for students and instructors has been assembled, including a spreadsheet-based tool that eliminates much of the drudgery of routine calculations that require large expenditures of time and have little instructional value.

The two authors of the first three editions acknowledge with gratitude the contributions of colleagues and students from the time work began on the book. Our thanks go to Dick Seagrave and the late Professors John Stevens and David Marsland, who read the first draft of the first edition and offered many suggestions for its improvement; our department head, the late Jim Ferrell, who gave us invaluable encouragement when we brashly (some might say, foolishly) launched into the book in our third year as faculty members; and our colleagues around the world who helped us prepare problems and case studies and suggested improvements to each successive edition. We raise our glasses to the students in the Fall 1973 offering of CHE 205 at N.C. State, who had the bad luck to get the first draft as a course text. We also thank the N.C. State graduate and undergraduate students who helped prepare the solution manuals, and the many N.C. State and Georgia Tech students who took the trouble to point out errors in the text. We know they did it out of a sense of professional responsibility and not just to collect the dollars.

The three authors of this edition thank our colleagues who contributed ideas for end-of-chapter problems in areas of expertise far removed from ours, whose names are acknowledged in footnotes. We are particularly grateful to Stephanie Farrell, Mariano Savelski, and Stewart Slater of Rowan University for contributing several excellent problems from a library of pharmaceutical engineering problems (see <*www.PharmaHUB.org*>). Support for the development of the library was provided by a grant from the National Science Foundation through the Engineering Research Center for Structured Organic Particulate Systems, ECC0540855.

Support for the development of the problems on climbing Kilimanjaro was provided by grants from the National Science Foundation through the Division of Undergraduate Education grants # 0088437 and 1140631. These problems were contributed by Stephanie Farrell of Rowan University.

Our heartfelt thanks also go to Emma Barber, Michael Burroughs, Andrew Drake, David Hurrelbrink, Samuel Jasper, Michael Jones, William Kappler, Katie Kirkley, Manami Kudoh, George Marshall, Jonathan Mihu, Adam Mullis, Kaitlyn Nilsen, Cailean Pritchard, Jordan Shack, Gitanjali Talreja, and Kristen

Twidt, who contributed to the development and testing of the fourth edition on-line content and solution manual, and especially to Karen Uffalussy, who meticulously read every sentence and equation in the manuscript and caught a frightening number of mistakes, some of which dated back to the first edition.

Finally, we thank our Wiley colleagues Dan Sayre and Jenny Welter for their help in bringing this and previous editions into existence; Rebecca, Sandra, and Michael for many years of unfailing encouragement and support; and the late Magnificent Mary Wade, who uncomplainingly and with great good humor typed revision after revision of the first edition, until the authors, unable to stand any more, declared the book done.

RMF
RWR
LGB

Notes to Instructors

Topical coverage

The organization of this text has been planned to provide enough flexibility to accommodate classes with diverse backgrounds within the scope of a one-semester or two-quarter course. We anticipate that semester-long courses in which most students have traditional first-year engineering backgrounds will cover most of the first nine chapters, and a one-quarter course should cover Chapters 1 through 6. Students who have been exposed to dimensional analysis and elementary data correlation can skip or skim Chapter 2, and students whose freshman chemistry courses provided a detailed coverage of process variable definitions and the systematic use of units to describe and analyze chemical processes may omit Chapter 3. The time gained as a result of these omissions may be used to cover additional sections in Chapters 4 through 9 or to add Chapter 10 on transient balances.

Teaching and promoting a systematic approach to process analysis

We have consistently found that the key to student success in this course is approaching problems systematically: drawing and labeling flow charts, counting degrees of freedom to make sure that problems are solvable, and formulating solution plans before doing any calculations. We have also found that students are remarkably resistant to this process, preferring to launch directly into writing equations in the hope that sooner or later a solution will emerge. The students who make the transition to the systematic approach generally do well, while those who continue to resist it frequently fail.

In our experience, the only way students learn to use this approach is by repeatedly practicing it. Hundreds of chapter-end problems in the text are structured to provide this practice. Representative assignment schedules are given in the instructor's resources, and there is enough duplication of problem types for the schedules to be varied considerably from one course offering to another.

Support for a wide range of course learning outcomes

Most of the problems in the book focus on setting up and solving basic material and energy balance problems, which is as it should be. Not all of them, however: many exercises focus on learning objectives beyond analytical problem-solving skills, including developing critical and creative thinking skills and understanding the industrial and social contexts of many of the processes treated in the chapter-end problems. (All of those learning outcomes, we might add, map onto required learning outcomes of the ABET Engineering Criteria.) Some of the exercises are included in the problems, and others are separate "*creativity exercises*" and "*explore and discover exercises*."

We encourage instructors to use these exercises as focal points for in-class activities, include them in homework assignments, and put similar exercises on tests after ample practice has been provided in assignments. The exercises can convey to the students a sense of the challenging and intellectually stimulating possibilities in a chemical engineering career, which may be the most important task that the introductory course can accomplish.

Digital Resources and *WileyPLUS*

WileyPLUS

WileyPLUS is an online environment that provides educational resources to teachers and students. When instructors choose to adopt *WileyPLUS* for their course, their students obtain access via a registration code that may be added to a print edition or purchased for online-only access. In this section, we first describe resources available to all users of *Elementary Principles of Chemical Processes*, and then we provide more information about the resources provided to instructors and students in classes in which *WileyPLUS* has been adopted.

Resources for all instructors

Two websites provide resources for instructors using the textbook.

- **Instructor Companion Website: www.wiley.com/college/felder**

This publisher-maintained site contains a section-problem concordance, sample assignment schedules, sample responses to creativity exercises, reproductions of selected figures from the text, solutions to chapter-end problems, a *Visual Encyclopedia of Chemical Engineering Equipment*, and *Notes with Gaps*, a resource new to the fourth edition. The password-protected site is accessible only to certified course instructors.

The ***Visual Encyclopedia of Chemical Engineering Equipment*** is an online tool developed by Susan Montgomery of the University of Michigan that provides photos, cutaway diagrams, videos, animations, and explanations of many common chemical processing equipment items. Icons referencing the Visual Encyclopedia are found throughout the text.

Notes with Gaps is an extensively class-tested set of lecture notes for Chapters 2–9 of the text. There are two versions of the set. One is for students and includes blank spaces (gaps) in which to fill in answers to imbedded questions, curves on plots for which only the axes are shown, stream labels on flowcharts, numbers in degrees-of-freedom analyses, and critical steps in derivations and problem solutions. On the second set of notes, which is for instructors, the gaps are filled in.

The student version of the notes can be loaded on a tablet computer and projected in class, or it can be printed, duplicated, and bound into a coursepack that students bring to every class session. The instructor can direct the students to read through completely straightforward parts of the notes (short simple paragraphs, definitions of terms and system variables, and routine algebraic calculations), which students can do in much less time than it would take to present the same information in a traditional lecture. When instructors reach gaps, they may either lecture on them traditionally or (better) direct the students to fill in the gaps in active learning exercises. The students don't have to spend a lot of time taking notes on straightforward content but can focus almost entirely on the key methods and concepts in the lecture, and they get practice and immediate feedback on hard or tricky parts of the methods. Research has shown that handing out partial notes of this type leads to deeper learning than either requiring students to take all their own notes or giving them complete sets of notes either before or after class.

- **Author-maintained website: http://epcp.wordpress.ncsu.edu**

This site contains frequently updated errata lists for the text, a website for the material and energy balance course with a sample syllabus and representative study guides and tests, and links to several publications describing how to teach the course effectively.

Resources for adopters of *WileyPLUS*

- **Introductory videos for all chapters.** The authors introduce each chapter, highlight important chapter content, and explain how the chapter fits in with the rest of the text, and the two original authors describe the history of the text. Award-winning professor Michael Dickey of North Carolina State University carries out demonstration experiments that illustrate key course concepts.
- **Algorithmic problems.** Individualized machine-gradable on-line homework problems (in which each student has unique values for key variables) can provide students with feedback, hints, and scaffolded tutorials to assist their learning. Instructors can determine the level of feedback (no feedback, final answer, full solution, or fully guided solution with feedback on each step) that students receive and the number of submissions that are allowed. Students can use on-line reading questions as a qualitative self-check to ensure that they have mastered the learning objectives for each section (similar to the more quantitative *Test Yourself* questions in the text), while instructor-assigned reading questions can be used to quiz students prior to class (in a flipped classroom environment) or after class.
- **APEx (Analyzing Processes with Excel)**, an Excel add-in developed by David Silverstein of the University of Kentucky, enables users to easily perform time-consuming tasks required to solve the text's chapter-end problems. APEx automates the processes of looking up physical properties of chemical species at specified phases, temperatures, and pressures; calculating vapor pressures and boiling points of species at specified temperatures or pressures; integrating tabulated heat capacity formulas to determine enthalpy changes for heating and cooling species between specified temperatures; inserting tabulated and calculated values into system equations; and solving the equations using Excel's Solver.
- **Library of case studies.** Nine case studies demonstrate the role of the calculations illustrated in Chapters 2–9 in the analysis of authentic industrial processes. The case studies are designed to be worked on as term projects by individuals or small teams of students.

Postscript: Introduction to an Author

Many instructors and students who have used this book can't tell you its title without looking at the cover. Since the first edition appeared in 1978, the text has generally been referred to as "Felder and Rousseau." The practice of using authors' last names to refer to textbooks is common, and it has become so universal for this one that one of us has occasionally begun talks by informing the audience that his first name is Ronald, not Felderand. So whether or not you know the title, if you've used the book before you probably noticed that the list of authors has metamorphosed in this edition to FelderandRousseauandBullard.

Who is Bullard, you might be asking. Before we formally introduce Lisa, let us give you a little history. We began work on this book when we were young untenured assistant professors. That was in 1972. By the time we started work on the fourth edition, we were neither untenured nor assistant professors, and you can do the math on "young" for yourself. We agreed that our careers and interests had moved in different directions, and if there were to be more editions after this one, someone else would have to play a major role in writing them. It made sense to bring in that individual to work with us and help assure a smooth transition in the future.

We quickly assembled a shopping list of desirable attributes for our future coauthor. We wanted to find an outstanding teacher with an extensive background in teaching material and energy balances; an experienced engineer with first-hand knowledge of both the science and the art of the practice of chemical engineering; and a good writer, who could carry on the work long after the original authors had begun to fully devote themselves to their children, grandchildren, good books, plays, operas, excellent food and wine, and occasional stays in five-star inns in the beautiful places in the world. (Look, you have your fantasies, we have ours.)

We found some excellent candidates, and then we got to Lisa Bullard and our search was over. Lisa was all of those things, as well as the finest academic advisor her N.C. State coauthor had ever seen or heard of and an author of papers and presenter of national and international seminars and workshops on effective teaching and advising. And so we invited her to join us, and she accepted. Our good fortune. And yours.

Felder & Rousseau

Nomenclature

The variables to be listed will be expressed in SI units for illustrative purposes, but they could be expressed equally well in any dimensionally consistent units.

a, b, c, d	Arbitrary constants, or parameters in an equation of state, or coefficients of a polynomial expression for heat capacity, such as those listed in Appendix B.2.
C_p[kJ/(mol·K)], C_v[kJ/(mol·K)]	Heat capacities at constant pressure and constant volume, respectively.
E_k(kJ), $\dot{E}_k$(kJ/s)	Kinetic energy, rate of kinetic energy transport by a flowing stream.
E_p(kJ), $\dot{E}_p$(kJ/s)	Potential energy, rate of potential energy transport by a flowing stream.
f	Fractional conversion.
$\hat{F}$(kJ/mol)	Friction loss.
g(m/s^2)	Gravitational acceleration constant, equal to 9.8066 m/s^2 or 32.174 ft/s^2 at sea level.
H(kJ), $\dot{H}$(kJ/s), $\hat{H}$(kJ/mol)	Enthalpy of a system (H), rate of transport of enthalpy by a process stream ($\dot{H}$), specific enthalpy ($\hat{H}$). $\hat{H} = \hat{U} + P\hat{V}$, all determined relative to a specified reference state.
m(kg), $\dot{m}$(kg/s)	Mass (m) or mass flow rate ($\dot{m}$) of a process stream or stream component.
M(g/mol)	Molecular weight of a species.
n(mol), $\dot{n}$(mol/s)	Number of moles (n) or molar flow rate ($\dot{n}$) of a process stream or stream component.
p_A(atm)	Partial pressure of species A in a mixture of gaseous species, $= y_A P$.
$p_A^*(T)$ (atm)	Vapor pressure of species A at temperature T.
P(atm)	Total pressure of a system. Unless specifically told otherwise, assume that P is absolute pressure and not gauge pressure.
P_c(atm)	Critical pressure. Values of this property are listed in Table B.1.
P_r	Reduced pressure. Ratio of system pressure to the critical pressure, P/P_c.
Q(kJ), $\dot{Q}$(kJ/s)	Total heat transferred to or from a system (Q), rate of heat transfer to or from a system ($\dot{Q}$). Q is defined to be positive if heat is transferred to the system.
R[kJ/(mol·K)]	Gas constant, given in different units on the inside back cover of the text.
SCMH, SCLH, SCFH.	Abbreviations for standard cubic meters per hour [m^3(STP)/h], standard liters per hour [L(STP/h)], and standard cubic feet per hour [ft^3(STP)/h], respectively: the volumetric flow rate of a gas stream if the stream were brought from its actual temperature and pressure to standard temperature and pressure (0°C and 1 atm).
SG	Specific gravity, or ratio of the density of a species to the density of a reference species. The abbreviation is always used for liquids and solids in this text and usually refers to species for which specific gravities are listed in Table B.1.
t(s)	Time.
T(K)	Temperature.
T_m, T_b, T_c(K)	Melting point temperature, boiling point temperature, and critical temperature, respectively. The *normal* melting and boiling points are the values of those properties at a pressure of one atmosphere. Values of these properties are listed in Table B.1.
T_r	Reduced temperature. Ratio of system temperature to the critical temperature, T/T_c.
u(m/s)	Velocity.
U(kJ), $\dot{U}$(kJ/s), $\hat{U}$(kJ/mol)	Internal energy of a system (U), rate of transport of internal energy by a process stream ($\dot{U}$), specific internal energy ($\hat{U}$).

v_A (m^3)	Pure component volume of species A in a mixture of gaseous species, $= y_A V$.
$V(m^3)$, $\dot{V}(m^3/s)$, $\hat{V}(m^3/mol)$	Volume (V), volumetric flow rate ($\dot{V}$) of a process stream, specific volume ($\hat{V}$) of a process material.
W(kJ), $\dot{W}_s$ (kJ/s)	Work transferred to or from a system (W), rate of transfer of shaft work to or from a continuous process system ($\dot{W}_s$). Work is defined to be positive (in this text) if it is transferred to a system from its surroundings.
x, y, z	Mass fraction or mole fraction of a species in a mixture. (Subscripts are usually used to identify the species.) In liquid-vapor systems, x usually denotes fraction in the liquid and y denotes fraction in the vapor. z may also denote the compressibility factor of a gas.

GREEK LETTERS

Δ	In batch (closed) systems, ΔX denotes the difference $X_{final} - X_{initial}$, where X is any system property. In continuous (open) systems, $\Delta\dot{X}$ denotes the difference $\dot{X}_{output} - \dot{X}_{input}$.
$\Delta\hat{H}^\circ_c$(kJ/mol)	Standard heat of combustion, the enthalpy change when one g-mole of a species at 25°C and 1 atm undergoes complete combustion and the products are at the same temperature and pressure. Standard heats of combustion are listed in Table B.1.
$\Delta\hat{H}^\circ_f$(kJ/mol)	Standard heat of formation, the enthalpy change when one g-mole of a species at 25°C and 1 atm is formed from its elements in their naturally occurring states (e.g., H_2, O_2). Standard heats of formation are listed in Table B.1.
$\Delta\hat{H}_m(T, P)$ (kJ/mol)	Heat of melting (fusion) at temperature T and pressure P, the enthalpy change when one g-mole of a species goes from solid to liquid at a constant temperature and pressure. Heats of melting at 1 atm and the normal melting point are listed in Table B.1.
$\Delta\hat{H}_v(T, P)$ (kJ/mol)	Heat of vaporization at temperature T and pressure P, the enthalpy change when one g-mole of a species goes from liquid to vapor at a constant temperature and pressure. Heats of vaporization at 1 atm and the normal boiling point are listed in Table B.1.
$\Delta H_r(T)$ (kJ)	Heat of reaction, the enthalpy change when stoichiometric quantities of reactants at temperature T react completely at constant temperature.
ν_A(mol), $\dot{\nu}_A$(mol/s)	Stoichiometric coefficient of species A in a chemical reaction, defined to be positive for products, negative for reactants. For $N_2 + 3H_2 \rightarrow 2NH_3$, $\nu_{N_2} = -1$ mol, $\nu_{H_2} = -3$ mol, $\nu_{NH_3} = 2$ mol.
ξ	Extent of reaction. If n_{A0} (mol) of reactive species A is initially present in a reactor and n_A (mol) is present some time later, then the extent of reaction at that time is $\xi = (n_{A0} - n_A)/\nu_A$, where ν_A (mol A) is the stoichiometric number of moles of A. If A is a product whose stoichiometric coefficient is 2, then ν_A in the equation for ξ would be 2 mol A; if A is a reactant, then ν_A would be −2 mol A. In a continuous system, n_A and ν_A would be replaced by $\dot{n}_A$(mol A/s) and $\dot{\nu}_A$ (mol A/s). The value of ξ is the same regardless of which reactant or product is chosen as species A.
ρ (kg/m^3)	Density.

OTHER SYMBOLS

$\dot{}$ (e.g., $\dot{m}$)	A dot over a term designates that it is a rate (e.g. mass flow rate).
$\hat{}$ (e.g., $\hat{U}$)	A caret over a term designates that it is a specific property, e.g. specific internal energy.
( )	Parentheses are used to express functional dependence, as in $p^*(T)$ to denote a vapor pressure that depends on temperature, and also to enclose units of variables, as in m(g) to denote a mass expressed in grams.

Glossary of Chemical Process Terms

Glossary terms indicated with @ can be found in the Equipment Encyclopedia at www.wiley.com/college/felder.

@ **Absorption** A process in which a gas mixture contacts a liquid solvent and a component (or several components) of the gas dissolves in the liquid. In an *absorption column* or *absorption tower* (or simply *absorber*), the solvent enters the top of a column, flows down, and emerges at the bottom, and the gas enters at the bottom, flows up (contacting the liquid), and leaves at the top.

Adiabatic A term applied to a process in which no heat is transferred between the process system and its surroundings.

@ **Adsorption** A process in which a gas or liquid mixture contacts a solid (the *adsorbent*) and a mixture component (the *adsorbate*) adheres to the surface of the solid.

Barometer A device that measures atmospheric pressure.

@ **Boiler** A process unit in which tubes pass through a combustion furnace. *Boiler feedwater* is fed into the tubes, and heat transferred from the hot combustion products through the tube walls converts the feedwater to steam.

Boiling point (at a given pressure) For a pure species, the temperature at which the liquid and vapor can coexist in equilibrium at the given pressure. When applied to the heating of a mixture of liquids exposed to a gas at the given pressure, the temperature at which the mixture begins to boil.

Bottoms product The product that leaves the bottom of a distillation column. The bottoms product is relatively rich in the less volatile components of the feed to the column.

Bubble point (of a mixture of liquids at a given pressure) The temperature at which the first vapor bubble appears when the mixture is heated.

Calibration (of a process variable measurement instrument) A procedure in which an instrument is used to measure several independently known process variable values, and a *calibration curve* of known variable values versus the corresponding instrument readings is plotted. Once the instrument has been calibrated, readings obtained with it can be converted to equivalent process variable values directly from the calibration curve.

@ **Catalyst** A substance that significantly increases the rate of a chemical reaction although it is neither a reactant nor a product.

Compressibility factor, z $z = PV/nRT$ for a gas. If $z = 1$, then $PV = nRT$ (the ideal-gas equation of state) and the gas is said to behave ideally.

@ **Compressor** A device that raises the pressure of a gas.

Condensation A process in which an entering gas is cooled and/or compressed, causing one or more of the gas components to liquefy. Uncondensed gases and liquid *condensate* leave the condenser as separate streams.

Critical pressure, P_c The highest pressure at which distinct vapor and liquid phases can coexist for a species.

Critical temperature, T_c The highest temperature at which distinct vapor and liquid phases can coexist for a species. The critical temperature and pressure, collectively referred to as the *critical constants*, are listed for various species in Table B.1.

@ **Crystallization** A process in which a liquid is cooled or solvent is evaporated to an extent that solid crystals form. The crystals in a *slurry* (suspension of solids in a liquid) leaving the crystallizer may subsequently be separated from the liquid in a filter or centrifuge.

Decanter A device in which two liquid phases or liquid and solid phases separate by gravity.

Degrees of freedom When applied to a general process, the difference between the number of unknown process variables and the number of equations relating those variables; the number of unknown variables for which values

must be specified before the remaining values can be calculated. When applied to a system at equilibrium, the number of intensive system variables for which values must be specified before the remaining values can be calculated. The degrees of freedom in the second sense is determined using the Gibbs Phase Rule.

Dew point (of a gas mixture at a given pressure) The temperature at which the first liquid droplet appears when the mixture is cooled at constant pressure.

@ **Distillation** A process in which a mixture of two or more species is fed to a vertical column that contains either a series of vertically spaced horizontal plates or solid packing through which fluid can flow. Liquid mixtures of the feed components flow down the column and vapor mixtures flow up. Interphase contact, partial condensation of the vapor, and partial vaporization of the liquid all take place throughout the column. The vapor flowing up the column becomes progressively richer in the more volatile components of the feed, and the liquid flowing down becomes richer in the less volatile components. The vapor leaving the top of the column is condensed: part of the condensate is taken off as the *overhead product* and the rest is recycled to the reactor as *reflux*, becoming the liquid stream that flows down the column. The liquid leaving the bottom of the column is partially vaporized: the vapor is recycled to the reactor as *boilup*, becoming the vapor stream that flows up the column, and the residual liquid is taken off as the *bottoms product*.

@ **Drying** A process in which a wet solid is heated or contacted with a hot gas stream, causing some or all of the entering liquid to evaporate. The vapor and the gas it evaporates into emerge as one outlet stream, and the solid and remaining residual liquid emerge as a second outlet stream.

Enthalpy (kJ) Property of a system defined as $H = U + PV$, where U = internal energy, P = absolute pressure, and V = volume of the system.

@ **Evaporation** (vaporization) A process in which a pure liquid, liquid mixture, or solvent in a solution is vaporized.

@ **Extraction** (liquid extraction) A process in which a liquid mixture of two species (the *solute* and the *feed carrier*) is contacted in a mixer with another liquid (the *solvent*) that is immiscible or nearly immiscible with the feed carrier. When the liquids are contacted, solute transfers from the feed carrier to the solvent. The combined mixture is then allowed to settle into two phases that are then separated by gravity.

@ **Filtration** A process in which a slurry of solid particles (often crystals) suspended in a liquid, most of which passes through the filter to form the *filtrate*; the solids and some entrained liquid are retained on the filter to form the *filter cake*. Filtration may also be used to separate solids or liquids from gases.

@ **Flash vaporization** A process in which a liquid feed at a high pressure is suddenly exposed to a lower pressure, causing some vaporization to occur. The vapor product is rich in the more volatile components of the feed and the residual liquid is rich in the less volatile components.

Flue gas See stack gas.

Heat Energy transferred between a system and its surroundings as a consequence of a temperature difference. Heat always flows from a higher temperature to a lower one. It is conventionally defined as positive when it flows to a system from its surroundings.

@ **Heat exchanger** A process unit through which two fluid streams at different temperatures flow on opposite sides of a metal barrier (e.g., a bundle of metal tubes). Heat is transferred from the stream at the higher temperature through the barrier to the other stream.

Internal energy (U) The total energy possessed by the individual molecules in a system (as opposed to the kinetic and potential energies of the system as a whole). U is a strong function of temperature, phase, and molecular structure and a weak function of pressure (it is independent of pressure for ideal gases). Its absolute value cannot be determined, so it is always expressed relative to a reference state at which it is defined to be zero.

@ **Membrane** A thin solid or liquid film through which one or more species in a process stream can permeate.

@ **Overhead product** The product that leaves the top of a distillation column. The overhead product is relatively rich in the most volatile components of the feed to the column.

Pump A device used to propel a liquid or slurry from one location to another, usually through a pipe or tube.

Scrubber An absorption column designed to remove an undesirable component from a gas stream.

Settler See decanter.

Shaft work All work transferred between a continuous system and its surroundings other than that done by or on the process fluid at the system entrance and exit.

Stack gas The gaseous products exiting from a combustion furnace.

Stripping A process in which a liquid containing a dissolved gas flows down a column and a gas (stripping gas) flows up the column at conditions such that the dissolved gas comes out of solution and is carried off with the stripping gas.

Vapor pressure The pressure at which pure liquid A can coexist with its vapor at a given temperature. In this text, vapor pressures can be determined from tabulated data (e.g., Tables B.3 and B5–B7 for water) or the Antoine equation (Table B.4).

Volume percent (% v/v) For liquid mixtures, the percentage of the total volume occupied by a particular component; for ideal gases, the same as mole percent. For nonideal gases the volume percent has no meaningful physical significance.

Work Energy transferred between a system and its surroundings as a consequence of motion against a restraining force, electricity or radiation, or any other driving force except a temperature difference. In this book, work is defined as positive if it flows to a system from its surroundings.

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Front cover photos: Some environments and products chemical engineers work on and with.

Top: Chemical plant (chemical, petrochemical, polymer, pharmaceutical, materials science and engineering, specialty chemical development and manufacturing)

Below, left: Printed circuit boards (microelectronic materials development and manufacturing, nanotechnology)

Below, center left and center right: Nucleic acid and the human body (biotechnology, biochemical engineering, biomedical engineering)

Below, right: Solar panels (clean fuel production and combustion, alternative energy sources)

FACTORS FOR UNIT CONVERSIONS

Quantity	Equivalent Values
Mass	1 kg $= 1000$ g $= 0.001$ metric ton (tonne) $= 2.20462$ $lb_m = 35.27392$ oz 1 $lb_m = 16$ oz $= 5 \times 10^{-4}$ ton $= 453.593$ g $= 0.453593$ kg
Length	1 m $= 100$ cm $= 1000$ mm $= 10^6$ microns (μm) $= 10^{10}$ angstroms (Å) $= 39.37$ in $= 3.2808$ ft $= 1.0936$ yd $= 0.0006214$ mile 1 ft $= 12$ in $= 1/3$ yd $= 0.3048$ m $= 30.48$ cm
Volume	1 $m^3 = 1000$ L $= 10^6$ $cm^3 = 10^6$ mL $= 35.3145$ ft^3 $= 219.97$ imperial gallons $= 264.17$ gal $= 1056.68$ qt 1 $ft^3 = 1728$ $in^3 = 7.4805$ gal $= 29.922$ qt $= 0.028317$ $m^3 = 28.317$ L
Density	1 $g/cm^3 = 1000$ $kg/m^3 = 62.43$ lb_m/ft^3 = density of liquid water at 4°C (reference for specific gravities)
Force	1 N $= 1$ $kg \cdot m/s^2 = 10^5$ dynes $= 10^5$ $g \cdot cm/s^2 = 0.22481$ lb_f 1 $lb_f = 32.174$ $lb_m \cdot ft/s^2 = 4.4482$ N $= 4.4482 \times 10^5$ dynes
Pressure	1 atm $= 1.01325 \times 10^5$ N/m^2 (Pa) $= 101.325$ kPa $= 1.01325$ bar $= 1.01325 \times 10^6$ dynes/$cm^2 = 14.696$ lb_f/in^2 (psi) $= 760$ mm Hg at 0°C (torr) $= 10.333$ m H_2O(l) at 4°C $= 29.921$ inches Hg at 0°C $= 406.8$ inches H_2O(l) at 4°C
Energy	1 J $= 1$ N·m $= 10^7$ ergs $= 10^7$ dyne·cm $= 1$ $kg \cdot m^2/s^2$ $= 2.778 \times 10^{-7}$ kW·h $= 0.23901$ cal $= 0.23901 \times 10^{-3}$ kcal (food calorie) $= 0.7376$ $ft \cdot lb_f = 9.486 \times 10^{-4}$ Btu
Power	1 W $= 1$ J/s $= 1$ N·m/s $= 0.23901$ cal/s $= 0.7376$ $ft \cdot lb_f/s$ $= 9.486 \times 10^{-4}$ Btu/s $= 1.341 \times 10^{-3}$ hp

Example: The factor to convert grams to lb_m is $\left(\frac{2.20462\ lb_m}{1000\ g}\right)$ or $\left(\frac{1\ lb_m}{453.593\ g}\right)$.

ATOMIC WEIGHTS AND NUMBERS

Atomic weights apply to naturally occurring isotopic compositions and are based on an atomic mass of $^{12}C = 12$

Element	Symbol	Atomic Number	Atomic Weight	Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	—	Iridium	Ir	77	192.2
Aluminum	Al	13	26.9815	Iron	Fe	26	55.847
Americium	Am	95	—	Krypton	Kr	36	83.80
Antimony	Sb	51	121.75	Lanthanum	La	57	138.91
Argon	Ar	18	39.948	Lawrencium	Lr	103	—
Arsenic	As	33	74.9216	Lead	Pb	82	207.19
Astatine	At	85	—	Lithium	Li	3	6.939
Barium	Ba	56	137.34	Lutetium	Lu	71	174.97
Berkelium	Bk	97	—	Magnesium	Mg	12	24.312
Beryllium	Be	4	9.0122	Manganese	Mn	25	54.9380
Bismuth	Bi	83	208.980	Mendelevium	Md	101	—
Boron	B	5	10.811	Mercury	Hg	80	200.59
Bromine	Br	35	79.904	Molybdenum	Mo	42	95.94
Cadmium	Cd	48	112.40	Neodymium	Nd	60	144.24
Calcium	Ca	20	40.08	Neon	Ne	10	20.183
Californium	Cf	98	—	Neptunium	Np	93	—
Carbon	C	6	12.01115	Nickel	Ni	28	58.71
Cerium	Ce	58	140.12	Niobium	Nb	41	92.906
Cesium	Cs	55	132.905	Nitrogen	N	7	14.0067
Chlorine	Cl	17	35.453	Nobelium	No	102	—
Chromium	Cr	24	51.996	Osmium	Os	75	190.2
Cobalt	Co	27	58.9332	Oxygen	O	8	15.9994
Copper	Cu	29	63.546	Palladium	Pd	46	106.4
Curium	Cm	96	—	Phosphorus	P	15	30.9738
Dysprosium	Dy	66	162.50	Platinum	Pt	78	195.09
Einsteinium	Es	99	—	Plutonium	Pu	94	—
Erbium	Er	68	167.26	Polonium	Po	84	—
Europium	Eu	63	151.96	Potassium	K	19	39.102
Fermium	Fm	100	—	Praseodymium	Pr	59	140.907
Fluorine	F	9	18.9984	Promethium	Pm	61	—
Francium	Fr	87	—	Protactinium	Pa	91	—
Gadolinium	Gd	64	157.25	Radium	Ra	88	—
Gallium	Ga	31	69.72	Radon	Rn	86	—
Germanium	Ge	32	72.59	Rhenium	Re	75	186.2
Gold	Au	79	196.967	Rhodium	Rh	45	102.905
Hafnium	Hf	72	178.49	Rubidium	Rb	37	84.57
Helium	He	2	4.0026	Ruthenium	Ru	44	101.07
Holmium	Ho	67	164.930	Samarium	Sm	62	150.35
Hydrogen	H	1	1.00797	Scandium	Sc	21	44.956
Indium	In	49	114.82	Selenium	Se	34	78.96
Iodine	I	53	126.9044	Silicon	Si	14	28.086

Atomic weights apply to naturally occurring isotopic compositions and are based on an atomic mass of $^{12}C = 12$

Element	Symbol	Atomic Number	Atomic Weight	Element	Symbol	Atomic Number	Atomic Weight
Silver	Ag	47	107.868	Tin	Sn	50	118.69
Sodium	Na	11	22.9898	Titanium	Ti	22	47.90
Strontium	Sr	38	87.62	Tungsten	W	74	183.85
Sulfur	S	16	32.064	Uranium	U	92	238.03
Tantalum	Ta	73	180.948	Vanadium	V	23	50.942
Technetium	Tc	43	—	Xenon	Xe	54	131.30
Tellurium	Te	52	127.60	Ytterbium	Yb	70	173.04
Terbium	Tb	65	158.924	Yttrium	Y	39	88.905
Thallium	Tl	81	204.37	Zinc	Zn	30	65.37
Thorium	Th	90	232.038	Zirconium	Zr	40	91.22
Thulium	Tm	69	168.934				

THE GAS CONSTANT (*R*)

8.314 $m^3 \cdot Pa/(mol \cdot K)$

0.08314 L·bar/(mol·K)

0.08206 L·atm/(mol·K)

62.36 L·mm Hg/(mol·K)

0.7302 $ft^3 \cdot atm/(lb\text{-}mole \cdot °R)$

10.73 $ft^3 \cdot psia/(lb\text{-}mole \cdot °R)$

8.314 J/(mol·K)

1.987 cal/(mol·K)

1.987 Btu/(lb-mole·°R)

PART 1

Engineering Problem Analysis

CHAPTER 1

What Some Chemical Engineers Do for a Living

Last May, thousands of chemical engineering seniors took their last final examination, attended their graduation ceremonies, flipped their tassels and threw their mortarboards in the air, enjoyed their farewell parties, said goodbye to one another and promised faithfully to stay in touch, and headed off in an impressive variety of geographical and career directions.

Since you bought this book, you are probably thinking about following in the footsteps of those graduates—spending the next few years learning to be a chemical engineer and possibly the next 40 applying what you learn in a career. Even so, it is a fairly safe bet that, like most people in your position, you have only a limited idea of what chemical engineering is or what chemical engineers do. A logical way for us to begin this book might therefore be with a definition of chemical engineering.

Unfortunately, no universally accepted definition of chemical engineering exists, and almost every type of skilled work you can think of is done somewhere by people educated as chemical engineers. Providing a definition has recently become even more difficult as university chemical engineering departments have morphed into departments of chemical and biomolecular engineering or chemical and materials engineering or chemical and environmental engineering. We will therefore abandon the idea of formulating a simple definition, and instead take a closer look at what those recent graduates did either immediately after graduation or following a well-earned vacation. We will also do some speculating about what they might do several years after graduating, based on our experiences with graduates from previous classes. Consider these examples and see if any of them sound like the sort of career you can see yourself pursuing and enjoying.

- About 45% of the class went to work for chemical, petrochemical, pulp and paper, and polymer (plastics) manufacturing firms.
- Another 35% went to work for government agencies and design and consulting firms (many specializing in environmental regulation and pollution control), companies in fields such as microelectronics and information technology that have not been traditionally associated with chemical engineering, and firms specializing in emerging areas such as biotechnology and sustainable development (development that addresses economic, ecological, cultural, and political considerations).
- About 10% of the class went directly into graduate school in chemical engineering. The master's degree candidates will get advanced training in traditional chemical engineering areas (thermodynamics, chemical reactor analysis and design, fluid dynamics, mass and heat transfer, and chemical process design and control) and emerging areas such as biotechnology, biomedicine, materials science and engineering, nanotechnology, and sustainable development. They will have access to most of the jobs available to the bachelor's degree holders plus jobs in those emerging areas that require additional training. The doctoral degree candidates will get more advanced training and work on major research projects, and in four to five years most will graduate and either go into industrial research and development or join university faculties.
- A small number were drawn to entrepreneurship, and within a few years after graduation will start their own companies in areas that might or might not have anything to do with their college backgrounds.

- The remaining 10% of the class went into graduate school in areas other than engineering, discovering that their chemical engineering backgrounds made them strongly competitive for admission to top universities. Several who took biology electives in their undergraduate programs went to medical school. Others went to law school, planning to go into patent or corporate law, and still others enrolled in Master of Business Administration programs with the goal of moving into management in industry.
- One graduate joined the Peace Corps for a two-year stint in East Africa helping local communities develop sanitary waste disposal systems and also teaching science and English in a rural school. When she returns, she will complete a Ph.D. program in environmental engineering, join a chemical engineering faculty, write a definitive book on environmental applications of chemical engineering principles, quickly rise through the ranks to become a full professor, resign after 10 years to run for the United States Senate, win two terms, and eventually become head of a large and highly successful private foundation dedicated to improving education in economically deprived communities. She will attribute her career successes in part to the problem-solving skills she acquired in her undergraduate training in chemical engineering.
- At various points in their careers, some of the graduates will work in chemical or biochemical or biomedical or material science laboratories doing research and development or quality engineering, at computer terminals designing processes and products and control systems, at field locations managing the construction and startup of manufacturing plants, on production floors supervising and troubleshooting and improving operations, on the road doing technical sales and service, in executive offices performing administrative functions, in government agencies responsible for environmental and occupational health and safety, in hospitals and clinics practicing medicine or biomedical engineering, in law offices specializing in chemical process-related patent work, and in classrooms teaching the next generation of students.

The careers just described are clearly too diverse to fall into a single category. They involve disciplines including physics, chemistry, biology, environmental science, medicine, law, applied mathematics, statistics, information technology, economics, research, design, construction, sales and service, production supervision, and business administration. The single feature they have in common is that chemical engineers can be found doing them. Some of the specific knowledge needed to carry out the tasks will be presented later in the chemical engineering curriculum, and most of it must be learned after graduation. There are, however, basic techniques that have been developed for setting up and attacking technical problems that apply across a broad range of disciplines. What some of these techniques are and how and when to use them are the subjects of this book.

CHAPTER 2

Introduction to Engineering Calculations

Chapter 1 suggests the range of problems encompassed by chemical engineering,[1] both in traditional areas of chemical processing and in relatively new fields such as environmental science and engineering, bioengineering, and semiconductor manufacturing. Differences between the areas mentioned in the chapter—chemical manufacturing, genetic engineering, and pollution control—are obvious. In this book, we examine the similarities.

One similarity is that all of the systems described involve **processes** designed to transform raw materials into desired products. Many of the problems that arise in connection with the design of a new process or the analysis of an existing one are of a certain type: given amounts and properties of the raw materials, calculate amounts and properties of the products, or vice versa.

The object of this text is to present a systematic approach to the solution of problems of this type. This chapter presents basic techniques for expressing the values of system variables and for setting up and solving equations that relate these variables. In Chapter 3 we discuss the variables of specific concern in process analysis—temperatures, pressures, chemical compositions, and amounts or flow rates of process streams—describing how they are defined, calculated, and, in some cases, measured. Parts Two and Three of the book deal with the laws of conservation of mass and energy, which relate the inputs and outputs of manufacturing systems, power plants, and the human body. The laws of nature constitute the underlying structure of all process design and analysis, including the techniques we present in the book.

2.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- Convert a quantity expressed in one set of units into its equivalent in any other dimensionally consistent units using appropriate conversion factors. [For example, convert a heat flux of 235 $kJ/(m^2 \cdot s)$ into its equivalent in $Btu/(ft^2 \cdot h)$.]
- Identify the units commonly used to express both mass and weight in SI, CGS, and U.S. customary units. Calculate weights from given masses in either natural units (e.g., $kg \cdot m/s^2$ or $lb_m \cdot ft/s^2$) or defined units (N, lb_f).
- Identify the number of significant figures in a given value expressed in either decimal or scientific notation and state the precision with which the value is known based on its significant figures. Determine the correct number of significant figures in the result of a series of arithmetic operations (adding, subtracting, multiplying, and dividing).
- Validate a quantitative problem solution by applying back-substitution, order-of-magnitude estimation, and the test of reasonableness.
- Given a set of measured values, calculate the sample mean, range, sample variance, and sample standard deviation. Explain in your own words what each of the calculated quantities means and why it is important.

[1] When we refer to chemical engineering, we intend to encompass all aspects of a discipline that includes applications in biology as well as a number of other fields.

- Explain the concept of dimensional homogeneity of equations. Given the units of some terms in an equation, use this concept to assign units to other terms.
- Given tabulated data for two variables (x and y), use linear interpolation between two data points to estimate the value of one variable for a given value of the other. Sketch a plot of y versus x and use it to illustrate how and when linear interpolation can lead to significant errors in estimated values.
- Given two points on a straight-line plot of y versus x, derive the expression for $y(x)$. Given tabulated data for x and y, fit a straight line by visual inspection.
- Given a two-parameter expression relating two variables [such as $y = a\sin(2x) + b$ or $P = 1/(aQ^3 + b)$ and two adjustable parameters (a and b), state what you would plot to generate a straight line. Given data for x and y, generate the plot and estimate the parameters a and b.
- Given a power-law or exponential expression involving two variables (such as $y = ax^b$ or $k = ae^{b/T}$), state what you would plot on rectangular, semilog, or logarithmic axes that would generate a straight line. Given a linear plot involving two variables on any of the three types of axes and two points on the line, determine the expression relating the two variables and the values of the two parameters.

2.1 UNITS AND DIMENSIONS

A measured or counted quantity has a numerical **value** (2.47) and a **unit** (whatever there are 2.47 of). It is useful in most engineering calculations—and essential in many—to write both the value and the unit of each quantity appearing in an equation:

$$2 \text{ meters}, \quad \tfrac{1}{3} \text{ second}, \quad 4.29 \text{ kilograms}, \quad 5 \text{ gold rings}$$

A **dimension** is a property that can be measured, such as length, time, mass, or temperature, or calculated by multiplying or dividing other dimensions, such as length/time (velocity), length^3 (volume), or mass/length^3 (density). Measurable units (as opposed to countable units) are specific values of dimensions that have been defined by convention, custom, or law, such as grams for mass, seconds for time, and centimeters or feet for length.

Units can be treated like algebraic variables when quantities are added, subtracted, multiplied, or divided. *Two quantities may be added or subtracted only if their units are the same.*

$$3 \text{ cm} - 1 \text{ cm} = 2 \text{ cm} \qquad (3x - x = 2x)$$

but

$$3 \text{ cm} - 1 \text{ mm (or 1 s)} = ? \qquad (3x - y = ?)$$

On the other hand, *numerical values and their corresponding units may always be combined by multiplication or division.*

$$3 \text{ N} \times 4 \text{ m} = 12 \text{ N}\cdot\text{m}$$

$$\frac{5.0 \text{ km}}{2.0 \text{ h}} = 2.5 \text{ km/h}$$

$$7.0 \frac{\text{km}}{\text{h}} \times 4 \text{ h} = 28 \text{ km}$$

$$3 \text{ m} \times 4 \text{ m} = 12 \text{ m}^2$$

$$6 \text{ cm} \times 5 \frac{\text{cm}}{\text{s}} = 30 \text{ cm}^2/\text{s}$$

$$\frac{6 \text{ g}}{2 \text{ g}} = 3 \qquad (3 \text{ is a } \textit{dimensionless} \text{ quantity})$$

$$\left(5.0 \frac{\text{kg}}{\text{s}}\right) \Big/ \left(0.20 \frac{\text{kg}}{\text{m}^3}\right) = 25 \text{ m}^3/\text{s} \qquad (\text{Convince yourself})$$

2.2 CONVERSION OF UNITS

A measured quantity can be expressed in terms of any units having the appropriate dimension. A particular velocity, for instance, may be expressed in ft/s, miles/h, cm/yr, or any other ratio of a length unit to a time unit. The numerical value of the velocity naturally depends on the units chosen.

The equivalence between two expressions of the same quantity may be defined in terms of a ratio:

$$\frac{1\text{ cm}}{10\text{ mm}} \quad \text{(1 centimeter per 10 millimeters)} \tag{2.2-1}$$

$$\frac{10\text{ mm}}{1\text{ cm}} \quad \text{(10 millimeters per centimeter)} \tag{2.2-2}$$

$$\left[\frac{10\text{ mm}}{1\text{ cm}}\right]^2 = \frac{100\text{ mm}^2}{1\text{ cm}^2} \tag{2.2-3}$$

Ratios of the form of Equations 2.2-1, 2.2-2, and 2.2-3 are known as **conversion factors**.

To convert a quantity expressed in terms of one unit to its equivalent in terms of another unit, multiply the given quantity by the conversion factor (new unit/old unit). For example, to convert 36 mg to its equivalent in grams, write

$$36\text{ mg} \times \frac{1\text{ g}}{1000\text{ mg}} = 0.036\text{ g} \tag{2.2-4}$$

(Note how the old units cancel, leaving the desired unit.) An alternative way to write this equation is to use a vertical line instead of the multiplication symbol:

$$\frac{36\text{ mg} \mid 1\text{ g}}{\mid 1000\text{ mg}} = 0.036\text{ g}$$

Carrying along units in calculations of this type is the best way of avoiding the common mistake of multiplying when you mean to divide and vice versa. In the given example, the result is known to be correct because milligrams cancel leaving only grams on the left side, whereas

$$\frac{36\text{ mg} \mid 1000\text{ mg}}{\mid 1\text{ g}} = 36{,}000\text{ mg}^2/\text{g}$$

is clearly wrong. (More precisely, it is not what you intended to calculate.)

The practice of carrying units along with calculations will require discipline, but it is sure to save you from making countless errors. To illustrate, simply insert the phrase "unit conversion errors" in your favorite search engine, and a list of famous ones will be displayed. Our experience is that once you start carrying units, two things will happen: (1) you will make fewer mistakes in calculations, and (2) you often will gain understanding of otherwise incomprehensible mathematical expressions.

If you are given a quantity having a compound unit [e.g., miles/h, cal/(g·°C)], and you wish to convert it to its equivalent in terms of another set of units, set up a **dimensional equation**: write the given quantity and its units on the left, write the units of conversion factors that cancel the old units and replace them with the desired ones, fill in the values of the conversion factors, and carry out the indicated arithmetic to find the desired value. (See Example 2.2-1.)

Test Yourself

(Answers, p. 654)

1. What is a conversion factor?

2. What is the conversion factor for s/min (s = second)?

3. What is the conversion factor for min^2/s^2? (See Equation 2.2-3.)

4. What is the conversion factor for m^3/cm^3?

Example 2.2-1 Conversion of Units

Convert an acceleration of 1 cm/s^2 to its equivalent in km/yr^2.

Solution

$$\frac{1\text{ cm}}{\text{s}^2}\left|\frac{3600^2\text{ s}^2}{1^2\text{ h}^2}\right|\frac{24^2\text{ h}^2}{1^2\text{ day}^2}\left|\frac{365^2\text{ day}^2}{1^2\text{ yr}^2}\right|\frac{1\text{ m}}{10^2\text{ cm}}\left|\frac{1\text{ km}}{10^3\text{ m}}\right.$$

$$=\frac{(3600\times 24\times 365)^2}{10^2\times 10^3}\frac{\text{km}}{\text{yr}^2}=\boxed{9.95\times 10^9\text{ km/yr}^2}$$

A principle illustrated in this example is that raising a quantity (in particular, a conversion factor) to a power raises its units to the same power. The conversion factor for h^2/day^2 is therefore the square of the factor for h/day:

$$\left(\frac{24\text{ h}}{1\text{ day}}\right)^2=24^2\,\frac{\text{h}^2}{\text{day}^2}$$

2.3 SYSTEMS OF UNITS

A system of units has the following components:

1. ***Base units*** for mass, length, time, temperature, electrical current, and light intensity.
2. ***Multiple units,*** which are defined as multiples or fractions of base units such as minutes, hours, and milliseconds, all of which are defined in terms of the base unit of a second. Multiple units are defined for convenience rather than necessity; it is simply more convenient to refer to 3 yr than to 94,608,000 s.
3. ***Derived units,*** obtained in one of two ways:
   (a) By multiplying and dividing base or multiple units (cm^2, ft/min, kg·m/s^2, etc.). Derived units of this type are referred to as **compound units**.
   (b) As defined equivalents of compound units (e.g., 1 erg ≡ 1 g·cm/s^2, 1 lb$_f$ ≡ 32.174 lb$_m$·ft/s^2).

The "Système Internationale d'Unités," or **SI** for short, has gained widespread acceptance in the scientific and engineering community.[2] Two of the base SI units—the ampere for electrical current and the candela for luminous intensity—will not concern us in this book. A third, the kelvin for temperature, will be discussed later. The others are the meter (m) for length, the kilogram (kg) for mass, and the second (s) for time.

Prefixes are used in SI to indicate powers of ten. The most common of these prefixes and their abbreviations are mega (M) for 10^6 (1 megawatt = 1 MW = 10^6 watts), kilo (k) for 10^3, centi (c) for 10^{-2}, milli (m) for 10^{-3}, micro (μ) for 10^{-6}, and nano (n) for 10^{-9}. The conversion factors between, say, centimeters and meters are therefore 10^{-2} m/cm and 10^2 cm/m. The principal SI units and prefixes are summarized in Table 2.3-1.

The **CGS system** is almost identical to SI, the principal difference being that grams (g) and centimeters (cm) are used instead of kilograms and meters as the base units of mass and length. The principal units of the CGS system are shown in Table 2.3-1.

The base units of the **U.S. customary system** are the foot (ft) for length, the pound-mass (lb$_m$) for mass, and the second (s) for time. This system has two principal difficulties. The first is the occurrence of conversion factors (such as 1 ft/12 in), which, unlike those in the metric systems, are not multiples of 10; the second, which has to do with the unit of force, is discussed in the next section.

[2] For additional information about the SI system, including its history, see http://physics.nist.gov/cuu/Units/.

Factors for converting from one system of units to another may be determined by taking ratios of quantities listed in the table on the inside front cover of this book. A larger table of conversion factors is given on pp. 1-2 through 1-18 of *Perry's Chemical Engineers' Handbook*.[3]

TABLE 2.3-1 SI and CGS Units

Base Units

Quantity	Unit	Symbol
Length	meter (SI)	m
	centimeter (CGS)	cm
Mass	kilogram (SI)	kg
	gram (CGS)	g
Moles	gram-mole	mol or g-mole
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Light intensity	candela	cd

Multiple Unit Preferences

tera (T) = 10^{12}	centi (c) = 10^{-2}
giga (G) = 10^{9}	milli (m) = 10^{-3}
mega (M) = 10^{6}	micro (μ) = 10^{-6}
kilo (k) = 10^{3}	nano (n) = 10^{-9}

Derived Units

Quantity	Unit	Symbol	Equivalent in Terms of Base Units
Volume	liter	L	0.001 m^3
			1000 cm^3
Force	newton (SI)	N	1 kg·m/s^2
	dyne (CGS)		1 g·cm/s^2
Pressure	pascal (SI)	Pa	1 N/m^2
Energy, work	joule (SI)	J	1 N·m = 1 kg·m^2/s^2
	erg (CGS)		1 dyne·cm = 1 g·cm^2/s^2
	gram-calorie	cal	4.184 J = 4.184 kg·m^2/s^2
Power	watt	W	1 J/s = 1 kg·m^2/s^3

Test Yourself

(Answers, p. 654)

1. What are the factors (numerical values and units) needed to convert
- **(a)** meters to millimeters?
- **(b)** nanoseconds to seconds?
- **(c)** square centimeters to square meters?
- **(d)** cubic feet to cubic meters (use the conversion factor table on the inside front cover)?
- **(e)** horsepower to British thermal units per second?

2. What is the derived SI unit for velocity? The velocity unit in the CGS system? In U.S. customary units?

[3] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008.

Example 2.3-1 Conversion between Systems of Units

Convert 23 $lb_m \cdot ft/min^2$ to its equivalent in $kg \cdot cm/s^2$.

Solution As before, begin by writing the dimensional equation, fill in the units of conversion factors (new/old) and then the numerical values of these factors, and then do the arithmetic. The result is

$$\frac{23\ lb_m \cdot ft}{min^2}\left|\begin{array}{r|r|r}\dfrac{0.453593\ kg}{1\ lb_m} & \dfrac{100\ cm}{3.281\ ft} & \dfrac{1^2\ min^2}{(60)^2\ s^2}\end{array}\right. \quad \text{(Cancellation of units leaves } kg \cdot cm/s^2\text{)}$$

$$= \frac{(23)(0.453593)(100)}{(3.281)(3600)}\frac{kg \cdot cm}{s^2} = \boxed{0.088\frac{kg \cdot cm}{s^2}}$$

2.4 FORCE AND WEIGHT

According to Newton's second law of motion, force is proportional to the product of mass and acceleration (length/time^2). *Natural force units* are, therefore, $kg \cdot m/s^2$ (SI), $g \cdot cm/s^2$ (CGS), and $lb_m \cdot ft/s^2$ (U.S. customary). To avoid having to carry around these complex units in all calculations involving forces, *derived force units* have been defined in each system. In the metric systems, the derived force units (the **newton** in SI, the **dyne** in the CGS system) are defined to equal the natural units:

$$1\ \text{newton (N)} \equiv 1\ kg \cdot m/s^2 \qquad \textbf{(2.4-1)}$$

$$1\ \text{dyne} \equiv 1\ g \cdot cm/s^2 \qquad \textbf{(2.4-2)}$$

In U.S. customary units, the derived force unit—called a **pound-force** (lb_f)—is defined as the product of a unit mass (1 lb_m) and the acceleration of gravity at sea level and 45° latitude, which is 32.174 ft/s^2:

$$1\ lb_f \equiv 32.174\ lb_m \cdot ft/s^2 \qquad \textbf{(2.4-3)}$$

Equations 2.4-1 through 2.4-3 define conversion factors between natural and derived force units. For example, the force in newtons required to accelerate a mass of 4.00 kg at a rate of 9.00 m/s^2 is

$$F = \frac{4.00\ kg}{}\left|\begin{array}{r|r}\dfrac{9.00\ m}{s^2} & \dfrac{1\ N}{1\ kg \cdot m/s^2}\end{array}\right. = 36.0\ N$$

The force in lb_f required to accelerate a mass of 4.00 lb_m at a rate of 9.00 ft/s^2 is

$$F = \frac{4.00\ lb_m}{}\left|\begin{array}{r|r}\dfrac{9.00\ ft}{s^2} & \dfrac{1\ lb_f}{32.174\ lb_m \cdot ft/s^2}\end{array}\right. = 1.12\ lb_f$$

Factors needed to convert from one force unit to another are summarized in the table on the inside front cover. The symbol g_c is sometimes used to denote the conversion factor from natural to derived force units: for example,

$$g_c = \frac{1\ kg \cdot m/s^2}{1\ N} = \frac{32.174\ lb_m \cdot ft/s^2}{1\ lb_f}$$

We will not use this symbol in the text, but if you should encounter it elsewhere remember that it is simply a conversion factor (not to be confused with gravitational acceleration, which is usually denoted by g).

The **weight** of an object is the force exerted on the object by gravitational attraction. Suppose that an object of mass m is subjected to a gravitational force W (W is by definition the weight of the object) and that if this object were falling freely its acceleration would be g. The weight, mass, and free-fall acceleration of the object are related by Equation 2.4-4:

$$W = mg \tag{2.4-4}$$

The gravitational acceleration (g) varies directly with the mass of the attracting body (the earth, in most problems you will confront) and inversely with the square of the distance between the centers of mass of the attracting body and the object being attracted. The value of g at sea level and 45° latitude is given below in each system of units:

$$\boxed{\begin{aligned} g &= 9.8066 \text{ m/s}^2 \\ &= 980.66 \text{ cm/s}^2 \\ &= 32.174 \text{ ft/s}^2 \end{aligned}} \tag{2.4-5}$$

The acceleration of gravity does not vary much with position on the earth's surface and (within moderate limits) altitude, and the values in Equation 2.4-5 may accordingly be used for most conversions between mass and weight.

Test Yourself

(Answers, p. 654)

1. What is a force of 2 kg·m/s^2 equivalent to in newtons? What is a force of 2 lb_m·ft/s^2 equivalent to in lb_f?
2. If the acceleration of gravity at a point is $g = 9.8$ m/s^2 and an object is resting on the ground at this point, is this object accelerating at a rate of 9.8 m/s^2?
3. Suppose an object weighs 9.8 N at sea level. What is its mass? Would its mass be greater, less, or the same on the moon? How about its weight?
4. Suppose an object weighs 2 lb_f at sea level. What is its mass? Would its mass be greater, less, or the same at the center of the earth? How about its weight? (Careful!)

Example 2.4-1 Weight and Mass

Water has a density of 62.4 lb_m/ft^3. How much does 2.000 ft^3 of water weigh (1) at sea level and 45° latitude and (2) in Denver, Colorado, where the altitude is 5374 ft and the gravitational acceleration is 32.139 ft/s^2?

Solution The mass of the water is

$$M = \left(62.4 \frac{\text{lb}_\text{m}}{\text{ft}^3}\right)(2 \text{ ft}^3) = 124.8 \text{ lb}_\text{m}$$

The weight of the water is

$$W = (124.8 \text{ lb}_\text{m}) g \left(\frac{\text{ft}}{\text{s}^2}\right)\left(\frac{1 \text{ lb}_\text{f}}{32.174 \text{ lb}_\text{m}\cdot\text{ft/s}^2}\right)$$

1. At sea level, $g = 32.174$ ft/s^2, so that $W = 124.8$ lb_f.
2. In Denver, $g = 32.139$ ft/s^2, and $W = 124.7$ lb_f.

As this example illustrates, the error incurred by assuming that $g = 32.174$ ft/s^2 is normally quite small as long as you remain on the earth's surface. In a satellite or on another planet it would be a different story.

2.5 NUMERICAL CALCULATION AND ESTIMATION

2.5a Scientific Notation, Significant Figures, and Precision

Both very large and very small numbers are commonly encountered in process calculations. A convenient way to represent such numbers is to use **scientific notation**, in which a number is expressed as the product of another number (usually between 0.1 and 10) and a power of 10. Examples:

$$123{,}000{,}000 = 1.23 \times 10^8 \text{ (or } 0.123 \times 10^9\text{)}$$
$$0.000028 = 2.8 \times 10^{-5} \text{ (or } 0.28 \times 10^{-4}\text{)}$$

The **significant figures** of a number are the digits from the first nonzero digit on the left to either (a) the last digit (zero or nonzero) on the right if there is a decimal point, or (b) the last nonzero digit of the number if there is no decimal point. For example,

2300 or 2.3×10^3 has two significant figures.
2300. or 2.300×10^3 has four significant figures.
2300.0 or 2.3000×10^3 has five significant figures.
23,040 or 2.304×10^4 has four significant figures.
0.035 or 3.5×10^{-2} has two significant figures.
0.03500 or 3.500×10^{-2} has four significant figures.

(***Note:*** The number of significant figures is easily shown and seen if scientific notation is used.)

The number of significant figures in the reported value of a measured or calculated quantity provides an indication of the precision with which the quantity is known: the more significant figures, the more precise is the value. Generally, if you report the value of a measured quantity with three significant figures, you indicate that the value of the third of these figures may be off by as much as a half-unit. Thus, if you report a mass as 8.3 g (two significant figures), you indicate that the mass lies somewhere between 8.25 and 8.35 g, whereas if you give the value as 8.300 g (four significant figures) you indicate that the mass lies between 8.2995 and 8.3005 g.

Note, however, that this rule applies only to measured quantities or numbers calculated from measured quantities. If a quantity is known precisely—like a pure integer (2) or a counted rather than measured quantity (16 oranges)—its value implicitly contains an infinite number of significant figures (5 cows really means 5.0000 . . . cows).

When two or more quantities are combined by multiplication and/or division, the number of significant figures in the result should equal the lowest number of significant figures of any of the multiplicands or divisors. If the initial result of a calculation violates this rule, you must round off the result to reduce the number of significant figures to its maximum allowed value, although if several calculations are to be performed in sequence it is advisable to keep extra significant figures of intermediate quantities and to round off only the final result. Examples:

$$\overset{(3)}{(3.57)}\,\overset{(4)}{(4.286)} = \overset{(7)}{15.30102} \Longrightarrow \overset{(3)}{15.3}$$

$$\overset{(2)}{(5.2 \times 10^{-4})}\,\overset{(4)}{(0.1635 \times 10^{7})} / \overset{(3)}{(2.67)} = \overset{(9)}{318.426966} \Longrightarrow \overset{(2)}{3.2 \times 10^{2}} = \overset{(2)}{320}$$

(The raised quantities in parentheses denote the number of significant figures in the given numbers.)
Warning: If you calculate, say, 3×4, and your calculator or computer gives you an answer like 11.99999, and you copy this answer and hand it in, your instructor may become hysterical!

The rule for addition and subtraction concerns the position of the last significant figure in the sum—that is, the location of this figure relative to the decimal point. The rule is: *When two or more numbers are added or subtracted, the positions of the last significant figures of each number*

relative to the decimal point should be compared. Of these positions, the one farthest to the left is the position of the last permissible significant figure of the sum or difference.

Several examples of this rule follow, in which an arrow (↓) denotes the last significant figure of each number.

$$\begin{array}{r} \overset{\downarrow}{1530} \\ \underline{-\ \overset{\downarrow}{2.56}} \\ 1527.44 \Longrightarrow 1530 \end{array}$$

$$\overset{\uparrow}{1530}$$

$$\overset{\downarrow}{1.0000} + \overset{\downarrow}{0.036} + \overset{\downarrow}{0.22} = \overset{\downarrow}{1.2560} \Longrightarrow 1.26$$

$$2.75 \times 10^6 + 3.400 \times 10^4 = (\overset{\downarrow}{2.75} + \overset{\downarrow}{0.03400}) \times 10^6$$

$$= \overset{\downarrow}{2.784000} \times 10^6 \Longrightarrow 2.78 \times 10^6$$

Finally, a rule of thumb for rounding off numbers in which the digit to be dropped is a 5 is always to make the last digit of the rounded-off number even:

$$1.35 \Longrightarrow 1.4$$
$$1.25 \Longrightarrow 1.2$$

Test Yourself

(Answers, p. 654)

1. Express the following quantities in scientific notation and indicate how many significant figures each has.
(a) 12,200 **(b)** 12,200.0 **(c)** 0.003040

2. Express the following quantities in standard decimal form and indicate how many significant figures each has.
(a) 1.34×10^5 **(b)** 1.340×10^{-2} **(c)** 0.00420×10^6

3. How many significant figures would the solution of each of the following problems have? What are the solutions of (c) and (d)?
(a) $(5.74)(38.27)/(0.001250)$ **(c)** $1.000 + 10.2$
(b) $(1.76 \times 10^4)(0.12 \times 10^{-6})$ **(d)** $18.76 - 7$

4. Round off each of the following numbers to three significant figures.
(a) 1465 **(b)** 13.35 **(c)** 1.765×10^{-7}

5. When the value of a number is given, the significant figures provide an indication of the uncertainty in the value; for example, a value of 2.7 indicates that the number lies between 2.65 and 2.75. Give ranges within which each of the following values lie.
(a) 4.3 **(d)** 2500
(b) 4.30 **(e)** 2.500×10^3
(c) 2.778×10^{-3}

2.5b Validating Results

Every problem you will ever have to solve—in this and other courses and in your professional career—will involve two critical questions: (1) How do I get a solution? (2) When I get one, how do I know it's right? Most of this book is devoted to Question 1—that is, to methods of solving problems that arise in the design and analysis of chemical processes. However, Question 2 is

equally important, and serious problems can arise when it is not asked. All successful engineers get into the habit of asking it whenever they solve a problem and they develop a wide variety of strategies for answering it.

Among approaches you can use to validate a quantitative problem solution are *back-substitution, order-of-magnitude estimation*, and *the test of reasonableness*.

- Back-substitution is straightforward: after you solve a set of equations, substitute your solution back into the equations and make sure it works.
- Order-of-magnitude estimation means coming up with a crude and easy-to-obtain approximation of the answer to a problem and making sure that the more exact solution comes reasonably close to it.
- Applying the test of reasonableness means verifying that the solution makes sense. If, for example, a calculated velocity of water flowing in a pipe is faster than the speed of light or the calculated temperature in a chemical reactor is higher than the interior temperature of the sun, you should suspect that a mistake has been made somewhere.

The procedure for checking an arithmetic calculation by order-of-magnitude estimation is as follows:

1. Substitute simple integers for all numerical quantities, using powers of 10 (scientific notation) for very small and very large numbers.

$$\begin{aligned} 27.36 &\rightarrow 20 \text{ or } 30 \text{ (whichever makes the subsequent arithmetic easier)} \\ 63{,}472 &\rightarrow 6 \times 10^4 \\ 0.002887 &\rightarrow 3 \times 10^{-3} \end{aligned}$$

2. Do the resulting arithmetic by hand, continuing to round off intermediate answers.

$$\frac{(36{,}720)(0.0624)}{0.000478} \approx \frac{(4 \times 10^4)(5 \times 10^{-2})}{5 \times 10^{-4}} = 4 \times 10^{(4-2+4)} = 4 \times 10^6$$

The correct solution (obtained using a calculator) is 4.78×10^6. If you obtain this solution, since it is of the same magnitude as the estimate, you can be reasonably confident that you haven't made a gross error in the calculation.

3. If a number is added to a second, much smaller, number, drop the second number in the approximation.

$$\frac{1}{4.13 + \cancel{0.04762}} \approx \frac{1}{4} = 0.25$$

The calculator solution is 0.239.

Example 2.5-1 Order-of-Magnitude Estimation

A calculation has led to the following:

$$y = \left[\frac{254}{(0.879)(62.4)} + \frac{13}{(0.866)(62.4)}\right] \times \frac{1}{(31.3145)(60)}$$

Estimate y without using a calculator. (The exact solution is 0.00230.)

Solution

$$y \approx \left[\frac{250}{50} + \frac{\cancel{10}}{\cancel{60}}\right] \times \frac{1}{(4 \times 10^1)(6 \times 10^1)} \approx \frac{5}{25 \times 10^2} \approx 0.2 \times 10^{-2} = 0.002$$

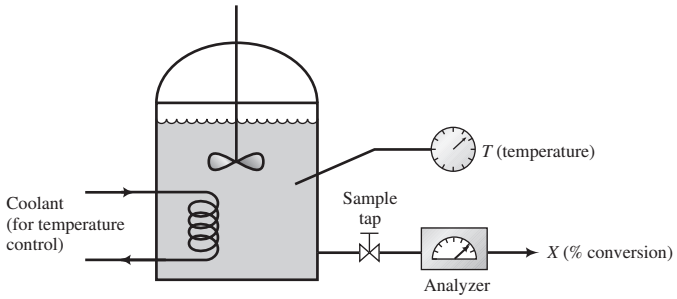
The third way to check a numerical result—and perhaps the first thing you should do when you get one—is to see if the answer is reasonable. If, for example, you calculate that a cylinder contains 4.23×10^{32} kg of hydrogen when the mass of the sun is only 2×10^{30} kg, it should motivate you to redo the calculation. You should similarly be concerned if you calculate a reactor volume larger than the earth (10^{21} m^3) or a room temperature hot enough to melt iron (1535°C). If you get in the habit of asking yourself, "Does this make sense?" every time you come up with a solution to a problem—in engineering and in the rest of your life—you will spare yourself considerable grief and embarrassment.

A sure way to embarrass yourself is to report the result of a calculation with excessive significant figures. For example, suppose you calculate that the required volume of a large vessel to be used in the production of a new bioproduct by fermentation is 1151.6 L. You may, in fact, have done all calculations correctly and had sufficient significant figures to include the 6 to the right of the decimal. Unless you really mean that a volume of that precision is required (which is inconceivable), you should not present it without comment to your colleagues, boss, vendor, or course instructor. Thus, at the end of your calculations, do something like the following:

$$V = 1151.6\,\text{L} \Longrightarrow \boxed{1150\,\text{L}}$$

2.5c Estimation of Measured Values: Sample Mean

Suppose we carry out a chemical reaction of the form A → Products, starting with pure A in the reactor and keeping the reactor temperature constant at 45°C. After two minutes we draw a sample from the reactor and analyze it to determine X, the percentage of the A fed that has reacted.



In theory X should have a unique value; however, in a real reactor X is a *random variable*, changing in an unpredictable manner from one run to another at the same experimental conditions. The values of X obtained after 10 successive runs might be as follows:

Run	1	2	3	4	5	6	7	8	9	10
X(%)	67.1	73.1	69.6	67.4	71.0	68.2	69.4	68.2	68.7	70.2

Why don't we get the same value of X in each run? There are several reasons.

- It is impossible to replicate experimental conditions exactly in successive experiments. If the temperature in the reactor varies by as little as 0.1 degree from one run to another, it could be enough to change the measured value of X.
- Even if conditions were identical in two runs, we could not possibly draw our sample at exactly $t = 2.000\ldots$ minutes both times, and a difference of a second could make a measurable difference in X.
- Variations in sampling and chemical analysis procedures invariably introduce scatter in measured values.

We might ask two questions about the system at this point.

1. *What is the true value of X?*

In principle there may be such a thing as the "true value"—that is, the value we would measure if we could set the temperature exactly to 45.0000 . . . degrees, start the reaction, keep the temperature and all other experimental variables that affect X perfectly constant, and then sample and analyze with complete accuracy at exactly $t = 2.0000\ldots$ minutes. In practice there is no way to do any of those things, however. We could also define the true value of X as the value we would calculate by performing an infinite number of measurements and averaging the results, but there is no practical way to do that either. The best we can ever do is to *estimate* the true value of X from a finite number of measured values.

2. *How can we estimate the true value of X?*

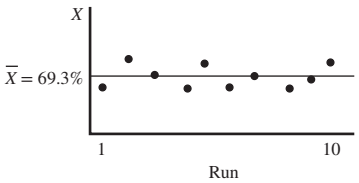
The most common estimate is the *sample mean* (or *arithmetic mean*). We collect N measured values of X $(X_1, X_2, \ldots, X_N)$ and then calculate

Sample Mean:
$$\overline{X} = \frac{1}{N}(X_1 + X_2 + \cdots + X_N) = \frac{1}{N}\sum_{j=1}^{N} X_j \qquad \textbf{(2.5-1)}$$

For the given data, we would estimate

$$\overline{X} = \frac{1}{10}(67.1\% + 73.1\% + \cdots + 70.2\%) = 69.3\%$$

Graphically, the data and sample mean might appear as shown below. The measured values scatter about the sample mean, as they must.



The more measurements of a random variable, the better the estimated value based on the sample mean. However, even with a huge number of measurements the sample mean is at best an approximation of the true value and could in fact be way off (e.g., if there is something wrong with the instruments or procedures used to measure X).

Test Yourself

(Answers, p. 654)

The weekly production rates of a pharmaceutical product over the past six weeks have been 37, 17, 39, 40, 40, and 40 batches per week.

1. Think of several possible explanations for the observed variation in the weekly production rate.
2. If you used the sample mean of the given data as a basis, what would you predict the next weekly production rate to be?
3. Come up with a better prediction, and explain your reasoning.

2.5d Sample Variance of Scattered Data

Consider two sets of measurements of the percentage conversion (X) in the same batch reactor measured using two different experimental techniques. Scatter plots of X versus run number are shown in Figure 2.5-1. The sample mean of each set is 70%, but the measured values scatter over a much narrower range for the first set (from 68% to 73%) than for the second set (from 52% to 88%).

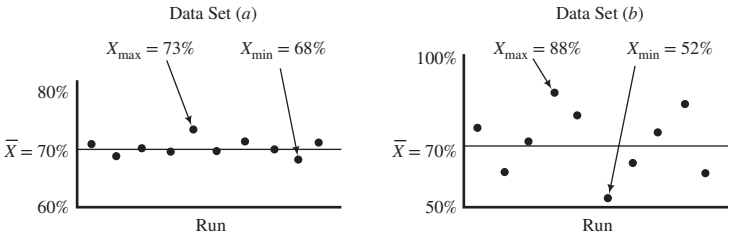


FIGURE 2.5-1 Scatter plots for two data sets with different levels of scatter.

In each case you would estimate the true value of X for the given experimental conditions as the sample mean, 70%, but you would clearly have more confidence in the estimate for Set (a) than in that for Set (b).

Three quantities—the *range*, the *sample variance*, and the *sample standard deviation*—are used to express the extent to which values of a random variable scatter about their mean value. The *range* is simply the difference between the highest and lowest values of X in the data set:

Range: $$R = X_{\max} - X_{\min} \tag{2.5-2}$$

In the first plot of Figure 2.5-1 the range of X is 5% $(73\% - 68\%)$ and in the second plot it is 36% $(88\% - 52\%)$.

The range is the crudest measure of scatter: it involves only two of the measured values and gives no indication of whether or not most of the values cluster close to the mean or scatter widely around it. The *sample variance* is a much better measure. To define it we calculate the *deviation* of each measured value from the sample mean, $X_j - \overline{X}$ $(j = 1, 2, \ldots, N)$, and then calculate

Sample Variance: $$s_X^2 = \frac{1}{N-1}\left[\left(X_1 - \overline{X}\right)^2 + \left(X_2 - \overline{X}\right)^2 + \cdots + \left(X_N - \overline{X}\right)^2\right] \tag{2.5-3}$$

The degree of scatter may also be expressed in terms of the *sample standard deviation*, by definition the square root of the sample variance:

Sample Standard Deviation: $$s_X = \sqrt{s_X^2} \tag{2.5-4}$$

The more a measured value (X_j) deviates from the mean, either positively or negatively, the greater the value of $(X_j - \overline{X})^2$ and hence the greater the value of the sample variance and sample standard deviation. If these quantities are calculated for the data sets of Figure 2.5-1, for example, relatively small values are obtained for Set (a) ($s_X^2 = 0.98$, $s_X = 0.99$) and large values are obtained for Set (b) ($s_X^2 = 132$, $s_X = 11.5$).

For typical random variables, roughly two-thirds of all measured values fall within one standard deviation of the mean; about 88% fall within two standard deviations; and about 99% fall within three standard deviations.[4] A graphical illustration of this statement is shown in Figure 2.5-2. Of the 37 measured values of X, 27 fall within one standard deviation of the mean, 33 within two standard deviations, and 36 within three standard deviations.

Values of measured variables are often reported with error limits, such as $X = 48.2 \pm 0.6$. This statement means that a single measured value of X is likely to fall between 47.6 and 48.8. The midpoint of the range ($X = 48.2$) is almost always the mean value of the data set used to generate this result; however, the significance of the given error limits (± 0.6) is not obvious unless more

[4] The exact percentages depend on how the measured values are distributed about the mean—whether they follow a *Gaussian (normal) distribution*, for example—and how many points are in the data set used to calculate the mean and standard deviation.

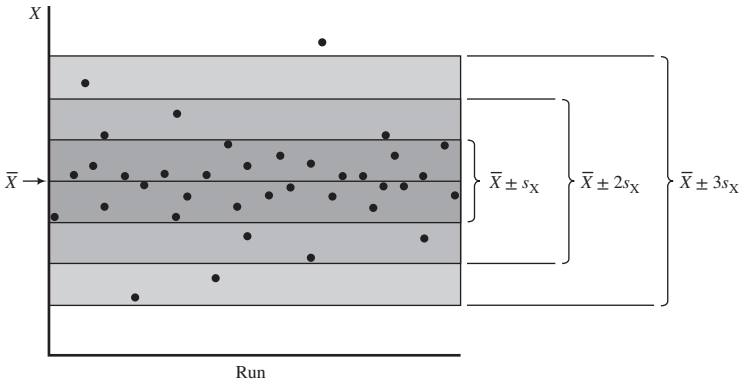


FIGURE 2.5-2 Data scatter about the mean.

information is given. The interval between 47.6 and 48.8 may represent the range of the data set ($X_{max} - X_{min}$) or ± 0.6 might represent $\pm s_X$, $\pm 2s_X$, or $\pm 3s_X$. (There are other possibilities, but they rarely occur.) If you report a variable value in this manner, make clear what your error limits mean.

Test Yourself

(Answers, p. 654)

The volumetric flow rate of a process fluid, $\dot{V}(\text{cm}^3/\text{s})$, is measured five times, with the following results:

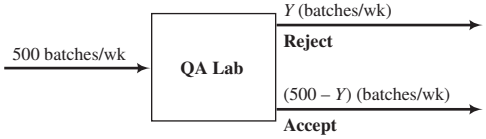
Measurement	1	2	3	4	5
$\dot{V}(\text{cm}^3/\text{s})$	232	248	227	241	239

(a) Calculate the sample mean ($\overline{V}$), range, sample variance (s_V^2), and sample standard deviation (s_V).

(b) There is a high probability (above 90%) that a measured value of $\dot{V}$ will fall within two standard deviations of the mean. Report the value of $\dot{V}$ in the form $\dot{V} = a \pm b$, choosing the values of a and b to define this range.

Example 2.5-2 Statistical Quality Control

Five hundred batches of a pigment are produced each week. In the plant's *quality assurance* (QA) program, each batch is subjected to a precise color analysis test. If a batch does not pass the test, it is rejected and sent back for reformulation.



Let Y be the number of bad batches produced per week, and suppose that QA test results for a 12-week base period are as follows:

Week	1	2	3	4	5	6	7	8	9	10	11	12
Y	17	27	18	18	23	19	18	21	20	19	21	18

The company policy is to regard the process operation as normal as long as the number of bad batches produced in a week is no more than three standard deviations above the mean value for the base period (i.e., as

long as $Y \leq \overline{Y} + 3s_Y$). If Y exceeds this value, the process is shut down for remedial maintenance (a long and costly procedure). Such large deviations from the mean might occur as part of the normal scatter of the process, but so infrequently that if it happens the existence of an abnormal problem in the process is considered the more likely explanation.

1. How many bad batches in a week would it take to shut down the process?
2. What would be the limiting value of Y if two standard deviations instead of three were used as the cutoff criterion? What would be the advantage and disadvantage of using this stricter criterion?

Solution

1. From Equations 2.5-1, 2.5-3, and 2.5-4, the sample mean, sample variance, and sample standard deviation of Y during the base period are

$$\overline{Y} = \frac{1}{12}\sum_{j=1}^{12}(17 + 27 + \cdots + 18) = 19.9 \text{ batches/wk}$$

$$s_Y^2 = \frac{1}{11}\left[(17 - 19.9)^2 + (27 - 19.9)^2 + \cdots + (18 - 19.9)^2\right] = 7.9 \text{ (batches/wk)}^2$$

$$s_Y = \sqrt{7.9} = 2.8 \text{ batches/wk}$$

The maximum allowed value of Y is

$$\overline{Y} + 3s_Y = 19.9 + (3)(2.8) = \boxed{28.3}$$

If 29 or more bad batches are produced in a week, the process must be shut down for maintenance.

2. $\overline{Y} + 2s_Y = 19.9 + (2)(2.8) = \boxed{25.5}$. If this criterion were used, 26 bad batches in a week would be enough to shut down the process. The advantage is that if something *has* gone wrong with the process the problem will be corrected sooner and fewer bad batches will be made in the long run. The disadvantage is that more costly shutdowns may take place when nothing is wrong, the large number of bad batches simply reflecting normal scatter in the process.

2.6 DIMENSIONAL HOMOGENEITY AND DIMENSIONLESS QUANTITIES

We began our discussion of units and dimensions by saying that quantities can be added and subtracted only if their units are the same. If the units are the same, it follows that the dimensions of each term must be the same. For example, if two quantities can be expressed in terms of grams/second, both must have the dimension (mass/time). This suggests the following rule:

Every valid equation must be dimensionally homogeneous: that is, all additive terms on both sides of the equation must have the same dimensions.

Consider the equation

$$u = u_0 + gt \tag{2.6-1}$$

where both u and u_0 have dimensions length/time, g has dimensions of length/time^2, and t is time. A simple check shows that each of the three groups of terms has dimensions of length/time, and therefore the equation is dimensionally homogeneous; on the other hand, $u = u_0 + g$ is not (why not?) and consequently cannot be a valid relationship.

While Equation 2.6-1 is dimensionally homogeneous, the units of each additive term must be identical for the equation to be valid. For instance, suppose that calculations using Equation 2.6-1 have been proceeding with time in seconds, but a new batch of data expresses t in minutes. The equation must then be written as

$$u(\text{m/s}) = u_0(\text{m/s}) + g(\text{m/s}^2)t(\text{min})(60 \text{ s/min})$$

The converse of the given rule is not necessarily true—an equation may be dimensionally homogeneous and invalid. For example, if M is the mass of an object, then the equation $M = 2M$ is dimensionally homogeneous, but it is also obviously incorrect except for one specific value of M.

Example 2.6-1 Dimensional Homogeneity

Consider the equation

$$D(\text{ft}) = 3t(\text{s}) + 4$$

1. If the equation is valid, what are the dimensions of the constants 3 and 4?
2. If the equation is consistent in its units, what are the units of 3 and 4?
3. Derive an equation for distance in meters in terms of time in minutes.

Solution

1. For the equation to be valid, it must be dimensionally homogeneous, so that each term must have the dimension of length. The constant 3 must therefore have the dimension $\boxed{\text{length/time}}$, and 4 must have the dimension $\boxed{\text{length}}$.
2. For consistency, the constants must be $\boxed{3\ \text{ft/s}}$ and $\boxed{4\ \text{ft}}$.
3. Define new variables $D'(\text{m})$ and $t'(\text{min})$. The equivalence relations between the old and new variables are

$$D(\text{ft}) = \frac{D'(\text{m}) \mid \dfrac{3.2808\ \text{ft}}{1\ \text{m}}}{} = 3.28D'$$

$$t(s) = \frac{t'(\text{min}) \mid \dfrac{60\ \text{s}}{1\ \text{min}}}{} = 60t'$$

Substitute these expressions in the given equation

$$3.28D' = (3)(60t') + 4$$

and simplify by dividing through by 3.28

$$\boxed{D'(\text{m}) = 55t'(\text{min}) + 1.22}$$

Exercise: What are the units of 55 and 1.22?

Example 2.6-1 illustrates a general procedure for rewriting an equation in terms of new variables having the same dimensions but different units:

1. Define new variables (e.g., by affixing primes to the old variable names) that have the desired units.
2. Write expressions for each old variable in terms of the corresponding new variable.
3. Substitute these expressions in the original equation and simplify.

A **dimensionless quantity** can be a pure number $(2, 1.3, \frac{5}{2})$ or a multiplicative combination of variables with no net dimensions. Two examples follow:

$$\frac{M(\text{g})}{M_o(\text{g})}, \qquad \frac{D(\text{cm})u(\text{cm/s})\rho(\text{g/cm}^3)}{\mu[\text{g/(cm}\cdot\text{s)}]}$$

A quantity such as M/M_o or $Du\rho/\mu$ is also called a **dimensionless group**.

Exponents (such as the 2 in X^2), transcendental functions (such as log, exp ≡ e, and sin), *and arguments of transcendental functions (such as the X in* sin X) *must be dimensionless quantities.* For example, 10^2 makes perfect sense, but $10^{2\,\text{ft}}$ is meaningless, as is log (20 s) or sin (3 dynes).

Example 2.6-2 Dimensional Homogeneity and Dimensionless Groups

A quantity k depends on the temperature T in the following manner:

$$k\left(\frac{\text{mol}}{\text{cm}^3\cdot\text{s}}\right) = 1.2\times 10^5 \exp\left(-\frac{20{,}000}{1.987T}\right)$$

The units of the quantity 20,000 are cal/mol, and T is in K (kelvin). What are the units of 1.2×10^5 and 1.987?

Solution Since the equation must be consistent in its units and exp is dimensionless, 1.2×10^5 should have the same units as k, mol/(cm^3·s). Moreover, since the argument of exp must be dimensionless, we can write

$$\frac{20{,}000\ \text{cal}}{\text{mol}} \left| \frac{1}{T(\text{K})} \right| \frac{\text{mol}\cdot\text{K}}{1.987\ \text{cal}} \quad \text{(All units cancel)}$$

The answers are thus

$$\boxed{1.2 \times 10^5\ \text{mol/(cm}^3\cdot\text{s)} \quad \text{and} \quad 1.987\ \text{cal/(mol}\cdot\text{K)}}$$

Test Yourself

(Answers, p. 654)

1. What is a dimensionally homogeneous equation? If an equation is dimensionally homogeneous, is it necessarily valid? If an equation is valid, is it necessarily dimensionally homogeneous?
2. If $y(\text{m/s}^2) = az(\text{m}^3)$, what are the units of a?
3. What is a dimensionless group? What multiplicative combination of r(m), s(m/s^2), and t(s) would constitute a dimensionless group?
4. If $z(\text{lb}_\text{f}) = a \sin(Q)$, what are the units of a and Q?

2.7 PROCESS DATA REPRESENTATION AND ANALYSIS

The operation of any chemical process is ultimately based on the measurement of process variables—temperatures, pressures, flow rates, concentrations, and so on. It is sometimes possible to measure these variables directly, but, as a rule, indirect techniques must be used.

Suppose, for example, that you wish to measure the concentration, C, of a solute in a solution. To do so, you normally measure a quantity, X—such as a thermal or electrical conductivity, a light absorbance, or the volume of a titer—that varies in a known manner with C, and then calculate C from the measured value of X. The relationship between C and X is determined in a separate **calibration** experiment in which solutions of known concentration are prepared and X is measured for each solution.

Consider a calibration in which a variable, y, is measured for several values of another variable, x:

x	1.0	2.0	3.0	4.0
y	0.3	0.7	1.2	1.8

In the terms of the first paragraph, y might be a reactant concentration or some other process variable and x would be a readily measured quantity (such as conductivity) whose value correlates with the value of y. Our object is to use the calibration data to estimate the value of y for a value of x between tabulated points (**interpolation**) or outside the range of the table data (**extrapolation**).

A number of interpolation and extrapolation methods are commonly used, including two-point linear interpolation, graphical interpolation, and curve fitting. Which one is most appropriate depends on the nature of the relationship between x and y.

Figure 2.7-1 shows several illustrative (x, y) plots. If the plot of a given data set looks like that shown in plot (a) or (b) of this figure, a straight line would probably be fitted to the data and used as the basis for subsequent interpolation or extrapolation. On the other hand, if the plot is distinctly

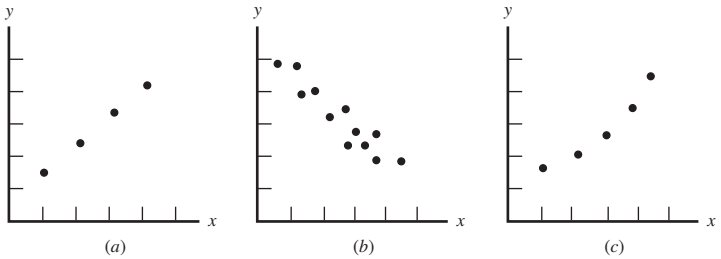


FIGURE 2.7-1 Representative plots of experimental data.

curved as in plot (*c*), a curve could be drawn in by inspection and used as the basis of interpolation, or straight-line segments could be fitted to successive pairs of points, or a nonlinear function $y(x)$ that fits the data could be sought.

The technique of drawing a line or curve through the data by inspection is self-explanatory. The other methods are reviewed in the sections that follow.

2.7a Two-Point Linear Interpolation

The equation of the line through (x_1, y_1) and (x_2, y_2) on a plot of y versus x is

$$y = y_1 + \frac{x - x_1}{x_2 - x_1}(y_2 - y_1) \tag{2.7-1}$$

(Can you prove it?) You may use this equation to estimate y for an x between x_1 and x_2; you may also use it to estimate y for an x outside of this range (i.e., to extrapolate the data), but with a much greater risk of inaccuracy.

If the points in a table are relatively close together, linear interpolation should provide an accurate estimate of y for any x and vice versa; on the other hand, if the points are widely separated or if the data are to be extrapolated, one of the curve-fitting techniques to be outlined in the next section should be used.

Test Yourself

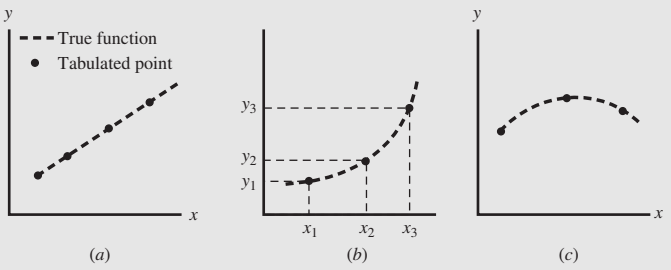
(Answers, p. 654)

1. Values of a variable (f) are measured at several times (t):

f	1	4	8
t	1	2	3

Show that if two-point linear interpolation is used (a) $f(t = 1.3) \approx 1.9$; (b) $t(f = 5) \approx 2.25$.

2. If a function $y(x)$ appears as shown in each of the diagrams shown below, would two-point linear interpolation yield estimates of y that are too high, too low, or correct? If the two-point linear interpolation formula (Equation 2.7-1) were used to estimate $y(x_3)$ from the tabulated values of (x_1, y_1) and (x_2, y_2) in plot (*b*), would the estimated value be too high or too low?



2.7b Fitting a Straight Line

A convenient way to indicate how one variable depends on another is with an equation:

$$y = 3x + 4$$
$$y = 4.24(x - 3)^2 - 23$$
$$y = 1.3 \times 10^7 \sin(2x)/(x^{1/2} + 58.4)$$

If you have an analytical expression for $y(x)$ like those shown above, you can calculate y for any given x or (with a somewhat greater effort) determine x for any given y, or you can write a simple program to perform these calculations.

Suppose the values of a dependent variable y have been measured for several values of an independent variable x, and a plot of y versus x on rectangular coordinates yields what appears to be a straight line. The equation you would use to represent the relationship between x and y is then

$$y = ax + b \tag{2.7-2}$$

If the points show relatively little scatter, like those in Figure 2.7-1*a*, a line may then be drawn through them by inspection, and if (x_1, y_1) and (x_2, y_2) are two points—which may or may not be data points—on the line, then

Slope:
$$a = \frac{y_2 - y_1}{x_2 - x_1} \tag{2.7-3}$$

Intercept:
$$b \begin{cases} = y_1 - ax_1 \\ = y_2 - ax_2 \end{cases} \tag{2.7-4}$$

Once a has been calculated from Equation 2.7-3 and b has been determined from either of Equations 2.7-4, it is good practice to check the result by verifying that Equation 2.7-2 is satisfied at the point—(x_1, y_1) or (x_2, y_2)—*not* used in the calculation of b.

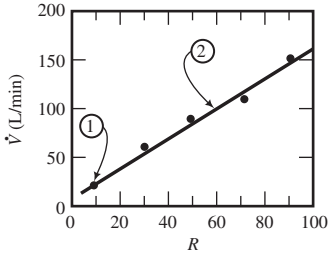
Example 2.7-1 Fitting a Straight Line to Flowmeter Calibration Data

Rotameter calibration data (flow rate versus rotameter reading) are as follows:

Flow Rate $\dot{V}$(L/min)	Rotameter Reading R
20.0	10
52.1	30
84.6	50
118.3	70
151.0	90

1. Draw a calibration curve and determine an equation for $\dot{V}(R)$.
2. Calculate the flow rate that corresponds to a rotameter reading of 36.

Solution **1.** The calibration curve appears as follows:



A line drawn through the data by visual inspection passes through the points ($R_1 = 10$, $\dot{V}_1 = 20$) and ($R_2 = 60$, $\dot{V}_2 = 101$). Therefore,

$$\dot{V} = aR + b \quad \text{(Since the data fall on a line)}$$

$$a = \frac{\dot{V}_2 - \dot{V}_1}{R_2 - R_1} = \frac{101 - 20}{60 - 10} = 1.62 \quad \text{(From Equation 2.7-3)}$$

$$b = \dot{V}_1 - aR_1 = 20 - (1.62)(10) = 3.8 \quad \text{(From Equation 2.7-4)}$$

The result is, therefore,

$$\boxed{\dot{V} = 1.62R + 3.8}$$

Check: At point ②,

$$aR_2 + b = (1.62)(60) + 3.8 = 101 = \dot{V}_2 \quad \checkmark$$

2. At $R = 36$, $\dot{V} = (1.62)(36) + 3.8 = \boxed{62.1 \text{ L/min}}$.

2.7c Fitting Nonlinear Data

During a recent week at a major university, 423 experimenters separately measured and plotted data and found that their data points did not lie on straight points; 416 of these people shrugged their shoulders, said "Close enough," and drew a line anyway; and the other seven went about finding an equation other than $y = ax + b$ to relate the variables.

Fitting a nonlinear equation (anything but $y = ax + b$) to data is usually much harder than fitting a line; however, with some nonlinear equations you can still use straight-line fitting if you plot the data in a suitable manner. Suppose, for example, that x and y are related by the equation $y^2 = ax^3 + b$. A plot of measured y versus x data would clearly be curved; however, a plot of y^2 versus x^3 would be a straight line with a slope a and intercept b. More generally, if any two quantities are related by an equation of the form

$$(\text{Quantity 1}) = a(\text{Quantity 2}) + b$$

then a plot of the first quantity (y^2 in the above example) versus the second (x^3) on rectangular coordinates yields a straight line with slope a and intercept b.

Here are several additional examples of plots that yield straight lines:

1. $y = ax^2 + b$. Plot y versus x^2.

2. $y^2 = \frac{a}{x} + b$. Plot y^2 versus $\frac{1}{x}$.

3. $\frac{1}{y} = a(x + 3) + b$. Plot $\frac{1}{y}$ versus $(x + 3)$.

4. $\sin y = a(x^2 - 4)$. Plot $\sin y$ versus $(x^2 - 4)$. The line through the data must be drawn through the origin. (Why?)

Even if the original equation is not in a proper form to generate a linear plot, you can sometimes rearrange it to get it into such a form:

5. $y = \dfrac{1}{C_1 x - C_2} \Longrightarrow \dfrac{1}{y} = C_1 x - C_2$

Plot $\frac{1}{y}$ versus x. Slope $= C_1$, intercept $= -C_2$.

6. $y = 1 + x(mx^2 + n)^{1/2} \Longrightarrow \dfrac{(y-1)^2}{x^2} = mx^2 + n$

Plot $\dfrac{(y-1)^2}{x^2}$ versus x^2. Slope $= m$, intercept $= n$.

Let us summarize the procedure. If you have (x, y) data that you wish to fit with an equation that can be written in the form $f(x, y) = ag(x, y) + b$,

1. Calculate $f(x, y)$ and $g(x, y)$ for each tabulated (x, y) point, and plot f versus g.
2. If the plotted points fall on a straight line, the equation fits the data. Choose two points on the line—(g_1, f_1) and (g_2, f_2)—and calculate a and b as outlined in the previous section.

$$a = \frac{f_2 - f_1}{g_2 - g_1} \qquad b = f_1 - ag_1 \qquad \text{or} \quad b = f_2 - ag_2$$

Example 2.7-2 Linear Curve-Fitting of Nonlinear Data

A mass flow rate $\dot{m}$(g/s) is measured as a function of temperature T(°C).

T	10	20	40	80
$\dot{m}$	14.76	20.14	27.73	38.47

There is reason to believe that $\dot{m}$ varies linearly with the square root of T:

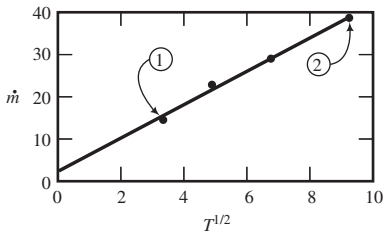
$$\dot{m} = aT^{1/2} + b$$

Use a straight-line plot to verify this relationship and determine a and b.

Solution If the given equation is correct, a plot of $\dot{m}$ versus $T^{1/2}$ should be linear, with slope $= a$ and intercept $= b$. The data table is augmented by adding a $T^{1/2}$ row:

T	10	20	40	80
$T^{1/2}$	3.162	4.472	6.325	8.944
$\dot{m}$	14.76	20.14	27.73	38.47

and $\dot{m}$ is plotted versus $T^{1/2}$.



Since the plot is linear, the proposed equation is verified. A line drawn through the data points passes through the first and last points, so these points may be used to calculate the slope and intercept:

$$\dot{m} = aT^{1/2} + b$$
$$\Downarrow \quad (T_1^{1/2} = 3.162, \dot{m}_1 = 14.76)$$
$$\Downarrow \quad (T_2^{1/2} = 8.944, \dot{m}_2 = 38.47)$$

Slope: $$a = \frac{\dot{m}_2 - \dot{m}_1}{T_2^{1/2} - T_1^{1/2}} = \frac{38.47 - 14.76}{8.944 - 3.162} = 4.10 \text{ g/(s·°C}^{1/2})$$

Intercept: $$b = \dot{m}_1 - aT_1^{1/2} = 14.76 - (4.10)(3.162) = 1.80 \text{ g/s}$$

(verify the units), so that

$$\boxed{\dot{m} = 4.10T^{1/2} + 1.80}$$

Check: At point ②, $4.10T_2^{1/2} + 1.80 = (4.10)(8.944) + 1.80 = 38.47 = \dot{m}_2$. ✓

Two nonlinear functions that often occur in process analysis are the **exponential function**, $y = ae^{bx}$ [or $y = a\exp(bx)$], where $e \approx 2.7182818$, and the **power law**, $y = ax^b$. Before we describe how the parameters of these functions may be determined by linear curve-fitting, let us review some algebra.

The natural logarithm (ln) is the inverse of the exponential function:

$$P = e^Q \Longleftrightarrow \ln P = Q \tag{2.7-5}$$

It follows that

$$\ln(e^Q) = Q \quad \text{and} \quad e^{\ln P} = P \tag{2.7-6}$$

The natural logarithm of a number may be calculated from the common logarithm ($\log_{10}$ or just log) using the relation

$$\ln x = 2.302585 \log_{10} x \tag{2.7-7}$$

The familiar rules for taking logarithms of products and powers are applicable to natural logarithms: if $y = ax$ then $\ln y = \ln a + \ln x$, and if $y = x^b$ then $\ln y = b \ln x$. These properties suggest ways to fit exponential and power law functions to (x, y) data:

$$\left\{\begin{array}{l} y = a\exp(bx) \Longrightarrow \ln y = \ln a + bx \\ \text{Plot } \ln y \text{ versus } x.\ \text{Slope} = b,\ \text{intercept} = \ln a. \end{array}\right\} \tag{2.7-8}$$

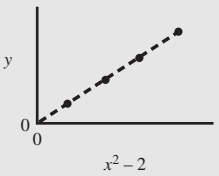
$$\left\{\begin{array}{l} y = ax^b \Longrightarrow \ln y = \ln a + b \ln x \\ \text{Plot } \ln y \text{ versus } \ln x.\ \text{Slope} = b,\ \text{intercept} = \ln a. \end{array}\right\} \tag{2.7-9}$$

Once you have determined $\ln a$ as the intercept of either of these plots, you can calculate a from Equation 2.7-6 as $\exp(\ln a)$; for example, if $\ln a = 3.00$, then $a = \exp(3.00) = 20.1$.

Test Yourself

(Answers, p. 654)

1. The following plot is generated from experimental (x, y) data:



What equation would you use to relate x and y?

2. How would you plot (x, y) data to get a straight line, and how would you determine a and b for each of the following functions?

(a) $y = a\sqrt{x} + b$

Solution: Plot y versus $\sqrt{x}$; let $\left(\sqrt{x_1}, y_1\right)$ and $\left(\sqrt{x_2}, y_2\right)$ be two points on the line; calculate $a = (y_2 - y_1)/\left(\sqrt{x_2} - \sqrt{x_1}\right)$, $b = y_1 - a\sqrt{x_1}$

(b) $1/y = a(x-3)^2 + b$

(c) $y = (ax^2 - b)^{1/3}$

(d) $\sin(y) = x(ax + b)^{-2}$

(e) $y = ae^{bx}$

(f) $y = ax^b$

2.7d Logarithmic Coordinates

Suppose you wish to fit an exponential function $y = a\exp(bx)$ to measured (x, y) data. The determination of a and b is simplified by plotting $\ln y$ as a function of x. There are two plotting

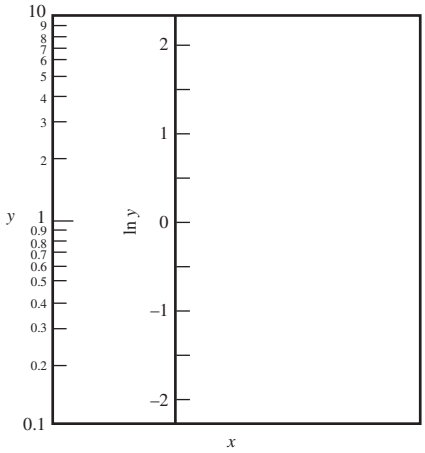


FIGURE 2.7-2 Construction of a logarithmic scale.

procedures you might use: (1) calculate ln y for each value of y, and plot ln y versus x on rectangular axes, or (2) plot y directly on a **logarithmic scale** versus x on a rectangular scale. Figure 2.7-2 illustrates the creation of a logarithmic scale, drawn parallel to a rectangular scale for ln y. All the values on the rectangular ln y scale are the natural logarithms of the adjacent values on the logarithmic y scale; conversely, all values on the y scale are the exponentials of the values on the ln y scale (that is, e raised to those values). Once you have the y scale, instead of having to calculate ln y for each tabulated y to plot the data points on the rectangular axis, you can directly locate and plot the y values on the logarithmic scale. If you wanted to plot a dependent variable versus ln x on a rectangular scale, you could draw a logarithmic scale parallel to the horizontal axis and plot x directly on it, avoiding the need to calculate ln x for each tabulated x value. A plot with logarithmic scales on both axes is called a **log plot**, and a plot with one logarithmic axis and one rectangular (equal interval) axis is called a **semilog plot**.

At one time, use of special graph paper in either log or semilog form was an essential feature of data graphing and analysis. Now, however, many computer programs (such as Excel and Kaleidagraph) will plot data using whatever type of graph you choose.

In short, *plotting values of a variable on a logarithmic scale in effect plots the logarithms of the variable on a rectangular scale*. Suppose, for example, that y and x are related by the equation $y = a \exp(bx)$, or equivalently, $\ln y = \ln a + bx$. To determine a and b you may plot y versus x on a semilog plot, choosing two points (x_1, y_1) and (x_2, y_2) on the resulting line, or you may plot ln y versus x on rectangular axes, drawing the line through the corresponding two points $(x_1, \ln y_1)$ and $(x_2, \ln y_2)$. In either case, b and a are obtained as

$$b = \frac{\ln y_2 - \ln y_1}{x_2 - x_1} = \frac{\ln(y_2/y_1)}{x_2 - x_1}$$

$$\ln a = \ln y_1 - bx_1$$

$$\text{or} \qquad \Longrightarrow [a = \exp(\ln a)]$$

$$\ln a = \ln y_2 - bx_2$$

In summary,

1. If y versus x data appear linear on a semilog plot, then ln y versus x would be linear on a rectangular plot, and the data can therefore be correlated by an exponential function $y = a \exp(bx)$. (See Equation 2.7-8.)

2. If y versus x data appear linear on a log plot, then $\ln y$ versus $\ln x$ would be linear on a rectangular plot, and the data can therefore be correlated by a power law $y = ax^b$. (See Equation 2.7-9.)
3. When you plot values of a variable z on a logarithmic axis and your plot yields a straight line through two points with coordinate values z_1 and z_2, replace $z_2 - z_1$ with $\ln(z_2/z_1)(= \ln z_2 - \ln z_1)$ in the formula for the slope.
4. *Do not plot values of* $\ln z$ *on a logarithmic scale and expect anything useful to result.*

Example 2.7-3 Curve Fitting on Semilog and Log Plots

A plot of F versus t yields a line that passes through the points $(t_1 = 15, F_1 = 0.298)$ and $(t_2 = 30, F_2 = 0.0527)$ on (1) a semilog plot and (2) a log plot. For each case, calculate the equation that relates F and t.

Solution **1.** ***Semilog plot***

$$\begin{aligned} \ln F &= bt + \ln a \qquad \text{(since the plot appears linear)} \\ &\Downarrow \\ F &= ae^{bt} \\ b &= \frac{\ln(F_2/F_1)}{t_2 - t_1} = \frac{\ln(0.0527/0.298)}{(30-15)} = -0.1155 \\ \ln a &= \ln F_1 - bt_1 = \ln(0.298) + (0.1155)(15) = 0.5218 \\ &\Downarrow \\ a &= \exp(0.5218) = 1.685 \end{aligned}$$

or

$$\boxed{F = 1.685\exp(-0.1155t)}$$

Check: $F(t_2) = 1.685\exp(-0.1155 \times 30) = 0.0527$. ✔

2. ***Log plot***

$$\begin{aligned} \ln F &= b\ln t + \ln a \qquad \text{(since the plot appears linear)} \\ &\Downarrow \\ F &= at^b \\ b &= \frac{\ln(F_2/F_1)}{\ln(t_2/t_1)} = \frac{\ln(0.0527/0.298)}{\ln(30/15)} = -2.50 \\ \ln a &= \ln F_1 - b\ln t_1 = \ln(0.298) + 2.5\ln(15) = 5.559 \\ &\Downarrow \\ a &= \exp(5.559) = 260 \end{aligned}$$

or

$$\boxed{F = 260t^{-2.5}}$$

Check: $F(t_2) = 260(30)^{-2.5} = 0.0527$. ✔

Test Yourself

(Answers, p. 654)

1. The following plots yield straight lines. What are the equations that relate the variables?

(a) P versus t on rectangular coordinates.

(b) P (logarithmic axis) versus t on a semilog plot.

(c) P versus t on a log plot.

(d) $y^2 - 3$ (logarithmic axis) versus $1/x^2$ on a semilog plot. (Express the answer as an exponential function.)

(e) $1/F$ versus $t^2 - 4$ on a log plot. (Express the answer as a power law.)

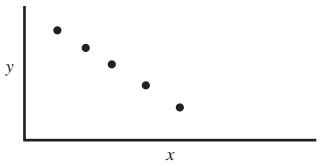
2. What would you plot against what on what kind of axes to get a straight line for the following relationships (a and b are constants)?

(a) $P = a \exp(bt)$ **(c)** $P^2 = \exp(at^3 + b)$

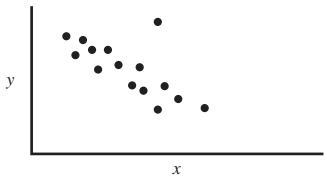
(b) $P = at^b$ **(d)** $1/P = a(t - 4)^{-b}$

2.7e Fitting a Line to Scattered Data

There is little problem fitting a line to data that look like this:



Life being the way it is, however, you are much more likely to come up with something more like this:



When data points are scattered, you can draw any number of lines that appear to fit the points equally well (or equally poorly, depending on your point of view). The question is which line to use.

A number of statistical techniques exist for fitting a function to a set of scattered data. The application of the most common of these techniques—*linear regression* or the *method of least squares*—to the fitting of a straight line to a series of y versus x data points is outlined and illustrated in Appendix A.1, and the use of this technique is required for the solution of Problems 2.48 through 2.53 at the end of this chapter. Alternatively, such fitting of an equation to data can be accomplished with commercial software (such as Excel and Kaleidagraph) and even on some calculators.

2.8 SUMMARY

This chapter introduces some fundamental problem-solving tools that you will need in the rest of this course, in subsequent engineering and science courses, and almost every time in your career when you perform mathematical calculations. The main points of the chapter are as follows.

- You can convert a quantity expressed in one set of units into its equivalent in other dimensionally consistent units using conversion factors, like those in the table on the inside front cover of the text.
- A *weight* is the force exerted on an object by gravitational attraction. The weight of an object of mass m may be calculated as $W = mg$, where g is the acceleration of gravity at the location of the object. At sea level on the earth, $g = 9.8066\ \text{m/s}^2 = 32.174\ \text{ft/s}^2$. To convert a weight (or any force) in natural units like $\text{kg}\cdot\text{m/s}^2$ or $\text{lb}_\text{m}\cdot\text{ft/s}^2$ to its equivalent in a derived force unit like N or lb_f, use the conversion factor table.
- The significant figures (s.f.) with which a number is reported specify the precision with which the number is known. For

instance, $x = 3.0$ (2 s.f.) states that x is somewhere between 2.95 and 3.05, while $x = 3.000$ (4 s.f.) states that it is between 2.9995 and 3.0005. When you multiply and divide numbers, the number of significant figures of the result equals the lowest number of significant figures of any of the factors. In complex calculations, keep the maximum number of significant figures until the final result is obtained, then round off.

- If X is a measured process variable, the *sample mean* of a set of measured values, $\overline{X}$, is the average of the set (the sum of the values divided by the number of values). It is an estimate of the true mean, the value that would be obtained by averaging an infinite number of measurements. The *sample variance* of the set, s_X^2, is a measure of the spread of the measured values about the sample mean. It is calculated from Equation (2.5-3). The *sample standard deviation*, s_X, is the square root of the sample variance.
- If $\overline{X}$ and s_X are determined from a set of normal process runs and a subsequently measured value of X falls more than $2s_X$ away from $\overline{X}$, the chances are that something has changed in the process—there is less than a 10% chance that normal scatter can account for the deviation. If the deviation is greater than $3s_X$, there is less than a 1% chance that normal scatter is the cause. The exact percentages depend on how the measured values are distributed about the mean—whether they follow a Gaussian distribution, for example—and how many points are in the data set used to calculate the mean and standard deviation.
- Suppose you are given a set of values of a dependent variable, y, corresponding to values of an independent variable, x, and you wish to estimate y for a specified x. You can either assume a straight-line dependence for the two data points that bracket the specified x and use two-point linear interpolation (Equation 2.7-1) or fit a function to the data points and use it for the desired estimation.
- If (x, y) data appear to scatter about a straight line on a plot of y versus x, you may fit a line using Equations (2.7-3) and (2.7-4) or, for greater precision and an estimate of the goodness of the fit, use the method of least squares (Appendix A.1). If a plot of y versus x is nonlinear, you may try to fit various nonlinear functions by plotting functions of x and y in a manner that should yield a straight line. For example, to fit a function $y^2 = a/x + b$ to (x, y) data, plot y^2 versus $1/x$. If the fit is good, the plot should be a straight line with slope a and intercept b.
- Plotting y (log scale) versus x (linear scale) on a semilog plot is equivalent to plotting $\ln y$ versus x on rectangular axes. If the plot is linear in either case, x and y are related by an exponential function, $y = ae^{bx}$.
- Plotting y versus x on logarithmic axes is equivalent to plotting $\ln y$ versus $\ln x$ on rectangular axes. If the plot is linear in either case, x and y are related by a power law function, $y = ax^b$.

PROBLEMS

2.1. Using dimensional equations, convert

(a) 2 wk to microseconds.

(b) 38.1 ft/s to kilometers/h.

(c) $554\ m^4/(day \cdot kg)$ to $ft^4/(min \cdot lb_m)$.

2.2. Using the table of conversion factors on the inside front cover, convert

(a) 1760 miles/h to km/s.

(b) $1400\ kg/m^3$ to lb_m/ft^3.

(c) 5.37×10^3 kJ/s to hp.

2.3. Using a single dimensional equation, estimate the number of baseballs it would take to fill your classroom.

2.4. Using a single dimensional equation, estimate the number of steps it would take you, walking at your normal stride, to walk from the Earth to Alpha Centauri, a distance of 4.3 light-years. The speed of light is 1.86×10^5 miles/s.

2.5. You have recently become interested in collecting used classic vinyl recordings. The jackets for these disks often have no liners to protect the records from dust and other sources of scratches, so you seek to purchase some liners from online vendors. Two web sites offer 12-in. inner plastic liners: site A advertises liners with a thickness of 50 microns, while the liners at site B are 3 mils thick. Which of the sites is selling the thicker liner? (*Note:* Neither of the given units of thickness is defined in the text, but definitions are available elsewhere.)

2.6. A frustrated professor once claimed that if all the reports she had graded in her career were stacked on top of one another, they would reach from the Earth to the moon. Assume that an average report is the thickness of about 10 sheets of printer paper and use a single dimensional equation to estimate the number of reports the professor would have had to grade for her claim to be valid.

2.7. You are trying to decide which of two automobiles to buy. The first is American-made, costs $28,500, and has a rated gasoline mileage of 28 miles/gal. The second car is of European manufacture, costs

$35,700, and has a rated mileage of 19 km/L. If the cost of gasoline is $3.25/gal and if the cars actually deliver their rated mileage, estimate how many miles you would have to drive for the lower fuel consumption of the second car to compensate for the higher cost of this car.

2.8. On a website devoted to answering engineering questions, viewers were invited to determine how much power a 100-MW power plant generates annually. The answer declared to be best was submitted by a civil engineering student, who stated, "It produces 100 MW/hr so over the year that's 100*24*365.25 & do the math."
(a) Carry out the calculation, showing all the units.
(b) What is wrong with the statement of the question?
(c) Why was the student wrong in saying that the plant produces 100 MW/hr?

2.9. Calculate
(a) the weight in lb_f of a 25.0-lb_m object.
(b) the mass in kg of an object that weighs 25 N.
(c) the weight in dynes of a 10-ton object (not metric tons).

2.10. A waste treatment pond is 50 m long and 25 m wide, and has an average depth of 2 m. The density of the waste is 75.3 lb_m/ft^3. Calculate the weight of the pond contents in lb_f, using a single dimensional equation for your calculation.

2.11. Five hundred lb_m of nitrogen is to be charged into a small metal cylinder at 25°C, at a pressure such that the gas density is 12.5 kg/m^3. Without using a calculator, estimate the required cylinder volume in ft^3. Show your work.

2.12. The daily production of carbon dioxide from an 880 MW coal-fired power plant is estimated to be 31,000 tons. A proposal has been made to capture and sequester the CO_2 at approximately 300 K and 140 atm. At these conditions, the specific volume of CO_2 is estimated to be 0.012 m^3/kg. What volume (m^3) of CO_2 would be collected during a one-year period?

ALTERNATIVE ENERGY →

2.13. The cost of a single solar panel lies in the range of $200 to $400, depending on the power output of the panel and the material it is made from. Before investing in equipping your home with solar power, it is wise to see whether the savings in the cost of electricity would justify the amount you would invest in the panels.
(a) Suppose your monthly electrical usage equals the national U.S. household average of 948 kWh. Assuming an average of five hours of sunlight per day and a 30-day month, calculate how many panels you would need to provide that amount of energy and what the total cost would be for each of the following two types of panels: (i) 140 W panel that costs $210; (ii) 240 W panel that costs $260. What is your conclusion?
(b) Suppose you decide to install the 240 W panels, and the average cost of electricity purchased over the next three years is $0.15/kWh. What would the total cost savings be over that 3-year period? What more would you need to know to determine whether the investment in the solar panels would pay off? (Remember that a solar power installation involves batteries, AC/DC converters, wires, and considerable hardware in addition to the solar panels themselves.)
(c) What might motivate someone to decide to install the solar panels even if the calculation of Part (b) shows that the installation would not be cost-effective?

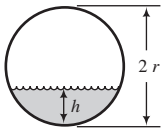
2.14. According to Archimedes' principle, the mass of a floating object equals the mass of the fluid displaced by the object. Use this principle to solve the following problems.
(a) A wooden cylinder 30.0 cm high floats vertically in a tub of water (density = 1.00 g/cm^3). The top of the cylinder is 13.5 cm above the surface of the liquid. What is the density of the wood?
(b) The same cylinder floats vertically in a liquid of unknown density. The top of the cylinder is 18.9 cm above the surface of the liquid. What is the liquid density?
(c) Explain why knowing the length and width of the wooden objects is unnecessary in solving Parts (a) and (b).

2.15. A right circular cone of base radius R, height H, and known density ρ_s floats base down in a liquid of unknown density ρ_f. A height h of the cone is above the liquid surface. Derive a formula for ρ_f in terms of ρ_s, R, and h/H, simplifying it algebraically to the greatest possible extent. [Recall Archimedes' principle, stated in the preceding problem, and note that the volume of a cone equals (base area)(height)/3.]

2.16. A horizontal drum, a cross-section of which is shown below, is being filled with benzene (density = 0.879 g/cm^3) at a constant rate $\dot{m}$(kg/min). The drum has a length L and radius r, and the level of benzene in the drum is h. The expression for the volume of benzene in the drum is

$$V = L\left[r^2 \cos^{-1}\left(\frac{r-h}{r}\right) - (r-h)\sqrt{r^2-(r-h)^2}\right]$$

(a) Show that the equation gives reasonable results for $h = 0$, $h = r$, and $h = 2r$.
(b) Estimate the mass of benzene (kg) in the tank if $L = 10$ ft, $r = 2$ ft, and $h = 4$ in.
(c) Suppose there is a sight glass on the side of the tank that allows observation of the height of liquid in the tank. Use a spreadsheet to prepare a graph that can be posted next to the sight glass so that an operator can estimate the mass that is in the tank without going through calculations like that in Part (b).



2.17. A **poundal** is the force required to accelerate a mass of 1 lb$_m$ at a rate of 1 ft/s^2, and a **slug** is the mass of an object that will accelerate at a rate of 1 ft/s^2 when subjected to a force of 1 lb$_f$.
(a) Calculate the mass in slugs and the weight in poundals of a 135 lb$_m$ woman (i) on earth and (ii) on the moon, where the acceleration of gravity is one-sixth of its value on earth.
(b) A force of 405 poundals is exerted on a 35.0-slug object. At what rate (m/s^2) does the object accelerate?

2.18. The **doozy** is defined as the unit of force required to accelerate a unit of mass, called the **cuz**, with the gravitational acceleration on the surface of the moon, which is one-sixth of the normal gravitational acceleration on earth.
(a) What is the conversion factor that would be used to convert a force from the natural unit to the derived unit in this system? (Give both its numerical value and its units.)
(b) What is the weight in doozies of a 3-cuz object on the moon? What does the same object weigh in Lizard Lick, North Carolina?

SAFETY

*2.19. During the early part of the 20th century, sulfanilamide (an antibacterial drug) was only administered by injection or in a solid pill. In 1937, a pharmaceutical company decided to market a liquid formulation of the drug. Since sulfanilamide was known to be highly insoluble in water and other common pharmaceutical solvents, a number of alternative solvents were tested and the drug was found to be soluble in diethylene glycol (DEG). After satisfactory results were obtained in tests of flavor, appearance, and fragrance, 240 gallons of sulfanilamide in DEG were manufactured and marketed as Elixir Sulfanilamide. After a number of deaths were determined to have been caused by the formulation, the Food and Drug Administration (FDA) mounted a campaign to recall the drug and recovered about 232 gallons. By this time, 107 people had died. The incident led to passage of the 1938 Federal Food, Drug, and Cosmetic Act that significantly tightened FDA safety requirements.

Not all of the quantities needed in solving the following problems can be found in the text. Give sources of such information and list all assumptions.
(a) The dosage instructions for the elixir were to "take 2 to 3 teaspoons in water every four hours." Assume each teaspoon was pure DEG, and estimate the volume (mL) of DEG a patient would have consumed in a day.
(b) The lethal oral dose of diethylene glycol has been estimated to be 1.4 mL DEG/kg body mass. Determine the maximum patient mass (lb$_m$) for which the daily dose estimated in Part (a) would be

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater, "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses—Part I" (2010), http://pharmahub.org/resources/360.

fatal. If you need values of quantities you cannot find in this text, use the Internet. Suggest three reasons why that dose could be dangerous to a patient whose mass is well above the calculated value.

(c) Estimate how many people would have been poisoned if the total production of the drug had been consumed.

(d) List steps the company should have taken that would have prevented this tragedy.

2.20. Perform the following calculations. In each case, first estimate the solution without using a calculator, following the procedure outlined in Section 2.5b, and then do the calculation, paying attention to significant figures.

(a) $(2.7)(8.632)$

(b) $(3.600 \times 10^{-4})/45$

(c) $2.365 + 125.2$

(d) $(4.753 \times 10^{4}) - (9 \times 10^{2})$

2.21. The following expression has occurred in a problem solution:

$$R = \frac{(0.6700)(264{,}980)(6)(5.386 \times 10^{4})}{(3.14159)(0.479 \times 10^{7})}$$

The factor 6 is a pure integer. Estimate the value of R without using a calculator, following the procedure outlined in Section 2.5b. Then calculate R, expressing your answer in both scientific and decimal notation and making sure it has the correct number of significant figures.

Equipment Encyclopedia
thermocouple
@
www.wiley.com/college/felder

2.22. Two thermocouples (temperature measurement devices) are tested by inserting their probes in boiling water, recording the readings, removing and drying the probes, and then doing it again. The results of five measurements are as follows:

T(°C)—Thermocouple A	72.4	73.1	72.6	72.8	73.0
T(°C)—Thermocouple B	97.3	101.4	98.7	103.1	100.4

(a) For each set of temperature readings, calculate the sample mean, the range, and the sample standard deviation.

(b) Which thermocouple readings exhibit the higher degree of scatter? Which thermocouple is more accurate? Explain your answers.

2.23. Product quality assurance (QA) is a particularly tricky business in the dye manufacturing industry. A slight variation in reaction conditions can lead to a measurable change in the color of the product, and since customers usually require extremely high color reproducibility from one shipment to another, even a small color change can lead to rejection of a product batch.

Suppose the various color frequency and intensity values that comprise a color analysis are combined into a single numerical value, C, for a particular yellow dye. During a test period in which the reactor conditions are carefully controlled and the reactor is thoroughly cleaned between successive batches (not the usual procedure), product analyses of 12 batches run on successive days yield the following color readings:

Batch	1	2	3	4	5	6	7	8	9	10	11	12
C	74.3	71.8	72.0	73.1	75.1	72.6	75.3	73.4	74.8	72.6	73.0	73.7

(a) The QA specification for routine production is that a batch that falls more than two standard deviations away from the test period mean must be rejected and sent for reworking. Determine the minimum and maximum acceptable values of C.

(b) A statistician working in quality assurance and a production engineer are having an argument. One of them, Frank, wants to raise the QA specification to three standard deviations and the other, Joanne, wants to lower it to one. Reworking is time-consuming, expensive, and very unpopular with the engineers who have to do it. Who is more likely to be the statistician and who the engineer? Explain.

(c) Suppose that in the first few weeks of operation relatively few unacceptable batches are produced, but then the number begins to climb steadily. Think of up to five possible causes, and state how you might go about determining whether or not each of them might in fact be responsible for the drop in quality.

2.24. Your company manufactures plastic wrap for food storage. The tear resistance of the wrap, denoted by X, must be controlled so that the wrap can be torn off the roll without too much effort but it does not tear too easily when in use.

In a series of test runs, 15 rolls of wrap are made under carefully controlled conditions and the tear resistance of each roll is measured. The results are used as the basis of a *quality assurance specification* (see Problem 2.23). If X for a subsequently produced roll falls more than two standard deviations away from the test period average, the process is declared out of specification and production is suspended for routine maintenance.

The test series data are as follows:

Roll	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
X	134	131	129	133	135	131	134	130	131	136	129	130	133	130	133

(a) Write a spreadsheet to take as input the test series data and calculate the sample mean ($\overline{X}$) and sample standard deviation (s_X), preferably using built-in functions for the calculations.

(b) The following tear resistance values are obtained for rolls produced in 14 consecutive production runs subsequent to the test series: 128, 131, 133, 130, 133, 129, 133, 135, 137, 133, 137, 136, 137, 139. On the spreadsheet (preferably using the spreadsheet plotting capability), plot a control chart of X versus run number, showing horizontal lines for the values corresponding to $\overline{X}$, $\overline{X} - 2s_X$, and $\overline{X} + 2s_X$ from the test period, and show the points corresponding to the 14 production runs. (See Figure 2.5-2.) Which measurements led to suspension of production?

(c) Following the last of the production runs, the chief plant engineer returns from vacation, examines the plant logs, and says that routine maintenance was clearly not sufficient and a process shutdown and full system overhaul should have been ordered at one point during the two weeks he was away. When would it have been reasonable to take this step, and why?

2.25. A variable, Q, is reported to have a value of 2.360×10^{-4} kg·m^2/h.

(a) Write a dimensional equation for Q', the equivalent variable value expressed in U.S. customary units, using seconds as the unit for time.

(b) Estimate Q' without using a calculator, following the procedure outlined in Section 2.5b. (Show your calculations.) Then determine Q' with a calculator, expressing your answer in both scientific and decimal notation and making sure it has the correct number of significant figures.

2.26. The **Prandtl number**, N_{Pr}, is a dimensionless group important in heat-transfer calculations. It is defined as $C_p\mu/k$, where C_p is the heat capacity of a fluid, μ is the fluid viscosity, and k is the thermal conductivity. For a particular fluid, $C_p = 0.583$ J/(g·°C), $k = 0.286$ W/(m·°C), and $\mu = 1936$ lb$_m$/(ft·h). Estimate the value of N_{Pr} without using a calculator (remember, it is dimensionless), showing your calculations; then determine it with a calculator.

2.27. The **Reynolds number** is a dimensionless group defined for a fluid flowing in a pipe as

$$Re = Du\rho/\mu$$

where D is pipe diameter, u is fluid velocity, ρ is fluid density, and μ is fluid viscosity. When the value of the Reynolds number is less than about 2100, the flow is *laminar*—that is, the fluid flows in smooth streamlines. For Reynolds numbers above 2100, the flow is *turbulent*, characterized by a great deal of agitation.

Liquid methyl ethyl ketone (MEK) flows through a pipe with an inner diameter of 2.067 inches at an average velocity of 0.48 ft/s. At the fluid temperature of 20°C the density of liquid MEK is 0.805 g/cm^3 and the viscosity is 0.43 centipoise [1 cP $= 1.00 \times 10^{-3}$ kg/(m·s)]. Without using a calculator, determine whether the flow is laminar or turbulent. Show your calculations.

2.28. The following empirical equation correlates the values of variables in a system in which solid particles are suspended in a flowing gas:

$$\frac{k_g d_p y}{D} = 2.00 + 0.600\left(\frac{\mu}{\rho D}\right)^{1/3}\left(\frac{d_p u \rho}{\mu}\right)^{1/2}$$

Both $(\mu/\rho D)$ and $(d_p u\rho/\mu)$ are dimensionless groups; k_g is a coefficient that expresses the rate at which a particular species transfers from the gas to the solid particles; and the coefficients 2.00 and 0.600 are dimensionless constants obtained by fitting experimental data covering a wide range of values of the equation variables.

The value of k_g is needed to design a catalytic reactor. Since this coefficient is difficult to determine directly, values of the other variables are measured or estimated and k_g is calculated from the given correlation. The variable values are as follows:

$$\begin{aligned} d_p &= 5.00\,\text{mm} \\ y &= 0.100 \quad \text{(dimensionless)} \\ D &= 0.100\,\text{cm}^2/\text{s} \\ \mu &= 1.00 \times 10^{-5}\,\text{N}\cdot\text{s/m}^2 \\ \rho &= 1.00 \times 10^{-3}\,\text{g/cm}^3 \\ u &= 10.0\,\text{m/s} \end{aligned}$$

(a) What is the estimated value of k_g? (Give its value and units.)

(b) Why might the true value of k_g in the reactor be significantly different from the value estimated in Part (a)? (Give several possible reasons.)

(c) Create a spreadsheet in which up to five sets of values of the given variables (d_p through u) are entered in columns and the corresponding values of k_g are calculated. Test your program using the following variable sets: (i) the values given above; (ii) as above, only double the particle diameter d_p (making it 10.00 mm); (iii) as above, only double the diffusivity D; (iv) as above, only double the viscosity μ; (v) as above, only double the velocity u. Report all five calculated values of k_g.

2.29. A seed crystal of diameter D (mm) is placed in a solution of dissolved salt, and new crystals are observed to nucleate (form) at a constant rate r (crystals/min). Experiments with seed crystals of different sizes show that the rate of nucleation varies with the seed crystal diameter as

$$r(\text{crystals/min}) = 200D - 10D^2 \qquad (D \text{ in mm})$$

(a) What are the units of the constants 200 and 10? (Assume the given equation is valid and therefore dimensionally homogeneous.)

(b) Calculate the crystal nucleation rate in crystals/s corresponding to a crystal diameter of 0.050 inch.

(c) Derive a formula for r(crystals/s) in terms of D(inches). (See Example 2.6-1.) Check the formula using the result of Part (b).

Exploratory Exercise—Research and Discover

(d) The given equation is empirical; that is, instead of being developed from first principles, it was obtained simply by fitting an equation to experimental data. In the experiment, seed crystals of known size were immersed in a well-mixed *supersaturated* solution. After a fixed run time, agitation was ceased and the crystals formed during the experiment were allowed to settle to the bottom of the apparatus, where they could be counted. Explain what it is about the equation that gives away its empirical nature. (*Hint:* Consider what the equation predicts as D continues to increase.)

2.30. The density of a fluid is given by the empirical equation

$$\rho = 70.5 \exp(8.27 \times 10^{-7} P)$$

where ρ is density ($\text{lb}_\text{m}/\text{ft}^3$) and P is pressure ($\text{lb}_\text{f}/\text{in}^2$).

(a) What are the units of 70.5 and 8.27×10^{-7}?

(b) Calculate the density in g/cm^3 for a pressure of $9.00 \times 10^6\ \text{N/m}^2$.

(c) Derive a formula for $\rho(\text{g/cm}^3)$ as a function of $P(\text{N/m}^2)$. (See Example 2.6-1.) Check your result using the solution of Part (b).

BIOENGINEERING

2.31. The volume of a microbial culture is observed to increase according to the formula

$$V(\text{cm}^3) = ae^{bt}$$

where t is time in seconds.

(a) Calculate the expression for $V(\text{in}^3)$ in terms of t(h).

(b) Since both the exponential function and its argument must be dimensionless, what must be the units of a and b?

2.32. A concentration C (mol/L) varies with time (min) according to the equation

$$C = 3.00 \exp(-2.00t)$$

(a) What are the implicit units of 3.00 and 2.00?
(b) Suppose the concentration is measured at $t = 0$ and $t = 1$ min. Use two-point linear interpolation or extrapolation to estimate $C(t = 0.6 \text{ min})$ and $t(C = 0.10 \text{ mol/L})$ from the measured values, and compare these results with the true values of these quantities.
(c) Sketch a curve of C versus t, and show graphically the points you determined in Part (b).

BIOENGINEERING

2.33. The following table is a summary of data taken on the growth of yeast cells in a bioreactor:

Time, t(h)	Yeast Concentration, X(g/L)
0	0.010
4	0.048
8	0.152
12	0.733
16	2.457

The data can be fit with the function

$$X = X_0 \exp(\mu t)$$

where X is the concentration of cells at any time t, X_0 is the starting concentration of cells, and μ is the *specific growth rate*.
(a) Based on the data in the table, what are the units of the specific growth rate?
(b) Give two ways to plot the data so as to obtain a straight line. Each of your responses should be of the form "plot ____ versus ____ on ____ axes."
(c) Plot the data in one of the ways suggested in Part (b) and determine μ from the plot.
(d) How much time is required for the yeast population to double?

BIOENGINEERING

*2.34. You arrive at your lab at 8 A.M. and add an indeterminate quantity of bacterial cells to a flask. At 11 A.M. you measure the number of cells using a spectrophotometer (the absorbance of light is directly related to the number of cells) and determine from a previous calibration that the flask contains 3850 cells, and at 5 P.M. the cell count has reached 36,530.
(a) Fit each of the following formulas to the two given data points (that is, determine the values of the two constants in each formula): linear growth, $C = C_0 + kt$; exponential growth, $C = C_0 e^{kt}$; power-law growth, $C = kt^b$. In these expressions, C_0 is the initial cell concentration and k and b are constants.
(b) Select the most reasonable of the three formulas and justify your selection.
(c) Estimate the initial number of cells present at 8 A.M. ($t = 0$). State any assumptions you make.
(d) The culture needs to be split into two equal parts once the number of cells reaches 2 million. Estimate the time at which you would have to come back to perform this task. State any assumptions you make. If this is a routine operation that you must perform often, what does your result suggest about the scheduling of the experiment?

BIOENGINEERING

**2.35. Bacteria can serve as catalysts for the conversion of low-cost chemicals, such as glucose, into higher value compounds, including commodity chemicals (with large production rates) and high-value specialty chemicals such as pharmaceuticals, dyes, and cosmetics. Commodity chemicals are produced from bacteria in very large bioreactors. For example, cultures up to 130,000 gallons are used to produce antibiotics and other therapeutics, industrial enzymes, and polymer intermediates.

When a healthy bacteria culture is placed in a suitable environment with abundant nutrients, the bacteria experience balanced growth, meaning that they continue to double in number in the same fixed period of time. The doubling time of *mesophilic* bacteria (bacteria that live comfortably at temperatures

* Adapted from a problem contributed by John Falconer and Garret Nicodemus of the University of Colorado at Boulder.

** Adapted from a problem contributed by Claire Komives of San Jose State University.

between 35°C and 40°C) ranges anywhere from 20 minutes to a few hours. During balanced growth, the rate of growth of the bacteria is given by the expression

$$\frac{dC}{dt} = \mu C$$

where C(g/L) is the concentration of bacteria in the culture and μ is called *the specific growth rate* of the bacteria (also described in Problem 2.33). The balanced growth phase eventually comes to an end, due either to the presence of a toxic byproduct or the lack of a key nutrient.

The following data were measured for the growth of a particular species of mesophilic bacteria at a constant temperature:

t(h)	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
C(g/L)	0.008	0.021	0.030	0.068	0.150	0.240	0.560	1.10

(a) If bacteria are used in the production of a commodity chemical, would a low or high value of μ be desirable? Explain.

(b) In the rate expression, separate the variables and integrate to derive an expression of the form $f(C, C_0) = \mu t$, where C_0 is the bacteria concentration that would be measured at $t = 0$ if balanced growth extended back that far. (It might not.) What would you plot versus what on what kind of coordinates (rectangular, semilog, or log) to get a straight line if growth is balanced, and how would you determine μ and C_0 from the plot? (Review Section 2.7 if necessary.)

(c) From the given data, determine whether balanced growth was maintained between $t = 1$ h and $t = 8$ h. If it was, calculate the specific growth rate. (Give both its numerical value and its units.)

(d) Derive an expression for the doubling time of a bacterial species in balanced growth in terms of μ. [You may make use of your calculations in Part (b).] Calculate the doubling time of the species for which the data are given.

SAFETY

*__2.36.__ The following reactions take place in a batch reactor:

$$\text{A} + \text{B} \rightarrow \text{C (desired product)}$$
$$\text{B} + \text{C} \rightarrow \text{D (hazardous product)}$$

As the reaction proceeds, D builds up in the reactor and could cause an explosion if its concentration exceeds 15 mol/L. To ensure the safety of the plant personnel, the reaction is quenched (e.g., by cooling the reactor contents to a low temperature) and the products are extracted when the concentration of D reaches 10 mol/L.

The concentration of C is measured in real-time, and samples are periodically taken and analyzed to determine the concentration of D. The data are shown below:

C_C (mol/L)	C_D (mol/L)
2.8	1.4
10	2.27
20	2.95
40	3.84
70	4.74
110	5.63
160	6.49
220	7.32

* Adapted from a problem contributed by Matthew Cooper of North Carolina State University.

(a) What would be the general form of an expression for C_D as a function of C_C?
(b) Derive the expression.
(c) At what concentration of C is the reactor stopped?
(d) Someone proposed not stopping the reaction until $C_D = 13$ mol/L, and someone else strongly objected. What would be the major arguments for and against that proposal?

2.37. The vapor pressures of 1-chlorotetradecane at several temperatures are tabulated here.

T(°C)	98.5	131.8	148.2	166.2	199.8	215.5
p^*(mm Hg)	1	5	10	20	60	100

(a) Use two-point linear interpolation to estimate the value of p^* at $T = 185$°C.
(b) Suppose you only know the data at 98.5°C and 215.5°C. Use two-point linear interpolation to estimate the vapor pressure at 148.2°C. Assume the measured vapor pressure in the table is the true value, and calculate the percentage error in your interpolated value. Why would you expect the error associated with the estimate in Part (a) to be significantly less than that of Part (b)?

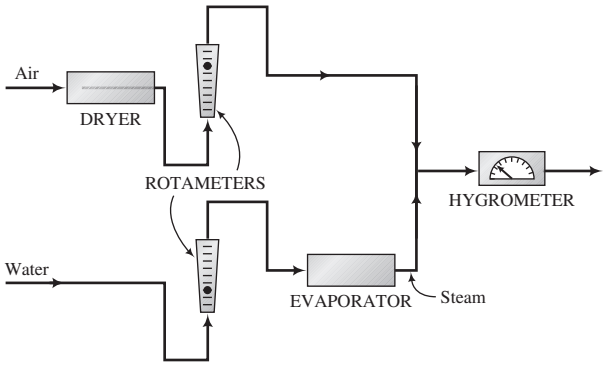
2.38. Sketch the plots described below and calculate the equations for $y(x)$ from the given information. The plots are all straight lines. Note that the given coordinates refer to abscissa and ordinate values, not x and y values. [The solution of Part (a) is given as an example.]
(a) A plot of $\ln y$ versus x on rectangular coordinates passes through (1.0, 0.693) and (2.0, 0.0) (i.e., at the first point $x = 1.0$ and $\ln y = 0.693$).

Solution :
$$\ln y = bx + \ln a \Longrightarrow y = ae^{bx}$$
$$b = (\ln y_2 - \ln y_1)/(x_2 - x_1) = (0 - 0.693)/(2.0 - 1.0) = -0.693$$
$$\ln a = \ln y_1 - bx_1 = 0.693 + (0.693)(1.0) = 1.386 \Longrightarrow a = e^{1.386} = 4.00$$
$$\Downarrow$$
$$\boxed{y = 4.00e^{-0.693x}}$$

(b) A semilog plot of y (logarithmic axis) versus x passes through (1, 2) and (2, 1).
(c) A log plot of y versus x passes through (1, 2) and (2, 1).
(d) A semilog plot of xy (logarithmic axis) versus y/x passes through (1.0, 40.2) and (2.0, 807.0).
(e) A log plot of y^2/x versus $(x - 2)$ passes through (1.0, 40.2) and (2.0, 807.0).

2.39. State what you would plot to get a straight line if experimental (x, y) data are to be correlated by the following relations, and what the slopes and intercepts would be in terms of the relation parameters. If you could equally well use two different kinds of plots (e.g., rectangular or semilog), state what you would plot in each case. [The solution to Part (a) is given as an example.]
(a) $y^2 = ae^{-b/x}$.
Solution: Construct a semilog plot of y^2 versus $1/x$ or a plot of $\ln(y^2)$ versus $1/x$ on rectangular coordinates. Slope $= -b$, intercept $= \ln a$.
(b) $y^2 = mx^3 - n$
(c) $1/\ln(y - 3) = \left(1 + a\sqrt{x}\right)/b$
(d) $(y + 1)^2 = [a(x - 3)^3]^{-1}$
(e) $y = \exp\left(a\sqrt{x} + b\right)$
(f) $xy = 10^{[a(x^2+y^2)+b]}$
(g) $y = [ax + b/x]^{-1}$

2.40. A **hygrometer**, which measures the amount of moisture in a gas stream, is to be calibrated using the apparatus shown here:



Steam and dry air are fed at known flow rates and mixed to form a gas stream with a known water content, and the hygrometer reading is recorded; the flow rate of either the water or the air is changed to produce a stream with a different water content and the new reading is recorded, and so on. The following data are taken:

Mass Fraction of Water, y	Hygrometer Reading, R
0.011	5
0.044	20
0.083	40
0.126	60
0.170	80

(a) Draw a calibration curve and determine an equation for $y(R)$.
(b) Suppose a sample of a stack gas is inserted in the sample chamber of the hygrometer and a reading of $R = 43$ is obtained. If the mass flow rate of the stack gas is 1200 kg/h, what is the mass flow rate of water vapor in the gas?

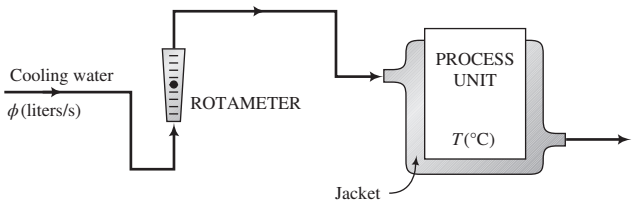
BIOENGINEERING

2.41. L-Serine is an amino acid important for its roles in synthesizing other amino acids and for its use in intravenous feeding solutions. It is often synthesized commercially by fermentation, and recovered by subjecting the fermentation broth to several processing steps and then crystallizing the serine from an aqueous solution. The solubilities of L-serine (L-Ser) in water have been measured at several temperatures, producing the following data:[5]

T(K)	283.4	285.9	289.3	299.1	316.0	317.8	322.9	327.1
x(mole fraction L-Ser)	0.0400	0.0426	0.0523	0.0702	0.1091	0.1144	0.1181	0.1248

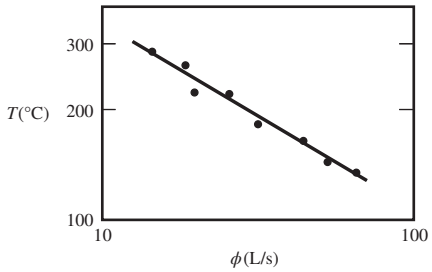
One of the ways such data can be represented is with the *van't Hoff equation*: $\ln x = (a/T) + b$. Graph the data so that the resulting plot is linear. Estimate a and b and give their units.

2.42. The temperature in a process unit is controlled by passing cooling water at a measured rate through a jacket that encloses the unit.



[5] C.-W. J. Luk, MS thesis, Georgia Institute of Technology, 2005.

The exact relationship between the unit temperature T(°C) and the water flow rate ϕ (L/s) is extremely complex, and it is desired to derive a simple empirical formula to approximate this relationship over a limited range of flow rates and temperatures. Data are taken for T versus ϕ. Plots of T versus ϕ on rectangular and semilog coordinates are distinctly curved (ruling out $T = a\phi + b$ and $T = ae^{b\phi}$ as possible empirical functions), but a log plot appears as follows:



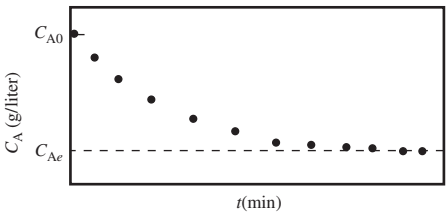
A line drawn through the data goes through the points ($\phi_1 = 25$ L/s, $T_1 = 210$°C) and ($\phi_2 = 40$ L/s, $T_2 = 120$°C).

(a) What is the empirical relationship between ϕ and T?

(b) Using your derived equation, estimate the cooling water flow rates needed to maintain the process unit temperature at 85°C, 175°C, and 290°C.

(c) In which of the three estimates in Part (b) would you have the most confidence and in which would you have the least confidence? Explain your reasoning.

2.43. A chemical reaction A → B is carried out in a closed vessel. The following data are taken for the concentration of A, C_A(g/L), as a function of time, t(min), from the start of the reaction:



t(min)	0	36	65	100	160	∞
C_A(g/liter)	0.1823	0.1453	0.1216	0.1025	0.0795	0.0495
	↑ C_{A0}					↑ C_{Ae}

A proposed reaction mechanism predicts that C_A and t should be related by the expression

$$\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = -kt$$

where k is the **reaction rate constant**.

(a) Do the data support this prediction? If so, plot the data appropriately to determine the value of k.

(b) If the tank volume is 125 L and there is no B in the tank at $t = 0$, how much B(g) does the tank contain after two hours?

(c) Estimate the time required for the final concentration of A to reach 1.1, 1.05, and 1.01 times C_{Ae}, and determine the mass of B produced at each of these conditions for the reactor described in Part (b).

2.44. The climactic moment in the film "The Eggplant That Ate New Jersey" comes when the brilliant young scientist announces his discovery of the equation for the volume of the eggplant:

$$V(\text{ft}^3) = 3.53 \times 10^{-2} \exp(2t^2)$$

where t is the time in hours from the moment the vampire injected the eggplant with a solution prepared from the blood of the beautiful dental hygienist.

(a) What are the units of 3.53×10^{-2} and 2?

(b) The scientist obtained the formula by measuring V versus t and determining the coefficients by linear regression. What would he have plotted versus what on what kind of coordinates? What would he have obtained as the slope and intercept of his plot?

(c) The European distributor of the film insists that the formula be given for the volume in m^3 as a function of t(s). Derive the formula.

2.45. The relationship between the pressure P and volume V of the air in a cylinder during the upstroke of a piston in an air compressor can be expressed as

$$PV^k = C$$

where k and C are constants. During a compression test, the following data are taken:

P(mm Hg)	760	1140	1520	2280	3040	3800
$V(cm^3)$	48.3	37.4	31.3	24.1	20.0	17.4

Determine the values of k and C that best fit the data. (Give both numerical values and units.)

2.46. In modeling the effect of an impurity on crystal growth, the following equation was derived:

$$\frac{G - G_L}{G_0 - G} = \frac{1}{K_L C^m}$$

where C is impurity concentration, G_L is a limiting growth rate, G_0 is the growth rate of the crystal with no impurity present, and K_L and m are model parameters.

In a particular experiment, $G_0 = 3.00 \times 10^{-3}$ mm/min, and $G_L = 1.80 \times 10^{-3}$ mm/min. Growth rates are measured for several impurity concentrations C (parts per million, or ppm), with the following results:

C(ppm)	50.0	75.0	100.0	125.0	150.0
G(mm/min) $\times 10^3$	2.50	2.20	2.04	1.95	1.90

(For example, when $C = 50.0$ ppm, $G = 2.50 \times 10^{-3}$ mm/min).

(a) Determine K_L and m, giving both numerical values and units.

(b) A solution is fed to a crystallizer in which the impurity concentration is 475 ppm. Estimate the expected crystal growth rate in (mm/min). Then state why you would be extremely skeptical about this result.

2.47. A process instrument reading, Z(volts), is thought to be related to a process stream flow rate $\dot{V}$(L/s) and pressure P(kPa) by the following expression:

$$Z = a\dot{V}^b P^c$$

Process data have been obtained in two sets of runs—one with $\dot{V}$ held constant, the other with P held constant. The data are as follows:

Point	1	2	3	4	5	6	7
$\dot{V}$(L/s)	0.65	1.02	1.75	3.43	1.02	1.02	1.02
P(kPa)	11.2	11.2	11.2	11.2	9.1	7.6	5.4
Z(volts)	2.27	2.58	3.72	5.21	3.50	4.19	5.89

(a) Suppose you had only performed runs 2, 3, and 5. Calculate a, b, and c algebraically from the data for these three runs.

(b) Now use a graphical method and all the data to calculate a, b, and c. Comment on why you would have more confidence in this result than in that of Part (a). (*Hint:* You will need at least two plots.)

2.48. Fit (a) a line and (b) a line through the origin to the following data using either the method of least squares (Appendix A.1) or graphics software:

x	0.3	1.9	3.2
y	0.4	2.1	3.1

On a single plot, show both fitted lines and the data points.

2.49. The following are measured values of a system temperature versus time:

t(min)	0.0	2.0	4.0	6.0	8.0	10.0
T(°C)	25.3	26.9	32.5	35.1	36.4	41.2

(a) Use the method of least squares (Appendix A.1) to fit a straight line to the data, showing your calculations. You may use a spreadsheet to evaluate the formulas in Appendix A.1, but do not use any plotting or statistical functions. Write the derived formula for $T(t)$, and convert it to a formula for $t(T)$.

(b) Transfer the data into two columns on an Excel spreadsheet, putting the t data (including the heading) in Cells A1–A7 and the T data (including the heading) in B1–B7. Following instructions for your version of Excel, insert a plot of T versus t into the spreadsheet, showing only the data points and not putting lines or curves between them. Then add a linear trendline to the plot (that is, fit a straight line to the data using the method of least squares) and instruct Excel to show the equation of the line and the R^2 value. The closer R^2 is to 1, the better the fit.

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2.50. A solution containing hazardous waste is charged into a storage tank and subjected to a chemical treatment that decomposes the waste to harmless products. The concentration of the decomposing waste, C, has been reported to vary with time according to the formula

$$C = 1/(a + bt)$$

When sufficient time has elapsed for the concentration to drop to 0.01 g/L, the contents of the tank are discharged appropriately.

The following data are taken for C and t:

t(h)	1.0	2.0	3.0	4.0	5.0
C(g/L)	1.43	1.02	0.73	0.53	0.38

(a) If the given formula is correct, what plot would yield a straight line that would enable you to determine the parameters a and b?

(b) Estimate a and b using the method of least squares (Appendix A.1) or graphics software. Check the goodness of fit by generating a plot of C versus t that shows both the measured and predicted values of C.

(c) Using the results of Part (b), estimate the initial concentration of the waste in the tank and the time required for C to reach its discharge level.

(d) You should have very little confidence in the time estimated in Part (c). Explain why.

(e) There are potential problems with the whole waste disposal procedure. Suggest several of them.

Exploratory Exercise—Research and Discover

(f) The problem statement includes the phrase "discharged appropriately." Recognizing that what is considered appropriate may change with time, list three different means of disposal and concerns with each.

2.51. The following (x, y) data are recorded:

x	0.5	1.4	84
y	2.20	4.30	6.15

(a) Plot the data on logarithmic axes.
(b) Determine the coefficients of a power law expression $y = ax^b$ using the method of least squares. (Remember what you are really plotting—there is no way to avoid taking logarithms of the data point coordinates in this case.)
(c) Draw your calculated line on the same plot as the data.

2.52. A published study of a chemical reaction, A → P, indicates that if the reactor initially contains A at a concentration C_{A0}(g/L) and the reaction temperature, T, is kept constant, then the concentration of P in the reactor increases with time according to the formula

$$C_P(\text{g/L}) = C_{A0}(1 - e^{-kt})$$

The *rate constant*, $k(\text{s}^{-1})$, is reportedly a function only of the reaction temperature.

To test this finding, the reaction is run in four different laboratories. The reported experimental results are given below.

	Lab 1 $T = 275°C$ $C_{A0} = 4.83$	**Lab 2** $T = 275°C$ $C_{A0} = 12.2$	**Lab 3** $T = 275°C$ $C_{A0} = 5.14$	**Lab 4** $T = 275°C$ $C_{A0} = 3.69$
t(s)	C_P (g/L)			
0	0.0	0.0	0.0	0.0
10	0.287	1.21	0.310	0.245
20	0.594	2.43	0.614	0.465
30	0.871	3.38	0.885	0.670
60	1.51	5.89	1.64	1.20
120	2.62	8.90	2.66	2.06
240	3.91	11.2	3.87	3.03
360	4.30	12.1	4.61	3.32
480	4.62	12.1	4.89	3.54
600	4.68	12.2	5.03	3.59

(a) What plot would yield a straight line if the given equation is correct?
(b) Enter the given data into a spreadsheet. For each data set (C_P versus t), generate the plot of Part (a) and determine the corresponding value of k. (Your spreadsheet program probably has a built-in function to perform a linear regression on the data in two specified columns.)
(c) Use the results in Part (b) to come up with a good estimate of the value of k at 275°C. Explain how you did it.
(d) If you did the calculation in Part (b) correctly, one of the calculated values of k should be considerably out of line with the others. Think of as many possible explanations for this result as you can (up to 10).

2.53. Suppose you have n data points (x_1, y_1), (x_2, y_2), . . . , (x_n, y_n) and you wish to fit a line through the origin ($y = ax$) to these data using the method of least squares. Derive Equation A.1-6 (Appendix A.1) for the slope of the line by writing the expression for the vertical distance d_i from the ith data point (x_i, y_i) to the line, then writing the expression for $\phi = \sum d_i^2$, and finding by differentiation the value of a that minimizes this function.

2.54. Use a spreadsheet program to fit a straight line ($y = ax + b$), to tabulated (x, y) data. Your program should evaluate the slope a and intercept b of the best fit to the data, and then calculate values of y using the estimated a and b for each tabulated value of x. Calculate the average deviation (*residual*) of the estimated y from the calculated value, and comment upon the quality of the fit to the data.

Test your program by fitting a line to the data in the following table:

x	1.0	1.5	2.0	2.5	3.0
y	2.35	5.53	8.92	12.15	15.38

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2.55. The rate at which a substance passes through a semipermeable membrane is determined by the *diffusivity* $D(\text{cm}^2/\text{s})$ of the gas. D varies with the membrane temperature $T(K)$ according to the *Arrhenius equation:*

$$D = D_0 \exp(-E/RT)$$

where D_0 = the *preexponential factor*
E = the *activation energy* for diffusion
$R = 1.987$ cal/(mol·K)

Diffusivities of SO_2 in a fluorosilicone rubber tube are measured at several temperatures, with the following results:

T(K)	$D(\text{cm}^2/\text{s}) \times 10^6$	
347.0	1.34	← (so that $D = 1.34 \times 10^{-6}$ cm^2/s)
374.2	2.50	
396.2	4.55	
420.7	8.52	
447.7	14.07	
471.2	19.99	

(a) What are the units of D_0 and E?
(b) How should the data be plotted to obtain a straight line on rectangular coordinates?
(c) Plot the data in the manner indicated in Part (b), and determine D_0 and E from the resulting line.
(d) Repeat Part (c) using a spreadsheet program.

CHAPTER 3

Processes and Process Variables

A **process** is any operation or series of operations by which a particular objective is accomplished. In this textbook, we address those operations that cause a physical or chemical change in a substance or mixture of substances. The material that enters a process is referred to as the **input** or **feed**, and that which leaves is the **output** or **product**. It is common for processes to consist of multiple steps, each of which is carried out in a **process unit**, and each process unit has associated with it a set of input and output **process streams**.

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As a chemical engineer, you are likely to be called upon to *design* or *operate* a process. **Design** includes formulation of a process flowchart (layout) as well as specification of individual process units (such as reactors, equipment to separate mixtures into their constituents, heat exchangers, pumps, and compressors) and associated process variables that specify the conditions at which the units are to be operated. In design, engineers usually work with a hypothetical process that has yet to be constructed. **Operation** involves the day-to-day performance of an existing process. The process is expected to produce a product at a specified rate with specified characteristics, and the engineer's tasks may involve controlling the individual units so that these objectives are met.

In addition to carrying out those two activities, you may be called upon to perform process **analysis**, with objectives that may vary from one process to another. For example, a task might be to identify ways to reduce costs associated with raw materials and energy consumption. The methodology could involve controlled tests on the actual process or a scaled-down version of it, or it may require developing a mathematical model to predict process outcomes at different operating conditions. Often, a combination of these approaches is used.

Examination of an operating process should be ongoing, but there is a special need when the process is functioning poorly and *troubleshooting* is required to identify the cause of the problem. Sometimes an increase in market demand requires an increase in production rate, and the required increase exceeds the capacity of the existing equipment. Identifying and modifying a step in the process that is limiting the production rate in order to obtain greater throughput is referred to as *debottlenecking*. When demand for the product falls, adjusting the process through *turndown* becomes important.

The links among all of the activities and functions described in the preceding discussion are the process streams connecting process units and forming the process flowchart. Performance of the functions requires knowledge of the amounts, compositions, and conditions of the process streams and materials within the process units. You must be able to measure or calculate such information for existing units or specify and calculate it for units being designed.

In this chapter we present definitions, illustrative measurement techniques, and methods of calculating variables that characterize the operation of processes and individual process units. In later chapters, we discuss how you can use the measured values of some of these variables to calculate process-related quantities that cannot be measured directly but must be known before the process can be fully designed or evaluated.

3.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- Explain in your own words and without the use of jargon (a) the difference between density and specific gravity; (b) the meaning of gram-mole, lb-mole, mol, and kmol; (c) at least two

methods for measuring temperature and at least two for measuring fluid pressure; (d) the meaning of the terms absolute pressure and gauge pressure; (e) why atmospheric pressure is not necessarily 1 atm.

- Calculate the density in g/cm^3 or lb_m/ft^3 of a liquid or solid species from a knowledge of the specific gravity, and vice versa.
- Calculate two of the quantities—mass (or mass flow rate), volume (or volumetric flow rate), and moles (or molar flow rate)—from a knowledge of the third quantity for any species of known density and molecular weight.
- Given the composition of a mixture expressed in terms of mass fractions, calculate the composition in terms of mole fractions, and vice versa.
- Determine the average molecular weight of a mixture from the mass or molar composition of the mixture.
- Convert a pressure expressed as a head of a fluid to the equivalent pressure expressed as a force per unit area, and vice versa.
- Convert a manometer reading into a pressure difference for an open-end manometer, a sealed-end manometer, and a differential manometer.
- Convert among temperatures expressed in K, °C, °F, and °R.

3.1 MASS AND VOLUME

The **density** of a substance is the mass per unit volume of the substance (kg/m^3, g/cm^3, lb_m/ft^3, etc.) The **specific volume** of a substance is the volume occupied by a unit mass of the substance; it is the inverse of density. Densities of pure solids and liquids are essentially independent of pressure and vary relatively slightly with temperature. The variation with temperature may be in either direction: the density of liquid water, for example, increases from 0.999868 g/cm^3 at 0°C to 1.00000 g/cm^3 at 3.98°C, and then decreases to 0.95838 g/cm^3 at 100°C. Densities of many pure compounds, solutions, and mixtures may be found in standard references (such as *Perry's Chemical Engineers' Handbook*,[1] pp. 2-7 through 2-47 and 2-96 through 2-123). Methods of estimating densities of gases and mixtures of liquids are given in Chapter 5 of this book.

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Carbon tetrachloride, CCl_4, was a common dry-cleaning solvent until it was found to cause liver damage. It also was an important precursor to manufacturing chlorofluorocarbons (CFCs), which were used extensively as refrigerants and aerosol propellants but have since been replaced with compounds less damaging to the environment.

The density of a substance can be used as a conversion factor to relate the mass and the volume of a quantity of the substance. For example, the density of carbon tetrachloride is 1.595 g/cm^3; the mass of 20.0 cm^3 of CCl_4 is therefore

$$\frac{20.0\ \text{cm}^3 \mid 1.595\ \text{g}}{\mid\ \text{cm}^3} = 31.9\ \text{g}$$

and the volume of 6.20 lb_m of CCl_4 is

$$\frac{6.20\ \text{lb}_\text{m} \mid 454\ \text{g} \mid 1\ \text{cm}^3}{\mid 1\ \text{lb}_\text{m} \mid 1.595\ \text{g}} = 1760\ \text{cm}^3$$

The **specific gravity** of a substance is the ratio of the density ρ of the substance to the density ρ_{ref} of a reference substance at a specific condition:

$$SG = \rho/\rho_{ref} \qquad \textbf{(3.1-1)}$$

[1] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008.

The reference most commonly used for solids and liquids is water at 4.0°C, which has the following density:

$$\begin{aligned}\rho_{H_2O(l)}(4°C) &= 1.000\ g/cm^3 \\ &= 1000\ kg/m^3 \\ &= 62.43\ lb_m/ft^3\end{aligned} \qquad \textbf{(3.1-2)}$$

Note that the density of a liquid or solid in g/cm^3 is numerically equal to the specific gravity of that substance. The notation

$$SG^{20°C/4°C} = 0.6$$

signifies that the specific gravity of a substance at 20°C with reference to water at 4°C is 0.6.

If you are given the specific gravity of a substance, multiply it by the reference density in any units to get the density of the substance in the same units. For example, if the specific gravity of a liquid is 2.00, its density is 2.00×10^3 kg/m^3 or 2.00 g/cm^3 or 125 lb_m/ft^3. Specific gravities of selected liquids and solids are given in Table B.1.

You can retrieve the specific gravity values tabulated in Table B.1 using the SG("species") function of APEx (see p. iv of the Preface). For example, if you enter the formula =SG("acetone") into a cell of a spreadsheet, the value 0.791 will be inserted into the cell.

Note: Special density units called degrees Baumé (°Bé), degrees API (°API), and degrees Twaddell (°Tw) are occasionally used, particularly in the petroleum industry. Definitions of and conversion factors for these units are given on p. 1-19 of *Perry's Chemical Engineers' Handbook*.

Test Yourself

(Answers, p. 654)

1. What are the units of specific gravity?
2. A liquid has a specific gravity of 0.50. What is its density in g/cm^3? What is its specific volume in cm^3/g? What is its density in lb_m/ft^3? What is the mass of 3.0 cm^3 of this liquid? What volume is occupied by 18 g?
3. If substance A and substance B each have a density of 1.34 g/cm^3, must 3 cm^3 of A have the same mass as 3 cm^3 of B?
4. If substance A and substance B each have a specific gravity of 1.34, must 3 cm^3 of A have the same mass as 3 cm^3 of B? Why not?
5. Freezing a sealed full bottle of water leads to a broken bottle, and freezing a sealed full flexible-walled container of *n*-butyl alcohol leads to a container with concave walls. What can you conclude about the densities of the solid and liquid forms of these two substances?
6. Does the density of liquid mercury increase or decrease with increasing temperature? Justify your answer using a thermometer as an illustration.

Example 3.1-1 Mass, Volume, and Density

Calculate the density of mercury in lb_m/ft^3 from a tabulated specific gravity, and calculate the volume in ft^3 occupied by 215 kg of mercury.

Solution Table B.1 lists the specific gravity of mercury at 20°C as 13.546. Therefore,

$$\rho_{Hg} = (13.546)\left(62.43\ \frac{lb_m}{ft^3}\right) = \boxed{845.7\ \frac{lb_m}{ft^3}}$$

$$V = \frac{215\ kg}{} \left| \begin{array}{c|c} 1\ lb_m & 1\ ft^3 \\ \hline 0.454\ kg & 845.7\ lb_m \end{array} \right. = \boxed{0.560\ ft^3}$$

The density could be calculated using APEx by inserting the formula =SG("mercury") * 62.43 or =SG("Hg") * 62.43 into a cell of a worksheet.

As stated earlier, temperature and pressure do not have large influences on the densities of solids and liquids. Nevertheless, the fact that mercury in a thermometer rises or falls with changing temperature shows that the effect of temperature on liquid density is measurable. Coefficients of linear and cubic (volume) thermal expansion of selected liquids and solids are given as empirical polynomial functions of temperature on pp. 2-133 to 2-136 of *Perry's Chemical Engineers' Handbook*. For example, the *Handbook* gives the dependence of the volume of mercury on temperature as

$$V(T) = V_0\left(1 + 0.18182 \times 10^{-3}T + 0.0078 \times 10^{-6}T^2\right) \qquad \textbf{(3.1-3)}$$

where $V(T)$ is the volume of a given mass of mercury at temperature T(°C) and V_0 is the volume of the same mass of mercury at 0°C.

Example 3.1-2 Effect of Temperature on Liquid Density

In Example 3.1-1, 215 kg of mercury was found to occupy 0.560 ft^3 at 20°C. (1) What volume would the mercury occupy at 100°C? (2) Suppose the mercury is contained in a cylinder having a diameter of 0.25 in. What change in height would be observed as the mercury is heated from 20°C to 100°C?

Solution

1. From Equation 3.1-3

$$V(100°C) = V_0[1 + 0.18182 \times 10^{-3}(100) + 0.0078 \times 10^{-6}(100)^2]$$

and

$$V(20°C) = 0.560\ ft^3 = V_0[1 + 0.18182 \times 10^{-3}(20) + 0.0078 \times 10^{-6}(20)^2]$$

Solving for V_0 from the second equation and substituting it into the first yields

$$V(100°C) = \boxed{0.568\ ft^3}$$

2. The volume of the mercury equals $\pi D^2 H/4$, where D is the cylinder diameter and H is its height. Since D is constant,

$$H(100°C) - H(20°C) = \frac{V(100°C) - V(20°C)}{\pi D^2/4}$$

$$\Downarrow \quad D = (0.25/12)\ ft$$

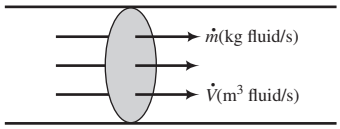
$$= \boxed{23.5\ ft}$$

3.2 FLOW RATE

3.2a Mass and Volumetric Flow Rate

Most processes involve the movement of material from one point to another—sometimes between process units, sometimes between a production facility and a transportation depot. The rate at which a material is transported through a process line is the **flow rate** of that material.

The flow rate of a process stream may be expressed as a **mass flow rate** (mass/time) or as a **volumetric flow rate** (volume/time). Suppose a fluid (gas or liquid) flows in the cylindrical pipe shown below, where the shaded area represents a section perpendicular to the direction of flow.



If the mass flow rate of the fluid is $\dot{m}$(kg/s),[2] then every second m kilograms of the fluid pass through the cross section. If the volumetric flow rate of the fluid at the given cross section is $\dot{V}$(m^3/s), then every second V cubic meters of the fluid pass through the cross section. However, the mass m and the volume V of a fluid—in this case, the fluid that passes through the cross section each second—are not independent quantities but are related through the fluid density, ρ:

$$\rho = m/V = \dot{m}/\dot{V} \qquad \textbf{(3.2-1)}$$

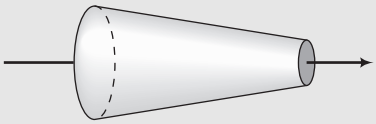
Thus, *the density of a fluid can be used to convert a known volumetric flow rate of a process stream to the mass flow rate of that stream or vice versa.*

The mass flow rates of process streams must be known for many process calculations, but it is frequently more convenient to measure volumetric flow rates. A common procedure is therefore to measure $\dot{V}$ and calculate $\dot{m}$ from $\dot{V}$ and the density of the stream fluid.

Test Yourself

(Answers, p. 654)

1. The mass flow rate of *n*-hexane ($\rho = 0.659$ g/cm^3) in a pipe is 6.59 g/s. What is the volumetric flow rate of the hexane?
2. The volumetric flow rate of CCl_4 ($\rho = 1.595$ g/cm^3) in a pipe is 100.0 cm^3/min. What is the mass flow rate of the CCl_4?
3. Suppose a gas is flowing through a cone-shaped pipe.



How do the mass flow rates of the gas at the inlet and outlet compare? (Remember the law of conservation of mass.) If the density of the gas is constant, how do the volumetric flow rates at these two points compare? What if the density decreases from inlet to outlet?

3.2b Flow Rate Measurement

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A **flowmeter** is a device mounted in a process line that provides a continuous reading of the flow rate in the line. Two commonly used flowmeters—the **rotameter** and the **orifice meter**—are shown schematically in Figure 3.2-1. *Perry's Chemical Engineers' Handbook*, pp. 10-14 through 10-24, describes many others.

The rotameter is a tapered vertical tube containing a float; the larger the flow rate, the higher the float rises in the tube. The orifice meter measures the pressure drop across an orifice (a small opening) in a thin plate restricting the flow in a conduit. Fluid flows through the orifice, and the pressure decreases from the upstream side of the orifice to the downstream side. The pressure difference, which varies with flow rate, may be measured with a number of devices, including a differential manometer, which is discussed in the next section. The greater the flow rate, the larger the pressure drop.

[2] Variables whose symbols include a dot (·) are rates; for example, $\dot{m}$ is mass flow rate and $\dot{V}$ is volumetric flow rate.

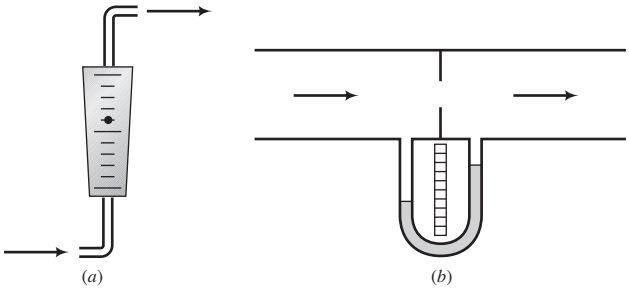

FIGURE 3.2-1 Flowmeters: (*a*) rotameter and (*b*) orifice meter.

Problems at the end of this chapter illustrate the calibration and use of both types of flowmeters.

Test Yourself

(Answers, p. 654)

1. A steadily flowing stream of water is funneled into a graduated cylinder for exactly 30 s, during which time 50 mL is collected. What is the volumetric flow rate of the stream? The mass flow rate?
2. What is a rotameter? An orifice meter?
3. A rotameter calibration curve (flow rate versus float position) obtained using a liquid is mistakenly used to measure a gas flow rate. Would you expect the gas flow rate determined in this manner to be too high or too low?

CREATIVITY EXERCISE

Given below is the first of a series of exercises contained in this book that we call Creativity Exercises. These exercises differ considerably from the kinds of problems you are accustomed to seeing in homework assignments and quizzes. In the latter, you are generally given information and asked to find the single correct solution to a problem. In the creativity exercises, you are asked to think of many possible responses without spending too much time doing so. There is no such thing as the "correct" response or even a "good" or "bad" response. The idea is to go for quantity rather than quality, imagination (even humor) rather than "correctness." Try to suspend your critical judgment completely and come up with as many ideas as you can, regardless of how likely they are to be efficient, cost-effective, or even to work at all.

In many situations, this "brainstorming" approach to creative problem solving is frequently used as the first step in solving difficult problems. Doing these exercises will help sharpen the skills you will need for successful brainstorming and at the same time will give you a broader understanding of the concepts contained in the text.

Here, then, is the first exercise. Invent as many devices as you can that might function as flowmeters for gases or liquids. In each case, describe the device and state what would be measured. (*Example:* Put a propeller in a flowing stream and measure its rotational speed.)

3.3 CHEMICAL COMPOSITION

Most materials encountered in nature and in chemical process systems are mixtures of various species. The physical properties of a mixture depend strongly on the mixture composition. In this section we will review different ways to express mixture compositions, and later in the book we will outline methods of estimating physical properties of a mixture from the properties of the pure components.

3.3a Moles and Molecular Weight

The **atomic weight** of an element is the mass of an atom on a scale that assigns ^{12}C (the isotope of carbon whose nucleus contains six protons and six neutrons) a mass of exactly 12. The atomic weights of all the elements in their naturally occurring isotopic proportions are listed in the table at the back cover of the book. The **molecular weight** of a compound is the sum of the atomic weights of the atoms that constitute a molecule of the compound: atomic oxygen (O), for example, has an atomic weight of approximately 16, and therefore molecular oxygen (O_2) has a molecular weight of approximately 32. Molecular weights of a number of compounds are given in Table B.1. You can retrieve the molecular weight of a compound with the APEx function =MW("species"). For example, if you enter =MW("oxygen") or =MW("O2") in a spreadsheet cell, the value 32 will be returned.

A **gram-mole** (g-mole or **mol** in SI units) of a species is the amount of that species whose mass in grams is numerically equal to its molecular weight. (If the species is an element, it is technically correct to refer to a gram-atom rather than a gram-mole. We will not observe this distinction, but will use moles for both elements and compounds.) Other types of moles (e.g., kg-moles or kmol, lb-moles, ton-moles) are similarly defined. Carbon monoxide (CO), for example, has a molecular weight of 28; 1 mol of CO therefore contains 28 g, 1 lb-mole contains 28 lb_m, 1 ton-mole contains 28 tons, and so on.

If the molecular weight of a substance is M, then there are M kg/kmol, *M* g/mol, *and M* lb_m/lb-mole *of this substance*. The molecular weight may thus be used as a conversion factor that relates the mass and the number of moles of a quantity of the substance. For example, 34 kg of ammonia (NH_3: $M = 17$) is equivalent to

$$\frac{34\ \text{kg NH}_3}{17\ \text{kg NH}_3}\left|\frac{1\ \text{kmol NH}_3}{}\right. = 2.0\ \text{kmol NH}_3 \qquad \textbf{(3.3-1)}$$

and 4.0 lb-moles of ammonia is equivalent to

$$\frac{4.0\ \text{lb-moles NH}_3}{1\ \text{lb-mole NH}_3}\left|\frac{17\ \text{lb}_\text{m}\ \text{NH}_3}{}\right. = 68\ \text{lb}_\text{m}\ \text{NH}_3 \qquad \textbf{(3.3-2)}$$

(It is often helpful in mass-mole conversions to include the chemical formula in the dimensional equation, as illustrated above.)

The same factors used to convert masses from one unit to another may be used to convert the equivalent molar units. Since 454 g/lb_m is a valid conversion factor, 454 mol/lb-mole must also be valid, regardless of the substance involved. (Prove it—convert 1 lb-mole of a substance with molecular weight M to gram-moles.)

One gram-mole of any species contains approximately 6.02×10^{23} *(Avogadro's number) molecules of that species*.

Example 3.3-1 Conversion Between Mass and Moles

How many of each of the following are contained in 100.0 g of CO_2 ($M = 44.01$)? (1) mol CO_2; (2) lb-moles CO_2; (3) mol C; (4) mol O; (5) mol O_2; (6) g O; (7) g O_2; (8) molecules of CO_2.

Solution

1.
$$\frac{100.0\ \text{g CO}_2}{44.01\ \text{g CO}_2}\left|\frac{1\ \text{mol CO}_2}{}\right. = \boxed{2.273\ \text{mol CO}_2}$$

2.
$$\frac{2.273\ \text{mol CO}_2}{453.6\ \text{mol}}\left|\frac{1\ \text{lb-mol}}{}\right. = \boxed{5.011 \times 10^{-3}\ \text{lb-mole CO}_2}$$

Each molecule of CO_2 contains one atom of C, one molecule of O_2, or two atoms of O. Therefore, each 6.02×10^{23} molecules of CO_2 (1 mol) contains 1 mol C, 1 mol O_2, or 2 mol O. Thus,

3. $$\frac{2.273 \text{ mol } CO_2 \mid 1 \text{ mol C}}{1 \text{ mol } CO_2} = \boxed{2.273 \text{ mol C}}$$

4. $$\frac{2.273 \text{ mol } CO_2 \mid 2 \text{ mol O}}{1 \text{ mol } CO_2} = \boxed{4.546 \text{ mol O}}$$

5. $$\frac{2.273 \text{ mol } CO_2 \mid 1 \text{ mol } O_2}{1 \text{ mol } CO_2} = \boxed{2.273 \text{ mol } O_2}$$

6. $$\frac{4.546 \text{ mol O} \mid 16.0 \text{ g O}}{1 \text{ mol O}} = \boxed{72.7 \text{ g O}}$$

7. $$\frac{2.273 \text{ mol } O_2 \mid 32.0 \text{ g } O_2}{1 \text{ mol } O_2} = \boxed{72.7 \text{ g } O_2}$$

8. $$\frac{2.273 \text{ mol } CO_2 \mid 6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = \boxed{1.37 \times 10^{24} \text{ molecules}}$$

Note: Part 7 could also be done by observing from the molecular formula that each 44.0 g of CO_2 contains 32.0 g of O_2 or O, so that

$$\frac{100.0 \text{ g } CO_2 \mid 32.0 \text{ g } O_2}{44.0 \text{ g } CO_2} = 72.7 \text{ g } O_2$$

The molecular weight of a species can be used to relate the mass flow rate of a continuous stream of this species to the corresponding molar flow rate. For example, if carbon dioxide (CO_2: $M = 44.0$) flows through a pipeline at a rate of 100 kg/h, the molar flow rate of the CO_2 is

$$\frac{100 \text{ kg } CO_2}{\text{h}} \left| \frac{1 \text{ kmol } CO_2}{44.0 \text{ kg } CO_2} \right. = 2.27 \frac{\text{kmol } CO_2}{\text{h}} \qquad \textbf{(3.3-3)}$$

If the output stream from a chemical reactor contains CO_2 flowing at a rate of 850 lb-moles/min, the corresponding mass flow rate is

$$\frac{850 \text{ lb-moles } CO_2}{\text{min}} \left| \frac{44.0 \text{ lb}_\text{m} \text{ } CO_2}{1 \text{ lb-mole } CO_2} \right. = 37{,}400 \frac{\text{lb}_\text{m} \text{ } CO_2}{\text{min}} \qquad \textbf{(3.3-4)}$$

The **dalton** (Da) is often used in discussions involving molecular weight and the size of molecules, especially when biochemical species are being discussed. The formal definition of a dalton is 1/12 of the mass of a ^{12}C atom; in other words, the mass of a carbon-12 atom is exactly 12 daltons, and the mass of a water molecule is almost exactly 18 daltons.

Test Yourself

(Answers, p. 654)

1. What is a mol of a species of molecular weight M, in terms of (a) a number of molecules? (b) a mass?
2. What is a ton-mole of a species?
3. How many lb-moles and lb_m of (a) H_2 and (b) H are contained in 1 lb-mole of H_2O?
4. How many gram-moles of C_3H_8 are contained in 2 kmol of this substance?

5. One hundred kilograms of molecular hydrogen (H_2) is fed into a reactor each hour. What is the molar flow rate of this stream in gram-moles/hour?

6. How many g-moles are in 2.0 g of chicken-egg white lysozyme?

3.3b Mass and Mole Fractions and Average Molecular Weight

Process streams occasionally contain one substance, but more often they consist of mixtures of liquids or gases, or solutions of one or more solutes in a liquid solvent.

The following terms may be used to define the composition of a mixture of substances that includes a species A.

Mass fraction:
$$x_A = \frac{\text{mass of A}}{\text{total mass}} \left(\frac{\text{kg A}}{\text{kg total}} \text{ or } \frac{\text{g A}}{\text{g total}} \text{ or } \frac{\text{lb}_\text{m}\text{ A}}{\text{lb}_\text{m}\text{ total}} \right) \tag{3.3-5}$$

Mole fraction:
$$y_A = \frac{\text{moles of A}}{\text{total moles}} \left(\frac{\text{kmol A}}{\text{kmol}} \text{ or } \frac{\text{mol A}}{\text{mol}} \text{ or } \frac{\text{lb-moles A}}{\text{lb-mole}} \right) \tag{3.3-6}$$

The **percent by mass** of A is $100x_A$, and the **mole percent** of A is $100y_A$.

Example 3.3-2 Conversions Using Mass and Mole Fractions

A solution contains 15% A by mass ($x_A = 0.15$) and 20 mole% B ($y_B = 0.20$).

1. Calculate the mass of A in 175 kg of the solution.

$$\frac{175 \text{ kg solution}}{} \left| \frac{0.15 \text{ kg A}}{\text{kg solution}} \right. = \boxed{26 \text{ kg A}}$$

2. Calculate the mass flow rate of A in a stream of solution flowing at a rate of 53 lb_m/h.

$$\frac{53 \text{ lb}_\text{m}}{\text{h}} \left| \frac{0.15 \text{ lb}_\text{m}\text{ A}}{\text{lb}_\text{m}} \right. = \boxed{8.0 \frac{\text{lb}_\text{m}\text{ A}}{\text{h}}}$$

(If a mass or molar unit—such as lb_m in 53 lb_m/h—is not followed by the name of a species, the unit should be understood to refer to the total mixture or solution rather than to a specific component.)

3. Calculate the molar flow rate of B in a stream flowing at a rate of 1000 mol/min.

$$\frac{1000 \text{ mol}}{\text{min}} \left| \frac{0.20 \text{ mol B}}{\text{mol}} \right. = \boxed{200 \frac{\text{mol B}}{\text{min}}}$$

4. Calculate the total solution flow rate that corresponds to a molar flow rate of 28 kmol B/s.

$$\frac{28 \text{ kmol B}}{\text{s}} \left| \frac{1 \text{ kmol solution}}{0.20 \text{ kmol B}} \right. = \boxed{140 \frac{\text{kmol solution}}{\text{s}}}$$

5. Calculate the mass of the solution that contains 300 lb_m of A.

$$\frac{300 \text{ lb}_\text{m}\text{ A}}{} \left| \frac{1 \text{ lb}_\text{m}\text{ solution}}{0.15 \text{ lb}_\text{m}\text{ A}} \right. = \boxed{2000 \text{ lb}_\text{m}\text{ solution}}$$

Note that *the numerical value of a mass or a mole fraction does not depend on the mass units in the numerator and denominator as long as these units are the same*. If the mass fraction of benzene (C_6H_6) in a mixture is 0.25, then $x_{C_6H_6}$ equals 0.25 kg C_6H_6/kg total, 0.25 g C_6H_6/g total,

0.25 lb_m C_6H_6/lb_m total, and so on. It is common practice to omit the word *total*, but here we include it for emphasis.

A set of mass fractions may be converted to an equivalent set of mole fractions by (a) assuming as a **basis of calculation** a mass of the mixture (e.g., 100 kg or 100 lb_m); (b) using the known mass fractions to calculate the mass of each component in the basis quantity, and converting these masses to moles; and (c) taking the ratio of the moles of each component to the total number of moles. An analogous procedure is followed to convert mole fractions to mass fractions, differing only in that a total number of moles (e.g., 100 mol or 100 lb-moles) is taken as a basis of calculation.

Example 3.3-3 Conversion from a Composition by Mass to a Molar Composition

A mixture of gases has the following composition by mass:

O_2	16%	(x_{O_2} = 0.16 g O_2/g total)
CO	4.0%	
CO_2	17%	
N_2	63%	

What is the molar composition?

Solution ***Basis: 100 g of the mixture.***

A convenient way to perform the calculations is to set them up in tabular form.

Component i	Mass Fraction x_i (g_i/g)	Mass (g) $m_i = x_i m_{total}$	Molecular Weight M_i (g/mol)	Moles $n_i = m_i/M_i$	Mole Fraction $y_i = n_i/n_{total}$
O_2	0.16	16	32	0.50	0.15
CO	0.04	4	28	0.14	0.04
CO_2	0.17	17	44	0.39	0.12
N_2	0.63	63	28	2.20	0.69
Total	1.00	100		3.28	1.00

The mass of a species is the product of the mass fraction of that species and total mass (basis of 100 g). The number of moles of a species is the mass of that species divided by the molecular weight of the species. Finally, the mole fraction of a species is the number of moles of that species divided by the total number of moles (3.279 mol).

The **average molecular weight** (or mean molecular weight) of a mixture, $\overline{M}$ (kg/kmol, lb_m/lb-mole, etc.), is the ratio of the mass of a sample of the mixture (m_t) to the number of moles of all species (n_t) in the sample. If y_i is the mole fraction of the ith component of the mixture and M_i is the molecular weight of this component, then

$$\overline{M} = y_1 M_1 + y_2 M_2 + \cdots = \sum_{\substack{\text{all} \\ \text{components}}} y_i M_i \qquad \textbf{(3.3-7)}$$

(*Exercise:* Derive Equation 3.3-7 by taking a basis of 1 mol of the mixture and calculating m_t following the procedure of Example 3.3-3.) If x_i is the mass fraction of the ith component, then

$$\frac{1}{\overline{M}} = \frac{x_1}{M_1} + \frac{x_2}{M_2} + \cdots = \sum_{\substack{\text{all} \\ \text{components}}} \frac{x_i}{M_i} \qquad \textbf{(3.3-8)}$$

(Prove it.)

Example 3.3-4 Calculation of an Average Molecular Weight

Calculate the average molecular weight of air (1) from its approximate molar composition of 79% N_2, 21% O_2 and (2) from its approximate composition by mass of 76.7% N_2, 23.3% O_2.

Solution

1. From Equation 3.3-7, with $y_{N_2} = 0.79$, $y_{O_2} = 0.21$,

$$\overline{M} = y_{N_2} M_{N_2} + y_{O_2} M_{O_2}$$

$$= \frac{0.79 \text{ kmol } N_2}{\text{kmol}} \left| \frac{28 \text{ kg } N_2}{\text{kmol}} \right. + \frac{0.21 \text{ kmol } O_2}{\text{kmol}} \left| \frac{32 \text{ kg } O_2}{\text{kmol}} \right.$$

$$= \boxed{29 \frac{\text{kg}}{\text{kmol}}} \left(= 29 \frac{\text{lb}_\text{m}}{\text{lb-mole}} = 29 \frac{\text{g}}{\text{mol}} \right)$$

2. From Equation 3.3-8,

$$\frac{1}{\overline{M}} = \frac{0.767 \text{ g } N_2/\text{g}}{28 \text{ g } N_2/\text{mol}} + \frac{0.233 \text{ g } O_2/\text{g}}{32 \text{ g } O_2/\text{mol}} = 0.035 \frac{\text{mol}}{\text{g}}$$

$$\Downarrow$$

$$\boxed{\overline{M} = 29 \text{ g/mol}}$$

Note: Air contains small amounts of carbon dioxide, argon, and other gases that have been neglected in this calculation, but whose presence does not significantly affect the calculated value of $\overline{M}$.

Test Yourself

(Answers, p. 655)

1. The molecular weight of atomic hydrogen is approximately 1, and that of atomic bromine is 80. What are (a) the mass fraction and (b) the mole fraction of bromine in pure HBr?
2. If 100 lb_m/min of A ($M_A = 2$) and 300 lb_m/min of B ($M_B = 3$) flow through a pipe, what are the mass fractions and mole fractions of A and B, the mass flow rate of A, the molar flow rate of B, the total mass flow rate, and the total molar flow rate of the mixture?

3.3c Concentration

The **mass concentration** of a component of a mixture or solution is the mass of this component per unit volume of the mixture (g/cm^3, lb_m/ft^3, kg/in^3, . . .). The **molar concentration** of a component is the number of moles of the component per unit volume of the mixture (kmol/m^3, lb-moles/ft^3, . . .). The **molarity** of a solution is the value of the molar concentration of the solute expressed in gram-moles solute/liter solution (e.g., a 2-molar solution of A contains 2 mol A/liter solution).

The concentration of a substance in a mixture or solution can be used as a conversion factor to relate the mass (or moles) of a component in a sample of the mixture to the sample volume, or to relate the mass (or molar) flow rate of a component of a continuous stream to the total volumetric flow rate of the stream. Consider, for example, a 0.02-molar solution of NaOH (i.e., a solution containing 0.02 mol NaOH/L): 5 L of this solution contains

$$\frac{5 \text{ L}}{} \left| \frac{0.02 \text{ mol NaOH}}{\text{L}} \right. = 0.1 \text{ mol NaOH}$$

and if a stream of this solution flows at a rate of 2 L/min, the molar flow rate of NaOH is

$$\frac{2 \text{ L}}{\text{min}} \left| \frac{0.02 \text{ mol NaOH}}{\text{L}} \right. = 0.04 \frac{\text{mol NaOH}}{\text{min}}$$

Test Yourself

(Answers, p. 655)

A solution with volume V(L) contains n(mol) of a solute A with a molecular weight of M_A(g A/mol). In terms of V, n, and M_A:

1. What is the molar concentration of A?
2. What is the mass concentration of A?

In terms of C_A(mol A/L) and c_A(g A/L):

3. What volume of the solution contains 20 mol of A?
4. What is the mass flow rate of A in a stream whose volumetric flow rate is 120 L/h?

Example 3.3-5 Conversion Between Mass, Molar, and Volumetric Flow Rates of a Solution

A 0.50-molar aqueous solution of sulfuric acid flows into a process unit at a rate of 1.25 m^3/min. The specific gravity of the solution is 1.03. Calculate (1) the mass concentration of H_2SO_4 in kg/m^3, (2) the mass flow rate of H_2SO_4 in kg/s, and (3) the mass fraction of H_2SO_4.

Solution

1. $$C_{H_2SO_4}\left(\frac{\text{kg } H_2SO_4}{m^3}\right) = \frac{0.50 \text{ mol } H_2SO_4}{\text{L}} \left| \frac{98 \text{ g}}{\text{mol}} \right| \frac{1 \text{ kg}}{10^3 \text{ g}} \left| \frac{10^3 \text{ L}}{1 \text{ m}^3} \right.$$

$$= \boxed{49 \frac{\text{kg } H_2SO_4}{m^3}}$$

2. $$\dot{m}_{H_2SO_4}\left(\frac{\text{kg } H_2SO_4}{\text{s}}\right) = \frac{1.25 \text{ m}^3}{\text{min}} \left| \frac{49 \text{ kg } H_2SO_4}{\text{m}^3} \right| \frac{1 \text{ min}}{60 \text{ s}} = \boxed{1.0 \frac{\text{kg } H_2SO_4}{\text{s}}}$$

3. The mass fraction of H_2SO_4 equals the ratio of the mass flow rate of H_2SO_4—which we know—to the total mass flow rate, which can be calculated from the total volumetric flow rate and the solution density.

$$\rho_{solution} = (1.03)\left(\frac{1000 \text{ kg}}{\text{m}^3}\right) = 1030 \frac{\text{kg}}{\text{m}^3}$$

$$\Downarrow$$

$$\dot{m}_{solution}\left(\frac{\text{kg}}{\text{s}}\right) = \frac{1.25 \text{ m}^3 \text{ solution}}{\text{min}} \left| \frac{1030 \text{ kg}}{\text{m}^3 \text{ solution}} \right| \frac{1 \text{ min}}{60 \text{ s}} = 21.46 \frac{\text{kg}}{\text{s}}$$

$$\Downarrow$$

$$x_{H_2SO_4} = \frac{\dot{m}_{H_2SO_4}}{\dot{m}_{solution}} = \frac{1.0 \text{ kg } H_2SO_4/\text{s}}{21.46 \text{ kg solution/s}} = \boxed{0.048 \frac{\text{kg } H_2SO_4}{\text{kg solution}}}$$

CREATIVITY EXERCISE

Itemize as many ways as you can think of to measure the concentration of a solute in a solution. (*Example:* If the solute absorbs light of a specific wavelength, pass a beam of light of this wavelength through the solution and measure the fractional light absorption.)

3.3d Parts per Million and Parts per Billion

The units **parts per million (ppm)** and **parts per billion (ppb)**[3] are used to express the concentrations of *trace species* (species present in minute amounts) in mixtures of gases or

[3] We are using the standard American definition of a billion as 10^9 or 1000 million, as opposed to the English definition of 10^{12}.

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A few parts per billion may seem like an insignificant amount, but for some chemicals it's a lot. For example, chemicals called aflatoxins *are potent carcinogens with acute toxicological effects in humans. They are often found in grains and peanut butter, and the FDA restricts their presence in milk to less than 0.5 ppb and in grain fed to dairy cattle to less than 20 ppb.*

liquids. The definitions may refer to mass ratios (usual for liquids) or mole ratios (usual for gases) and signify how many parts (grams, moles) of the species are present per million or billion parts (grams, moles) of the mixture. If y_i is the fraction of component i, then by definition

$$\text{ppm}_i = y_i \times 10^6 \tag{3.3-9}$$

$$\text{ppb}_i = y_i \times 10^9 \tag{3.3-10}$$

For example, suppose air in the vicinity of a power plant is said to contain 15 ppm SO_2 (15 parts per million sulfur dioxide). Assuming that a molar basis has been used (customary for gases), this statement means that every million moles of air contains 15 moles of SO_2, or equivalently, that the mole fraction of SO_2 in the air is 15×10^{-6}. Units such as ppm and ppb have become increasingly common in recent years as public concern about potentially hazardous trace species in the environment has grown.

Test Yourself

(Answers, p. 655)

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A blood sample is reported to contain 68 ppm creatinine (mass basis).

1. What is the mass fraction of creatinine in the blood?
2. How many milligrams of creatinine are contained in one kilogram of the blood?
3. What is the approximate concentration of creatinine in the blood in g/L?

3.4 PRESSURE

3.4a Fluid Pressure and Hydrostatic Head

A **pressure** is the ratio of a force to the area on which the force acts. Accordingly, pressure units are force units divided by area units (e.g., N/m^2, dynes/cm^2, and lb_f/in^2 or psi). The SI pressure unit, N/m^2, is called a **pascal** (Pa).

Consider a fluid (gas or liquid) contained in a closed vessel or flowing through a pipe, and suppose that a hole of area A is made in the wall of the containing vessel, as in Figure 3.4-1. The **fluid pressure** may be defined as the ratio F/A, where F is the minimum force that would have to be exerted on a frictionless plug in the hole to keep the fluid from emerging.

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tanks
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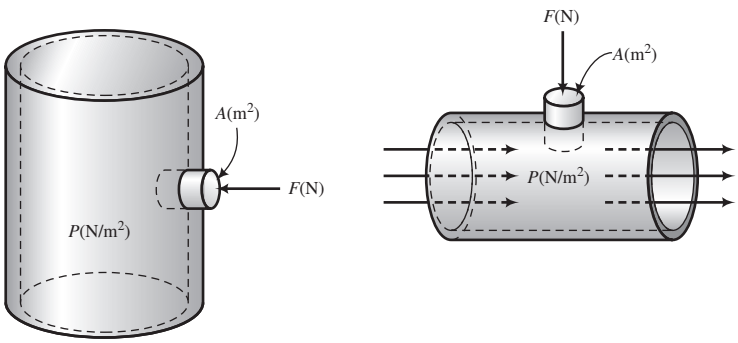

FIGURE 3.4-1 Fluid pressure in a tank and a pipe.

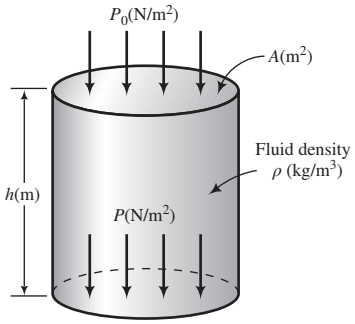

FIGURE 3.4-2 Pressure at the base of a fluid column.

We must introduce an additional definition of fluid pressure to explain the concept of atmospheric pressure and to discuss common methods for measuring pressures of fluids in tanks and pipes. Suppose a vertical column of fluid is h(m) high and has a uniform cross-sectional area A(m^2). Further suppose that the fluid has a density of ρ(kg/m^3), and that a pressure P_0(N/m^2) is exerted on the upper surface of the column. (See Figure 3.4-2.) The pressure P of the fluid at the base of the column—called the **hydrostatic pressure** of the fluid—is, by definition, the force F exerted on the base divided by the base area A. F thus equals the force on the top surface plus the weight of the fluid in the column. It is not difficult to show that:

$$\boxed{P = P_0 + \rho g h} \qquad \textbf{(3.4-1)}$$

(See if you can derive this equation.) Since A does not appear in this equation, the formula is applicable to a column of fluid as thin as a test tube or as wide as the ocean.

In addition to being expressible as a force per unit area, a pressure may be expressed as a **head** of a particular fluid—that is, as the height of a hypothetical column of this fluid that would exert the given pressure at its base if the pressure at the top were zero. You can thus speak of a pressure of 14.7 psi, or equivalently of a pressure (or head) of 33.9 ft of water (33.9 ft H_2O) or 76 cm of mercury (76 cm Hg). *The equivalence between a pressure P (force/area) and the corresponding head* P_h *(height of a fluid) is given by Equation* 3.4-1 *with* $P_0 = 0$:

$$P\left(\frac{\text{force}}{\text{area}}\right) = \rho_{\text{fluid}}\, g\, P_h(\text{head of fluid}) \qquad \textbf{(3.4-2)}$$

Example 3.4-1 Calculation of a Pressure as a Head of Fluid

Express a pressure of 2.00×10^5 Pa in terms of mm Hg.

Solution Solve Equation 3.4-2 for P_h(mm Hg), assuming that $g = 9.807$ m/s^2 and noting that the density of mercury is 13.6×1000 kg/m^3 = 13,600 kg/m^3.

$$P_h = \frac{P}{\rho_{Hg} g}$$

$$= \frac{2.00 \times 10^5 \text{ N}}{\text{m}^2} \left| \frac{\text{m}^3}{13{,}600 \text{ kg}} \right| \frac{\text{s}^2}{9.807 \text{ m}} \left| \frac{1 \text{ kg}\cdot\text{m/s}^2}{1 \text{ N}} \right| \frac{10^3 \text{ mm}}{1 \text{ m}} = \boxed{1.50 \times 10^3 \text{ mm Hg}}$$

The relationship between the pressure at the base of a column of fluid of height h and the pressure at the top is particularly simple if these pressures are expressed as heads of the given fluid: if the column is mercury, for example, then

$$\boxed{P_h(\text{mm Hg}) = P_0(\text{mm Hg}) + h(\text{mm Hg})} \qquad \textbf{(3.4-3)}$$

Any other length unit and chemical species may be substituted for mm Hg in this equation.

The conversion table on the inside front cover of this book lists values of a pressure expressed in several common force/area units and as heads of mercury and water. The use of this table for pressure unit conversion is illustrated by the conversion of 20.0 psi to cm Hg:

$$\frac{20.0\ \text{psi}}{} \left| \frac{76.0\ \text{cm Hg}}{14.696\ \text{psi}} \right. = 103\ \text{cm Hg}$$

Example 3.4-2 Pressure Below the Surface of a Fluid

What is the pressure 30.0 m below the surface of a lake? Atmospheric pressure (the pressure at the surface) is 10.4 m H_2O, and the density of water is 1000.0 kg/m^3. Assume that g is 9.807 m/s^2.

Solution First, the hard way, using Equation 3.4-1:

$$P_h = P_0 + \rho g h$$

$$\Downarrow$$

$$P_h = \frac{10.4\ \text{m H}_2\text{O}}{} \left| \frac{1.013 \times 10^5\ \text{N/m}^2}{10.33\ \text{m H}_2\text{O}} \right. + \frac{1000.0\ \text{kg/m}^3}{} \left| \frac{9.807\ \text{m}}{\text{s}^2} \right| \frac{30.0\ \text{m}}{} \left| \frac{1\ \text{N}}{1\ \text{kg}\cdot\text{m/s}^2} \right.$$

$$= \boxed{3.96 \times 10^5\ \text{N/m}^2\text{(Pa)}}$$

or

$$\boxed{P_h = 396\ \text{kPa}}$$

Next, the easy way, using Equation 3.4-3:

$$P_h = 10.4\ \text{m H}_2\text{O} + 30.0\ \text{m H}_2\text{O} = \boxed{40.4\ \text{m H}_2\text{O}}$$

(Verify that the two calculated pressures are equivalent.)

Note: We will henceforth use an unsubscripted P to denote pressure expressed as either (force/area) or as the head of a fluid.

Test Yourself

(Answers, p. 655)

1. Define (a) the pressure of a fluid flowing in a pipe, (b) hydrostatic pressure, and (c) a head of a fluid corresponding to a given pressure.
2. Consider the tank in Figure 3.4-1. Does the pressure at the plug depend on the height of the opening in the tank? (*Hint:* Yes.) Why? Would you expect the difference between the pressure at the top and that at the bottom to be very large if the fluid were air? How about water? Mercury?

3. Suppose the pressure in the tank of Figure 3.4-1 is given as 1300 mm Hg. Does this tell you anything about the height of the tank? If you were given the area of the hole (say, 4 cm^2), how would you calculate the force needed to hold the plug in the hole?
4. Suppose the pressure at a point within a column of mercury in a tube is 74 mm Hg. What is the pressure 5 mm below this point? (If this takes you more than one second, you are probably doing it wrong.)

3.4b Atmospheric Pressure, Absolute Pressure, and Gauge Pressure

The pressure of the atmosphere can be thought of as the pressure at the base of a column of fluid (air) located at the point of measurement (e.g., at sea level). Equation 3.4-1 can be used to calculate atmospheric pressure, assuming that the pressure at the top of the column (P_0) equals 0 and ρ and g are average values of the density of air and the acceleration of gravity between the top of the atmosphere and the measurement point.

A typical value of the atmospheric pressure at sea level, 760.0 mm Hg, has been designated as a standard pressure of 1 atmosphere. The conversion table on the inside front cover lists equivalent values of this pressure in various units.

The fluid pressures referred to so far are all **absolute pressures**, in that a pressure of zero corresponds to a perfect vacuum. Many pressure-measuring devices give the **gauge pressure** of a fluid, or the pressure relative to atmospheric pressure. A gauge pressure of zero indicates that the absolute pressure of the fluid is equal to atmospheric pressure. The relationship for converting between absolute and gauge pressure is

$$P_{\text{absolute}} = P_{\text{gauge}} + P_{\text{atmospheric}} \tag{3.4-4}$$

The abbreviations psia and psig are commonly used to denote absolute and gauge pressure in lb_f/in^2. Also, it is common to refer to negative gauge pressures (absolute pressures less than atmospheric) as positive amounts of vacuum: for example, a gauge pressure of −1 cm Hg (75.0 cm Hg absolute if atmospheric pressure is 76.0 cm Hg) may also be called 1 cm of vacuum.

Test Yourself

(Answers, p. 655)

1. Is atmospheric pressure always equal to 1 atm?
2. What is absolute pressure? Gauge pressure?
3. The gauge pressure of a gas is −20 mm Hg at a point where atmospheric pressure is 755 mm Hg. How else can the gas pressure be expressed in terms of mm Hg? (Give two values.)
4. A mercury column is open to the atmosphere on a day when atmospheric pressure is 29.9 inches Hg. What is the gauge pressure 4 inches below the surface? The absolute pressure? (Give the answers in inches Hg.)

3.4c Fluid Pressure Measurement

Perry's Chemical Engineers' Handbook (pp. 8-58 to 8-59) categorizes pressure-measurement devices as:

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- elastic-element methods—Bourdon tubes, bellows, or diaphragms
- liquid-column methods—manometers
- electrical methods—strain gauges, piezoresistive transducers, and piezoelectric transducers

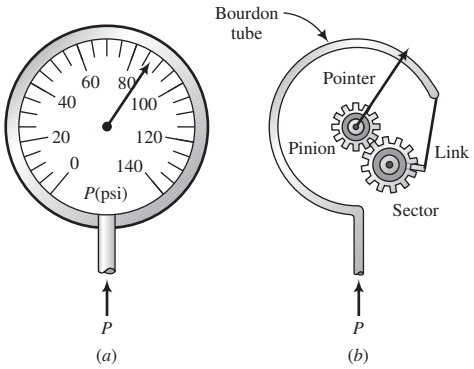

FIGURE 3.4-3 Bourdon gauge.

We limit our discussion here to Bourdon gauges and manometers but you should recognize the importance of other modern process sensors.

The most common mechanical device used for pressure measurement is a **Bourdon gauge**, a hollow tube closed at one end and bent into a C configuration. The open end of the tube is exposed to the fluid whose pressure is to be measured. As the pressure increases, the tube tends to straighten, causing a pointer attached to the tube to rotate. The position of the pointer on a calibrated dial gives the *gauge* pressure of the fluid. A schematic diagram of a Bourdon gauge is shown in Figure 3.4-3.

Bourdon gauges are used to measure fluid pressures from nearly perfect vacuums to about 7000 atm. More accurate measurements of pressures below about 3 atm are provided by **manometers**.

A manometer is a U-shaped tube partially filled with a fluid of known density (the **manometer fluid**). When the ends of the tube are exposed to different pressures, the liquid level drops in the high-pressure arm and rises in the low-pressure arm. The difference between the pressures can be calculated from the measured difference between the liquid levels in each arm.

Manometers are used in several different ways, as shown in Figure 3.4-4. In each diagram, pressure P_1 is greater than pressure P_2.

Figure 3.4-4*a* shows an **open-end manometer**: one end is exposed to a fluid whose pressure is to be measured, and the other is open to the atmosphere. Figure 3.4-4*b* shows a **differential manometer**, which is used to measure the pressure difference between two points in a process line. Figure 3.4-4*c* shows a **sealed-end manometer**, which has a near-vacuum enclosed at one

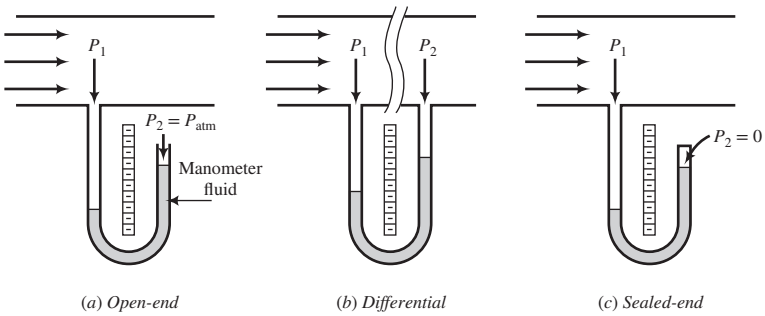

FIGURE 3.4-4 Manometers.

Equipment Encyclopedia
manometers
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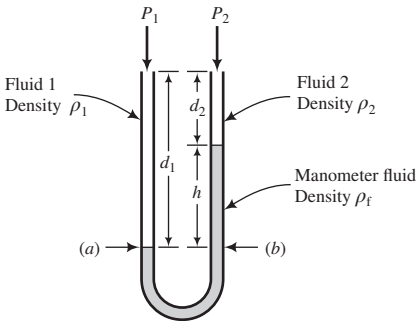


FIGURE 3.4-5 Manometer variables.

end. (Some of the enclosed fluid will vaporize into the empty space, thereby preventing the existence of a perfect vacuum.) If the open end of a sealed-end manometer is exposed to the atmosphere ($P_1 = P_{atm}$) the device functions as a **barometer**.

The formula that relates the pressure difference $P_1 - P_2$ to the difference in manometer fluid levels is based on the principle that the fluid pressure must be the same at any two points at the same height in a continuous fluid. In particular, *the pressure at the height of the lower surface of a manometer fluid is the same in both arms of the manometer*. (See Figure 3.4-5.) Writing and equating expressions for the pressures at points (*a*) and (*b*) in Figure 3.4-5 yields the general manometer equation

General Manometer Equation:

$$\boxed{P_1 + \rho_1 g d_1 = P_2 + \rho_2 g d_2 + \rho_f g h} \qquad \textbf{(3.4-5)}$$

In a differential manometer, fluids 1 and 2 are the same, and consequently $\rho_1 = \rho_2 = \rho$. The general manometer equation then reduces to

Differential Manometer Equation:

$$\boxed{P_1 - P_2 = (\rho_f - \rho) g h} \qquad \textbf{(3.4-6)}$$

If either fluid 1 or 2 is a gas at a moderate pressure (e.g., if one arm is open to the atmosphere), the density of this fluid is 100 to 1000 times lower than the density of the manometer fluid, so that the corresponding $\rho g d$ term in Equation 3.4-5 may be neglected. If *both* fluids are gases, then the equation becomes

$$P_1 - P_2 = \rho_f g h$$

and if both P_1 and P_2 are expressed as heads of the manometer fluid, then

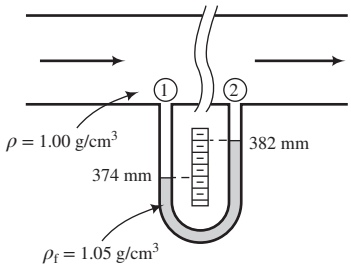
Manometer Formula for Gases:

$$\boxed{P_1 - P_2 = h} \qquad \textbf{(3.4-7)}$$

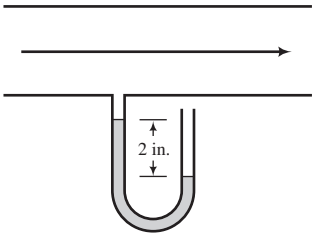
If P_2 is atmospheric pressure, then the gauge pressure at point 1 is simply the difference in the levels of the manometer fluid.

Example 3.4-3 Pressure Measurement with Manometers

1. A differential manometer is used to measure the drop in pressure between two points in a process line containing water. The specific gravity of the manometer fluid is 1.05. The measured levels in each arm are shown below. Calculate the pressure drop between points 1 and 2 in dynes/cm^2.



2. The pressure of gas being pulled through a line by a vacuum pump is measured with an open-end mercury manometer. A reading of −2 inches is obtained. What is the gauge pressure of the gas in inches of mercury? What is the absolute pressure if $P_{atm} = 30$ inches Hg?



Solution **1.** $h = (382 - 374)$ mm $= 8$ mm. From Equation 3.4-6,

$$P_1 - P_2 = (\rho_f - \rho)gh$$

$$= \frac{(1.05 - 1.00)\text{ g}}{\text{cm}^3} \left| \frac{980.7\text{ cm}}{\text{s}^2} \right| \frac{1\text{ dyne}}{1\text{ g}\cdot\text{cm/s}^2} \left| \frac{8\text{ mm}}{} \right| \frac{1\text{ cm}}{10\text{ mm}}$$

$$= \boxed{40\ \frac{\text{dynes}}{\text{cm}^2}}$$

2. From Equation 3.4-7 and the definition of a gauge pressure,

$$P_1 - P_{atm} = P_{gauge} = \boxed{-2\text{ in. Hg}}$$

$$\Downarrow$$

$$P_1 = P_{atm} + P_{gauge} = (30 - 2)\text{ in. Hg} = \boxed{28\text{ in. Hg}}$$

Test Yourself

(Answers, p. 655)

1. What is a Bourdon gauge? What range of pressures can it be used to measure? As it is normally calibrated, does it measure gauge or absolute pressure?

2. What is an open-end manometer? A differential manometer? A sealed-end manometer?

3. True or false?

(a) An open-end manometer provides a direct reading of the gauge pressure of a gas.

(b) A sealed-end manometer provides a direct reading of the absolute pressure of a gas, provided that the gas pressure in the sealed end may be neglected.

(c) The reading of a differential manometer does not depend on the density of the fluid in the pipeline but only on that of the manometer fluid.

4. The pressure of a gas in a pipeline is measured with an open-end mercury manometer. The mercury level in the arm connected to the line is 14 mm *higher* than the level in the open arm. What is the gauge pressure of the gas in the line?

CREATIVITY EXERCISE

Think of several devices that might be used to measure fluid pressures, being as imaginative as you can. (*Example:* Allow a gas at the pressure to be measured to fill a calibrated balloon, and measure the final balloon diameter.)

3.5 TEMPERATURE

Equipment Encyclopedia
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temperature measurement

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The temperature of a substance in a particular state of aggregation (solid, liquid, or gas) is a measure of the average kinetic energy possessed by the molecules of the substance. Since this energy cannot be measured directly, the temperature must be determined indirectly by measuring some physical property of the substance whose value depends on temperature in a known manner. Such properties and the temperature-measuring devices based on them include electrical resistance of a conductor (**resistance thermometer**), voltage at the junction of two dissimilar metals (**thermocouple**), spectrum of emitted radiation (**pyrometer**), and volume of a fixed mass of fluid (**thermometer**).

Temperature scales can be defined in terms of any of these properties, or in terms of physical phenomena, such as freezing and boiling, that take place at fixed temperatures and pressures. You might refer, for example, to "the temperature at which the resistivity of a copper wire is 1.92×10^{-6} ohms/cm^3" or to "the temperature two-thirds of the way from the boiling point of water at 1 atm to the melting point of NaCl."

It is convenient to have, in addition to these physical scales, a simple numerical temperature scale—among other reasons, so that you do not have to use 25 words to give the value of a single temperature. A defined temperature scale is obtained by arbitrarily assigning numerical values to two reproducibly measurable temperatures; for example, assign a value of 0 to the freezing point of water and a value of 100 to the boiling point of water at 1 atm. The assigned values completely specify the scale, since in addition to locating the two points they specify that the length of a unit temperature interval (called a **degree**) is $\frac{1}{100}$ of the distance between the two reference points on the scale.

The two most common temperature scales are defined using the freezing point (T_f) and boiling point (T_b) of water at a pressure of 1 atm.

Celsius (or centigrade) scale: T_f is assigned a value of 0°C, and T_b is assigned a value of 100°C. ***Absolute zero*** (theoretically the lowest temperature attainable in nature) on this scale falls at −273.15°C.

Fahrenheit scale: T_f is assigned a value of 32°F, and T_b is assigned a value of 212°F. Absolute zero falls at −459.67°F.

The **Kelvin** and **Rankine** scales are defined such that absolute zero has a value of 0 and the size of a degree is the same as a Celsius degree (Kelvin scale) or a Fahrenheit degree (Rankine scale).

The following relationships may be used to convert a temperature expressed in one defined scale unit to its equivalent in another:

$$T(\text{K}) = T(^\circ\text{C}) + 273.15 \qquad \textbf{(3.5-1)}$$

$$T(^\circ\text{R}) = T(^\circ\text{F}) + 459.67 \qquad \textbf{(3.5-2)}$$

$$T(^\circ\text{R}) = 1.8T(\text{K}) \qquad \textbf{(3.5-3)}$$

$$T(^\circ\text{F}) = 1.8T(^\circ\text{C}) + 32 \qquad \textbf{(3.5-4)}$$

Equations like these always have the form of the equation of a line ($y = ax + b$). If ($^\circ A$) and ($^\circ B$) stand for any two temperature units, to derive the equation for $T(^\circ B)$ in terms of $T(^\circ A)$ you must know equivalent values on each scale of two temperatures—say, T_1 and T_2. Then

1. Write $T(^\circ B) = aT(^\circ A) + b$
2. Substitute $T_1(^\circ B)$ and $T_1(^\circ A)$ in the equation—you then have one equation in two unknowns (a and b). Substitute $T_2(^\circ B)$ and $T_2(^\circ A)$ to get the second equation in the two unknowns, and solve for a and b.

Example 3.5-1 Derivation of a Temperature Conversion Formula

Derive Equation 3.5-4 for $T(°F)$ in terms of $T(°C)$. Use $T_1 = 0°C$ (32°F) and $T_2 = 100°C$ (212°F).

Solution

$$T(°F) = aT(°C) + b$$

Substitute T_1: $\quad 32 = (a)(0) + b \Longrightarrow b = 32$

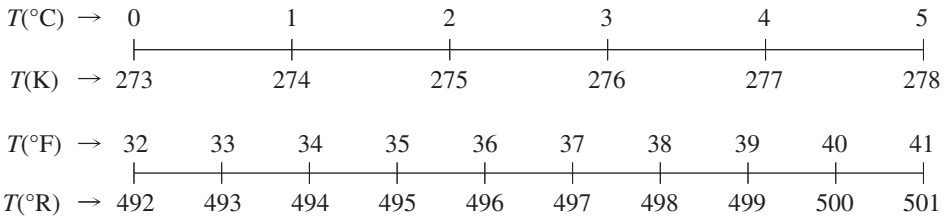
Substitute T_2: $\quad 212 = (a)(100) + 32 \Longrightarrow a = 1.8$

$$\Downarrow$$

$$T(°F) = 1.8T(°C) + 32$$

A degree can be both a temperature and a temperature interval, a fact that sometimes leads to confusion. Consider the temperature interval from 0°C to 5°C. There are nine Fahrenheit and nine Rankine degrees in this interval, and only five Celsius degrees and five kelvins. An interval of 1 Celsius degree or kelvin therefore contains 1.8 Fahrenheit or Rankine degrees, leading to the conversion factors

$$\frac{1.8°F}{1°C}, \frac{1.8°R}{1\ K}, \frac{1°F}{1°R}, \frac{1°C}{1\ K} \qquad \textbf{(3.5-5)}$$



Note: *These conversion factors refer to temperature intervals, not temperatures.*[4] For example, to find the number of Celsius degrees between 32°F and 212°F you can say that

$$\Delta T(°C) = \frac{(212 - 32)°F \mid 1°C}{\qquad\quad \mid 1.8°F} = 100°C$$

but to find the Celsius temperature corresponding to 32°F you must use Equation 3.5-4; you cannot say

$$T(°C) = \frac{32°F \mid 1°C}{\qquad \mid 1.8°F}$$

A temperature — A temperature interval

Test Yourself

(Answers, p. 655)

1. Suppose you were given a glass tube with mercury in it but no scale markings, and you were given only a beaker of water, a freezer, and a bunsen burner with which to work. How would you calibrate the thermometer to provide readings in °C?
2. Which is warmer, a temperature of 1°C or 1°F?
3. Which reflects a greater change in temperature, an increase of 1°C or 1°F?

[4] Some authors have proposed varying the position of the degree symbol to indicate whether a temperature or temperature interval is denoted; that is, 5°C refers to a temperature of five degrees Celsius, and 5C° means an interval of five Celsius degrees. This idea, while an excellent one in principle, has not caught on, so you will have to get used to making the distinction yourself from the context in which the unit appears.

Example 3.5-2 Temperature Conversion

Consider the interval from 20°F to 80°F.

1. Calculate the equivalent temperatures in °C and the interval between them.
2. Calculate directly the interval in °C between the temperatures.

Solution

1. From Equation 3.5-4,

$$T(°C) = \frac{T(°F) - 32}{1.8}$$

so that

$$T_1(20°F) = \left(\frac{20 - 32}{1.8}\right)°C = -6.7°C$$

$$T_2(80°F) = \left(\frac{80 - 32}{1.8}\right)°C = 26.6°C$$

and

$$T_2 - T_1 = (26.6 - (-6.7))°C = 33.3°C$$

2. From Equation 3.5-5,

$$\Delta T(°C) = \frac{\Delta T(°F)}{\left|\begin{array}{c} 1°C \\ \hline 1.8°F \end{array}\right.} = \frac{(80 - 20)°F}{\left|\begin{array}{c} 1°C \\ \hline 1.8°F \end{array}\right.} = 33.3°C$$

Example 3.5-3 Temperature Conversion and Dimensional Homogeneity

The heat capacity of ammonia, defined as the amount of heat required to raise the temperature of a unit mass of ammonia by precisely 1° at a constant pressure, is, over a limited temperature range, given by the expression

$$C_p\left(\frac{\text{Btu}}{\text{lb}_\text{m}\cdot°\text{F}}\right) = 0.487 + 2.29 \times 10^{-4} T(°F)$$

Determine the expression for C_p in J/(g·°C) in terms of T(°C).

Solution

The °F in the units of C_p refers to a temperature interval, while the unit of T is a temperature. The calculation is best done in two steps.

1. Substitute for T(°F) and simplify the resulting equation:

$$\begin{aligned} C_p\left(\frac{\text{Btu}}{\text{lb}_\text{m}\cdot°\text{F}}\right) &= 0.487 + 2.29 \times 10^{-4}[1.8T(°C) + 32] \\ &= 0.494 + 4.12 \times 10^{-4} T(°C) \end{aligned}$$

2. Convert to the desired temperature interval unit using Equation 3.5-5:

$$C_p\left(\frac{\text{J}}{\text{g}\cdot°\text{C}}\right) = \left[0.494 + 4.12 \times 10^{-4} T(°C)\right] \frac{(\text{Btu})}{(\text{lb}_\text{m}\cdot°\text{F})} \left|\begin{array}{c|c|c} 1.8°F & 1\text{ J} & 1\text{ lb}_\text{m} \\ \hline 1.0°C & 9.486 \times 10^{-4}\text{ Btu} & 454\text{ g} \end{array}\right.$$

$$\Downarrow$$

$$\boxed{C_p\left(\frac{\text{J}}{\text{g}\cdot°\text{C}}\right) = 2.06 + 1.72 \times 10^{-3} T(°C)}$$

CREATIVITY EXERCISES

1. Invent several temperature-measuring devices. For each, describe the device, and state what you would measure. (*Example:* Put a guinea pig on a treadmill and measure the rate at which he runs to keep warm.) (Well, it *could* work.)
2. Think of as many ways as you can to use a solid block as a temperature-measuring device. (*Example:* Put it in a furnace equipped with a window and observe the color with which it glows.)

3.6 SUMMARY

In this chapter, we have described how amounts of material, flow rates, compositions, pressures, and temperatures are determined from direct measurements or calculated from measurements and physical properties. We also have described how to convert between different methods of expressing these variables. Here are some highlights.

- The *density* of a substance is the ratio of its mass to its volume. For example, the density of liquid acetone at 20°C is 0.791 g/cm^3, so that one cubic centimeter of liquid acetone at 20°C has a mass of 0.791 gram. Density can be thought of as a conversion factor between mass and volume or between mass flow rate and volumetric flow rate.
- The *specific gravity* of a substance is the ratio of the density of the substance to the density of a reference material (typically water at 4°C). Specific gravities of many liquids and solids are given in Table B.1, with the reference density being that of liquid water at 4°C (1.00 g/cm^3, 1.00 kg/L, 62.43 lb$_m$/ft^3). The density of a substance is the product of its specific gravity and the reference density in the desired units.
- The *atomic weight* of an element is the mass of an atom of that element on a scale that assigns ^{12}C a mass of exactly 12. This quantity may be refered to as 12 daltons. Atomic weights of the elements in their naturally occurring isotopic proportions are listed in the table at the back of the book. The *molecular weight* of a compound is the sum of the atomic weights of the atoms that constitute a molecule of that compound.
- A *gram-mole* or *mol* of a compound is the molecular weight of the compound in grams; for example, 1 mol H_2O has a mass of 18.01 grams. *A pound-mole* or *lb-mole* is the molecular weight in pounds mass; for example, 1 lb-mole H_2O has a mass of 18.01 lb$_m$. The molecular weight of water may therefore be expressed as 18.01 g/mol, 18.01 lb$_m$/lb-mole, and so on, and it may be used to convert masses to moles or mass flow rates to molar flow rates, and vice versa.
- The *mass fraction* of a component in a mixture is the ratio of the mass of the component to the total mass of the mixture. If 100 grams of a mixture contains 30 grams of nitrogen, the mass fraction of nitrogen is 0.30 g N_2/g mixture. (The word "mixture" usually is omitted.) The mass fraction is also 0.30 kg N_2/kg and 0.30 lb$_m$ N_2/lb$_m$, and the *percent by mass* or *weight percent* of nitrogen is 30%. The *mole fraction* of a component is defined similarly. If 10.0 kmol of a mixture contains 6.0 kmol of methanol, the mole fraction of methanol is 0.60 kmol CH_3OH/kmol (= 0.60 lb-mole CH_3OH/lb-mole), and the mole percent of methanol is 60%.
- The *average molecular weight* of a mixture is the ratio of the total mass to the total number of moles of all species.
- The *concentration* of a component in a mixture is the ratio of the mass or moles of the component to the total mixture volume. The *molarity* of a component of a solution is the concentration of the component expressed in mol/L.
- The *pressure* at a point in a fluid (gas or liquid) is the force per unit area that the fluid would exert on a plane surface passing through the point. Standard units of fluid pressure are N/m^2 (pascal, or Pa) in the SI system, dyne/cm^2 in the CGS system, and lb$_f$/ft^2 in the U.S. customary system. The unit lb$_f$/in^2 (psi) is also common in the U.S. customary system.
- The pressure at the base of a vertical column of fluid of density ρ and height h is given by the expression

$$P = P_o + \rho g h \qquad \textbf{(3.4-1)}$$

  where P_o is the pressure exerted on the top of the column and g is the acceleration of gravity. This result gives rise to two ways of expressing fluid pressure: as force per unit area (e.g., $P = 14.7$ lb$_f$/in^2) or as an equivalent *pressure head*, $P_h = P/\rho g$ (e.g., $P_h = 760$ mm Hg), the height of a column of the specified fluid with zero pressure at the top that would exert the specified pressure at the bottom.
- The earth's atmosphere can be considered a column of fluid with zero pressure at the top. The fluid pressure at the base of this column is *atmospheric pressure* or *barometric pressure*, P_{atm}. Although atmospheric pressure varies with altitude and weather conditions, its value at sea level is always close to 1.01325×10^5 N/m^2 (= 14.696 lb$_f$/in^2 = 760 mm Hg). This pressure value has been designated *1 atmosphere*. Other equivalents to 1 atm in different units are given on the inside front cover of this text.
- The *absolute pressure* of a fluid is the pressure relative to a perfect vacuum ($P = 0$). The *gauge pressure* is the pressure relative to atmospheric pressure: $P_{gauge} = P_{abs} - P_{atm}$. Common pressure gauges like a Bourdon gauge and an open-end manometer provide a direct reading of gauge pressure. If

atmospheric pressure is not known from a weather report or a barometer reading, a value of $P_{atm} = 1$ atm is usually reasonable to assume when converting between absolute and gauge pressure.

- *Temperature scales* are obtained by assigning numerical values to two experimentally reproducible temperatures. For example, the Celsius scale is obtained by assigning a value of 0°C to the freezing point of pure water at 1 atm and a value of 100°C to the boiling point of pure water at 1 atm. A temperature of 40°C is consequently shorthand for "the temperature 40% of the way from the freezing point of water at 1 atm to the boiling point of water at 1 atm."
- The four most common temperature scales are Celsius (°C), Fahrenheit (°F), and the absolute temperature scales Kelvin (K) and Rankine (°R). Temperatures expressed in one of these scales may be converted to equivalent temperatures in another scale using Equations 3.5-1 through 3.5-4.
- Temperatures should not be confused with temperature intervals. For example, a temperature of 10°C is equivalent to a temperature of 50°F (from Equation 3.5-4), but a temperature interval of 10°C (e.g., the interval between $T = 10$°C and $T = 20$°C) is equivalent to a temperature interval of 18°F (the interval between 50°F and 68°F). An interval of 1 Celsius degree or 1 kelvin is equivalent to 1.8 Fahrenheit or Rankine degrees.

Note: This would be a good time to work through the first interactive tutorial.

WileyPLUS
Interactive Tutorial #1
Questions with Immediate Feedback

PROBLEMS

3.1. Perform the following estimations *without using a calculator*.
- **(a)** Estimate the mass of water (kg) in an Olympic-size swimming pool.
- **(b)** A drinking glass is being filled from a pitcher. Estimate the mass flow rate of the water (g/s).
- **(c)** Twelve male heavyweight boxers coincidentally get on the same elevator in Great Britain. Posted on the elevator wall is a sign that gives the maximum safe combined weight of the passengers, W_{max}, in stones. (A stone is a unit of mass equal to 14 lb_m. It is commonly used in England as a measure of body weight, which, like the numerical equivalence between the lb_m and lb_f, is only valid at or near sea level.) If you were one of the boxers, estimate the lowest value of W_{max} for which you would feel comfortable remaining on the elevator.
- **(d)** The Trans-Alaska Pipeline has an outside diameter of 4 ft and extends 800 miles from the North Slope of Alaska to the northernmost ice-free port in Valdez, Alaska. How many barrels of oil are required to fill the pipeline?
- **(e)** Estimate the volume of your body (cm^3) in two different ways. (Show your work.)
- **(f)** A solid block is dropped into water and very slowly sinks to the bottom. Estimate its specific gravity.

3.2. Calculate densities in lb_m/ft^3 of the following substances:
- **(a)** a liquid with density of 995 kg/m^3. Use (i) conversion factors from the table on the inside front cover and (ii) Equation 3.1-2.
- **(b)** a solid with a specific gravity of 5.7. What did you assume to come up with your answer?

3.3. The specific gravity of gasoline is approximately 0.70.
- **(a)** Estimate the mass (kg) of 50.0 liters of gasoline.
- **(b)** The mass flow rate of gasoline exiting a refinery tank is 1150 kg/min. Estimate the volumetric flow rate in liters/s.
- **(c)** Estimate the average mass flow rate (lb_m/min) delivered by a gasoline pump.
- **(d)** Gasoline and kerosene (specific gravity = 0.82) are blended to obtain a mixture with a specific gravity of 0.78. Calculate the volumetric ratio (volume of gasoline/volume of kerosene) of the two compounds in the mixture, assuming $V_{blend} = V_{gasoline} + V_{kerosene}$.

3.4. In September 2014 the average price of gasoline in France was 1.54 euro/liter, and the exchange rate was \$1.29 per euro (€). How much would you have paid, in dollars, for 50.0 kg of gasoline in France, assuming gasoline has a specific gravity of 0.71? What would the same quantity of gasoline have cost in the United States at the prevailing average price of \$3.81/gal?

3.5. Liquid benzene and liquid *n*-hexane are blended to form a stream flowing at a rate of 1700 lb_m/h. An on-line *densitometer* (an instrument used to determine density) indicates that the stream has a density of 0.810 g/mL. Using specific gravities from Table B.1, estimate the mass and volumetric feed rates of the

two hydrocarbons to the mixing vessel (in U.S. customary units). State at least two assumptions required to obtain the estimate from the recommended data.

*3.6. You purchase six oranges that weigh a total of 2 lb_f and 13 ounces. After cutting them open and squeezing all the juice your strength allows into a large measuring cup, you weigh the remaining pulp and orange peels. They weigh 1 lb_f and 12 ounces and the total volume of the juice is 1.75 cups. What is the specific gravity of orange juice? State any assumptions you make.

*3.7. A small family home in Tucson, Arizona, has a rooftop area of 1967 square feet, and it is possible to capture rain falling on about 56% of the roof. A typical annual rainfall is about 14 inches. If the family wanted to install a tank to capture the rain for an entire year, without using any of it, what would be the required volume of the tank in m^3 and in gallons? How much would the water weigh when the tank was full (in N and in lb_f)?

3.8. At 25°C, an aqueous solution containing 35.0 wt% H_2SO_4 has a specific gravity of 1.2563. A quantity of the 35% solution is needed that contains 195.5 kg of H_2SO_4.
(a) Calculate the required volume (L) of the solution using the given specific gravity.
(b) Estimate the percentage error that would have resulted if pure-component specific gravities of H_2SO_4 (SG = 1.8255) and water had been used for the calculation instead of the given specific gravity of the mixture.

3.9. Hot mix asphalt (HMA) is commonly used in the construction of roadways in the United States at a rate estimated to be 500,000,000 tons/year. A typical upper layer (there may be as many as 5 layers of different thicknesses and compositions) of a high-volume highway is composed of crushed stone (also known as crushed aggregate) and asphalt binder and is approximately 1.25 inches thick. The stone, which has a specific gravity of about 2.7, is mixed with asphalt binder (SG = 1.03) to form the HMA with a composition of approximately 95 wt% aggregate and 5% asphalt. What is the volume (ft^3) of asphalt binder and weight (tons) of HMA required for the top layer of a 15-mile segment of interstate highway with 5 lanes, each of which has a width of 12 ft?

3.10. A rectangular block of solid carbon (graphite) floats at the interface of two immiscible liquids. The bottom liquid is a relatively heavy lubricating oil, and the top liquid is water. Of the total block volume, 54.2% is immersed in the oil and the balance is in the water. In a separate experiment, an empty flask is weighed, 35.3 cm^3 of the lubricating oil is poured into the flask, and the flask is reweighed. If the scale reading was 124.8 g in the first weighing, what would it be in the second weighing? (*Suggestion:* Recall Archimedes' principle, and do a force balance on the block.)

3.11. A rectangular block floats in pure water with 0.5 inch above the surface and 1.5 inches below the surface. When placed in an aqueous solution, the block of material floats with 1 inch below the surface. Estimate the specific gravities of the block and the solution. (*Suggestion:* Call the horizontal cross-sectional area of the block A. A should cancel in your calculations.)

3.12. An object of density ρ_a, volume V_a, and weight W_a is thrown from a rowboat floating on the surface of a small pond and sinks to the bottom. The weight of the rowboat without the jettisoned object is W_b. Before the object was thrown out, the depth of the pond was h_{p1}, and the bottom of the boat was a distance h_{b1} above the pond bottom. After the object sinks, the values of these quantities are h_{p2} and h_{b2}. The area of the pond is A_p; that of the boat is A_b. A_b may be assumed constant, so that the volume of water displaced by the boat is $A_b(h_p - h_b)$.
(a) Derive an expression for the change in the pond depth $(h_{p2} - h_{p1})$. Does the liquid level of the pond rise or fall, or is it indeterminate?
(b) Derive an expression for the change in the height of the bottom of the boat above the bottom of the pond $(h_{b2} - h_{b1})$. Does the boat rise or fall relative to the pond bottom, or is it indeterminate?

3.13. Since the 1960s, the Free Expression Tunnel at North Carolina State University has been the University's way to combat graffiti on campus. The tunnel is painted almost daily by various student groups to advertise club meetings, praise athletic accomplishments, and declare undying love. You and your engineering classmates decide to decorate the tunnel with chemical process flowcharts and key

* Adapted from a problem contributed by Paul Blowers of the University of Arizona.

equations found in your favorite text, so you purchase a can of spray paint. The label indicates that the can holds nine fluid ounces, which should cover an area of approximately 25 ft^2.

(a) You measure the tunnel and find that it is roughly 8 feet wide, 12 feet high, and 148 feet long. Based on the stated coverage, how many cans of spray paint would it take to apply one coat to the walls and ceiling of the tunnel?

SAFETY →

(b) Having just heard a lecture on process safety in your engineering class, you want to take appropriate safety precautions while painting the tunnel. One useful source for this type of information is the Safety Data Sheet (SDS), a document used in industry to provide workers and emergency personnel with procedures for safely handling or working with a specified chemical. Other sources of information about hazardous substances can be found in handbooks,[5] and some countries, including the United States, have laws that require employers to provide their employees with Safety Data Sheets.[6] Besides composition information, the SDS contains information such as physical properties (melting point, boiling point, flash point, etc.), other threats to health and safety, recommended protective equipment, and recommended procedures for storage, disposal, first aid, and spill handling. The SDS can typically be found online for most common substances. Search the web for "spray paint SDS" and find a representative SDS for a typical spray paint product. Based on the document you find, what are the top three hazards that you might encounter during your tunnel painting project? Suggest one safety precaution for each listed hazard.

3.14. Limestone (calcium carbonate) particles are stored in 50-L bags. The **void fraction** of the particulate matter is 0.30 (liter of void space per liter of total volume) and the specific gravity of solid calcium carbonate is 2.93.

(a) Estimate the **bulk density** of the bag contents (kg $CaCO_3$/liter of total volume).

(b) Estimate the weight (W) of the filled bags. State what you are neglecting in your estimate.

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ball mill
@
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(c) The contents of three bags are fed to a **ball mill**, a device something like a rotating clothes dryer containing steel balls. The tumbling action of the balls crushes the limestone particles and turns them into a powder. (See pp. 21-64 of *Perry's Chemical Engineers' Handbook*, 8th ed.) The limestone coming out of the mill is put back into 50-L bags. Would the limestone (i) just fill three bags, (ii) fall short of filling three bags, or (iii) fill more than three bags? Briefly explain your answer.

BIOENGINEERING →

3.15. A useful measure of an individual's physical condition is the fraction of his or her body that consists of fat. This problem describes a simple technique for estimating this fraction by weighing the individual twice, once in air and once submerged in water.

(a) A man has body mass $m_b = 122.5$ kg. If he stands on a scale calibrated to read in newtons, what would the reading be? If he then stands on a scale while he is totally submerged in water at 30°C (specific gravity = 0.996) and the scale reads 44.0 N, what is the volume of his body (liters)? (*Hint:* Recall from Archimedes' principle that the weight of a submerged object equals the weight in air minus the buoyant force on the object, which in turn equals the weight of water displaced by the object. Neglect the buoyant force of air.) What is his body density, ρ_b (kg/L)?

(b) Suppose the body is divided into fat and nonfat components, and that x_f (kilograms of fat/kilogram of total body mass) is the fraction of the total body mass that is fat:

$$x_f = \frac{m_f}{m_b}$$

Prove that

$$x_f = \frac{\dfrac{1}{\rho_b} - \dfrac{1}{\rho_{nf}}}{\dfrac{1}{\rho_f} - \dfrac{1}{\rho_{nf}}}$$

[5] R. J. Lewis, *Sax's Dangerous Properties of Industrial Materials*, 10th Edition, John Wiley & Sons, New York, 2000.

[6] For an illustration of OSHA Form 174, which is issued by the Occupational Safety and Health Administration of the U.S. Department of Labor as a non-mandatory form for MSDS, see the website http://www.uschambersmallbusinessnation.com/toolkits/tool/osh174_m.

where ρ_b, ρ_f, and ρ_{nf} are the average densities of the whole body, the fat component, and the nonfat component, respectively. [*Suggestion:* Start by labeling the masses (m_f and m_b) and volumes (V_f and V_b) of the fat component of the body and the whole body, and then write expressions for the three densities in terms of these quantities. Then eliminate volumes algebraically and obtain an expression for m_f/m_b in terms of the densities.[7]]

(c) If the average specific gravity of body fat is 0.9 and that of nonfat tissue is 1.1, what fraction of the man's body in Part (a) consists of fat?

(d) The body volume calculated in Part (a) includes volumes occupied by gas in the digestive tract, sinuses, and lungs. The sum of the first two volumes is roughly 100 mL and the volume of the lungs is roughly 1.2 liters. The mass of the gas is negligible. Use this information to improve your estimate of x_f.

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3.16. In April 2010, the worst oil spill ever recorded occurred when an explosion and fire on the Deepwater Horizon offshore oil-drilling rig left 11 workers dead and began releasing oil into the Gulf of Mexico. One of the attempts to contain the spill involved pumping drilling mud into the well to balance the pressure of escaping oil against a column of fluid (the mud) having a density significantly higher than those of seawater and oil. In the following problems, you may assume that seawater has a specific gravity of 1.03 and that the subsea wellhead was 5053 ft below the surface of the Gulf.

(a) Estimate the gauge pressure (psig) in the Gulf at a depth of 5053 ft.

(b) Measurements indicate that the pressure inside the wellhead is 4400 psig. Suppose a pipe between the surface of the Gulf and the wellhead is filled with drilling mud and balances that pressure. Estimate the specific gravity of the drilling mud.

(c) The drilling mud is a stable slurry of seawater and barite (SG = 4.37). What is the mass fraction of barite in the slurry?

(d) What would you expect to happen if the barite weight fraction were significantly less than that estimated in Part (c)? Explain your reasoning.

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3.17. Aqueous solutions of the amino acid L-isoleucine (Ile) are prepared by putting 100.0 grams of pure water into each of six flasks and adding different precisely weighed quantities of Ile to each flask. The densities of the solutions at 50.0 ± 0.05°C are then measured with a precision densitometer, with the following results:

r (g Ile/100 g H_2O)	0.0000	0.8821	1.7683	2.6412	3.4093	4.2064
ρ (g solution/cm^3)	0.98803	0.98984	0.99148	0.99297	0.99439	0.99580

(a) Plot a calibration curve showing the mass ratio, r, as a function of solution density, ρ, and fit a straight line to the data to obtain an equation of the form $r = a\rho + b$.

(b) The volumetric flow rate of an aqueous Ile solution at a temperature of 50°C is 150 L/h. The density of a sample of the stream is measured at 50°C and found to be 0.9940 g/cm^3. Use the calibration equation to estimate the mass flow rate of Ile in the stream (kg Ile/h).

(c) It has just been discovered that the thermocouple used to measure the stream temperature was poorly calibrated and the temperature was actually 47°C. Would the Ile mass flow rate calculated in Part (b) be too high or too low? State any assumption you make and briefly explain your reasoning.

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3.18. The following data have been obtained for the effect of solvent composition on the solubility of a serine, an amino acid, at 10.0°C:

Volume % Methanol	0	10	20	30	40	60	80	100
Solubility (g/100 mL solvent)	22.72	18.98	11.58	6.415	4.205	1.805	0.85	0.65
Solution Density (g/mL)	1.00	0.98	0.97	0.95	0.94	0.91	0.88	0.79

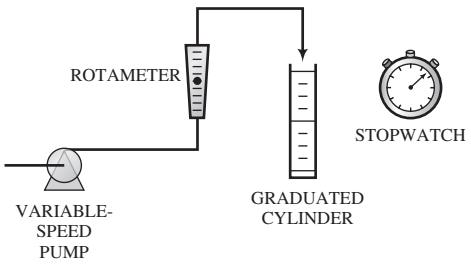
The data were obtained by mixing known volumes of methanol and water to obtain the desired solvent compositions, and then slowly adding measured amounts of serine to each mixture until no more would go into solution. The temperature was held constant at 10.0°C.

[7] If you can't work out the proof, take the given formula as valid and proceed to the next part.

(a) Derive an expression for solvent composition expressed as mass fraction of methanol, x, as a function of volume fraction of methanol, f.

(b) Prepare a table of solubility of serine (g serine/g solution) versus mass fraction of methanol.

3.19. Before a rotameter can be used to measure an unknown flow rate, a **calibration curve** of flow rate versus rotameter reading must be prepared. A calibration technique for liquids is illustrated below. A flow rate is set by adjusting the pump speed; the rotameter reading is recorded, and the effluent from the rotameter is collected in a graduated cylinder for a timed interval. The procedure is carried out twice for each of several pump settings.



Rotameter Reading	Collection Time (min)	Volume Collected (cm^3)
2	1	297
2	1	301
4	1	454
4	1	448
6	0.5	300
6	0.5	298
8	0.5	371
8	0.5	377
10	0.5	440
10	0.5	453

(a) Assuming the liquid is water at 25°C, draw a calibration curve of mass flow rate, $\dot{m}$ (kg/min), versus rotameter reading, R, and use it to estimate the mass flow rate of a water stream for which the rotameter reading is 5.3.

(b) The **mean difference between duplicates**, $\overline{D_i}$, provides an estimate of the standard deviation of a single measurement, which was given the symbol s_x in Eq. 2.5-4:

$$s_x \approx \frac{\sqrt{\pi}}{2}\,\overline{D_i} = 0.8862\overline{D_i}$$

Moreover, **confidence limits** on measured values can be estimated to a good approximation using the mean difference between duplicates. For example, if a single measurement of Y yields a value Y_{measured}, then there is a 95% probability that the true value of Y falls within the 95% confidence limits $(Y_{\text{measured}} - 1.74\overline{D_i})$ and $(Y_{\text{measured}} + 1.74\overline{D_i})$.[8] For a measured flow rate of 610 g/min, estimate the 95% confidence limits on the true flow rate.

3.20. How many of the following are found in 15.0 kmol of xylene (C_8H_{10})? (a) kg C_8H_{10}; (b) mol C_8H_{10}; (c) lb-mole C_8H_{10}; (d) mol (g-atom) C; (e) mol H; (f) g C; (g) g H; (h) molecules of C_8H_{10}.

3.21. Liquid toluene is flowing through a pipe at a rate of 175 m^3/h.

(a) What is the mass flow rate of this stream in kg/min?

(b) What is the molar flow rate in mol/s?

(c) In fact, the answer to Part (a) is only an approximation that is almost certain to be slightly in error. What did you have to assume to obtain the answer?

3.22. A mixture of methanol and propyl acetate contains 25.0 wt% methanol.

(a) Using a single dimensional equation, determine the g-moles of methanol in 200.0 kg of the mixture.

(b) The flow rate of propyl acetate in the mixture is to be 100.0 lb-mole/h. What must the mixture flow rate be in lb_m/h?

3.23. The feed to an ammonia synthesis reactor contains 25 mole% nitrogen and the balance hydrogen. The flow rate of the stream is 3000 kg/h. Calculate the rate of flow of nitrogen into the reactor in kg/h. (*Suggestion:* First calculate the average molecular weight of the mixture.)

[8] W. Volk, *Applied Statistics for Engineers*, McGraw-Hill, New York, pp. 113–115, 1958.

3.24. As described in Problem 3.16, a *drilling mud* is a slurry pumped into oil wells being drilled. The mud has several functions: It floats rock cuttings to the top of the well where they can easily be removed; lubricates and cools the drill bit; and keeps loose solids and water from leaking into the borehole. A drilling mud is prepared by blending barite (SG = 4.37) with seawater (SG = 1.03). The seawater has a dissolved salt content of approximately 3.5 wt%. You have been asked to determine the specific gravity of the mud and the wt% barite. You collect a sample of the mud from a blending tank on an oil platform and make the following observations: (i) The mud appears homogeneous, even after standing for 2 days; (ii) the tare mass of the calibrated vessel into which you pour the sample of mud is 118 g; (iii) the volume of the collected sample is 100 mL, and the mass of the collection vessel and sample is 323 g; and (iv) the mass of the vessel and residue remaining after completely evaporating water from the sample is 254 g.

(a) Estimate the specific gravity of the mud and the wt% barite.

(b) What is the practical importance of Observation (i)?

3.25. A mixture is 10.0 mole% methyl alcohol, 75.0 mole% methyl acetate ($C_3H_6O_2$), and 15.0 mole% acetic acid. Calculate the mass fractions of each compound. What is the average molecular weight of the mixture? What would be the mass (kg) of a sample containing 25.0 kmol of methyl acetate?

Equipment Encyclopedia
crystallizer, filter, dryer
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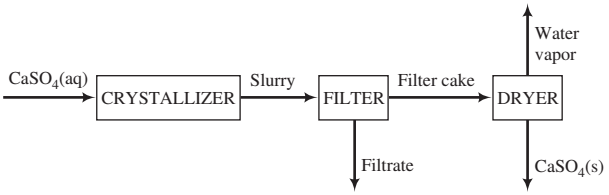
3.26. Certain solid substances, known as *hydrated* compounds, have well-defined molecular ratios of water to some other species. For example, calcium sulfate dihydrate (commonly known as *gypsum*, $CaSO_4 \cdot 2H_2O$), has 2 moles of water per mole of calcium sulfate; alternatively, it may be said that 1 mole of gypsum consists of 1 mole of calcium sulfate and 2 moles of water. The water in such substances is called *water of hydration*. (More information about hydrated salts is given in Chapter 6.)

In order to eliminate the discharge of sulfuric acid into the environment, a process has been developed in which the acid is reacted with aragonite ($CaCO_3$) to produce calcium sulfate. The calcium sulfate then comes out of solution in a crystallizer to form a *slurry* (a suspension of solid particles in a liquid) of solid gypsum particles suspended in an aqueous $CaSO_4$ solution. The slurry flows from the crystallizer to a filter in which the particles are collected as a *filter cake*. The filter cake, which is 95.0 wt% solid gypsum and the remainder $CaSO_4$ solution, is fed to a dryer in which all water (including the water of hydration in the crystals) is driven off to yield anhydrous (water-free) $CaSO_4$ as product. A flowchart and relevant process data are given below.

Solids content of slurry leaving crystallizer: 0.35 kg $CaSO_4 \cdot 2H_2O$/L slurry
$CaSO_4$ content of slurry liquid: 0.209 g $CaSO_4$/100 g H_2O
Specific gravities: $CaSO_4 \cdot 2H_2O$(s), 2.32; liquid solutions, 1.05



(a) Briefly explain in your own words the functions of the three units (crystallizer, filter, and dryer).

(b) Take a basis of one liter of solution leaving the crystallizer and calculate the mass (kg) and volume (L) of solid gypsum, the mass of $CaSO_4$ in the gypsum, and the mass of $CaSO_4$ in the liquid solution.

(c) Calculate the percentage recovery of $CaSO_4$—that is, the percentage of the total $CaSO_4$ (precipitated plus dissolved) leaving the crystallizer recovered as solid anhydrous $CaSO_4$.

(d) List five potential negative consequences of discharging H_2SO_4 into the river passing the plant.

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*__3.27.__ In the manufacture of pharmaceuticals, most active pharmaceutical ingredients (APIs) are made in solution and then recovered by separation. Acetaminophen, a pain-killing drug commercially marketed as Tylenol®, is synthesized in an aqueous solution and subsequently crystallized. The slurry of crystals is sent to a centrifuge from which two effluent streams emerge: (1) a wet cake containing 90.0 wt% solid acetaminophen (MW = 151 g/mol) and 10.0 wt% water (plus some acetaminophen and other dissolved substances, which we will neglect), and (2) a highly dilute aqueous solution of acetaminophen that is discharged from the process.

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater (2010), "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses—Part I," http://pharmahub.org/resources/360.

The wet cake is fed to a dryer where the water is completely evaporated, leaving the residual acetaminophen solids bone dry. If the evaporated water were condensed, its volumetric flow rate would be 50.0 L/h. Following is a flowchart of the process, which runs 24 h/day, 320 days/yr. A denotes acetaminophen.

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centrifuge

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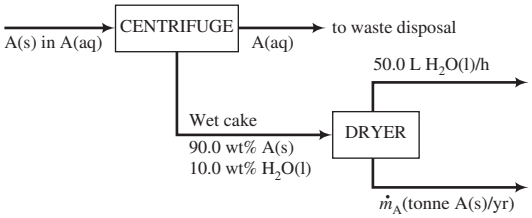

(a) Calculate the yearly production rate of solid acetaminophen (tonne/yr), using as few dimensional equations as possible.

(b) A proposal has been made to subject the liquid solution leaving the centrifuge to further processing to recover more of the dissolved acetaminophen instead of disposing of the solution. On what would the decision depend?

3.28. Things were going smoothly at the Breaux Bridge Drug Co. pilot plant during the midnight to 8 a.m. shift until Therèse Lagniappe, the reactor operator, let the run instruction sheet get too close to the Coleman stove that was being used to heat water to prepare Lagniappe's bihourly cup of Community Coffee. What followed ended in a total loss of the run sheet, the coffee, and a substantial portion of the novel Lagniappe was writing.

Remembering the less than enthusiastic reaction she got the last time she telephoned her supervisor in the middle of the night, Lagniappe decided to rely on her memory of the required flow-rate settings. The two liquids being fed to a stirred-tank reactor were circulostoic acid (CSA: MW = 75, SG = 0.90) and flubitol (FB: MW = 90, SG = 0.75). The product from the system was a popular over-the-counter drug that simultaneously cures high blood pressure and clumsiness. The molar ratio of the two feed streams had to be between 1.05 and 1.10 mol CSA/mol FB to keep the contents of the reactor from forming a solid plug. At the time of the accident, the flow rate of CSA was 45.8 L/min. Lagniappe set the flow of flubitol to the value she thought had been in the run sheet: 55.2 L/min. Was she right? If not, how would she have been likely to learn of her mistake? (*Note:* The reactor was stainless steel, so she could not see the contents.)

3.29. A mixture of methanol (methyl alcohol) and water contains 60.0% water by mass.

(a) Assuming volume additivity of the components, estimate the specific gravity of the mixture at 20°C. What volume (in liters) of this mixture is required to provide 150 mol of methanol?

(b) Repeat Part (a) with the additional information that the specific gravity of the mixture at 20°C is 0.9345 (making it unnecessary to assume volume additivity). What percentage error results from the volume-additivity assumption?

3.30. Coal being used in a power plant at a rate of 8000 lb_m/min has the following composition:

Component	Weight % (dry basis)
Ash	7.2
Sulfur	3.5
Hydrogen	5.0
Carbon	75.2
Nitrogen	1.6
Oxygen	7.5

In addition, there are 4.58 lb_m H_2O per lb_m of coal. Determine the molar flow rate of each element in the coal (including water) other than ash.

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*3.31. *Drop-on-demand (DoD) technology* is an emerging form of drug delivery in which a reservoir is filled with a solution of an active pharmaceutical ingredient (API) dissolved in a volatile liquid, and a device

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater (2010), "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses—Part I," http://pharmahub.org/resources/360.

sprays nanometer-scale drops of the solution onto an edible substrate, such as a small strip the size of a stick of chewing gum. The liquid evaporates very rapidly, causing the API to crystallize on the substrate. The exact dose required by a patient can be administered based on the known concentration of the API in the reservoir and the volume of solution deposited on the substrate, enabling greater dosage accuracy than can be provided by administering fractions of tablets.

(a) A DoD device is charged with a 1.20 molar solution of ibuprofen (the API) in *n*-hexane. The molecular weight of ibuprofen is 206.3 g/mol. If a prescribed dosage is 5.0 mg ibuprofen/kg patient weight, how many milliliters of solution should be sprayed for a 245-pound man and a 65-pound child? How many drops are in each dose, assuming that each drop is a sphere with a radius of 1 nm?

(b) The DoD device is to be automated, so that the operator enters a patient's body weight into a computer that determines the required solution volume and causes that volume to be sprayed on the substrate. Derive a formula for the volume, V_{dose} (mL), in terms of the following variables:

M_s (mol API/L) = molarity of reservoir solution
SG_s = specific gravity of reservoir solution
MW_{API} (g/mol) = molecular weight of API
D (mg API/kg body weight) = prescribed dosage
W_p (lb_f) = patient's weight
Check your formula by verifying your solution to Part (a).

(c) Calculate the surface-to-volume ratio of a sphere of radius r. Then calculate the total drop surface area of 1 mL (= 1 cm^3) of the solution if it were sprayed as drops of (i) radius 1 nm and (ii) 1 mm. Speculate on the likely reason for spraying nanoscale drops instead of much larger drops.

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3.32. A mixture of methane and air is capable of being ignited only if the mole percent of methane is between 5% and 15%. A mixture containing 9.0 mole% methane in air flowing at a rate of 7.00×10^2 kg/h is to be diluted with pure air to reduce the methane concentration to the lower flammability limit. Calculate the required flow rate of air in mol/h and the percent *by mass* of oxygen in the product gas. (*Note:* Air may be taken to consist of 21 mole% O_2 and 79% N_2 and to have an average molecular weight of 29.0.)

3.33. In the manufacture of paper, logs are cut into small chips, which are stirred into an alkaline solution that dissolves several of the chemical constituents of wood but not cellulose. The slurry of undissolved chips in solution is further processed to recover most of the original solution constituents and dried wood pulp. In one such process, wood chips with a specific gravity of 0.64 containing 45 wt% water and 47 wt% (dry basis) cellulose are treated to produce 1400 tons/day of dry wood pulp containing 85 wt% cellulose. Estimate the feed rate of logs (logs/min), assuming that the logs have an average diameter of 8 inches and an average length of 7 feet.

3.34. A liquid mixture is prepared by combining N different liquids with densities $\rho_1, \rho_2, \ldots, \rho_N$. The volume of component i added to the mixture is V_i, and the mass fraction of this component in the mixture is x_i. The components are completely miscible.

The following two formulas provide estimates of the density of the liquid mixture, $\overline{\rho}$, if the volume of the mixture equals the sum of the pure-component volumes.[9] Only one of the formulas is correct, however.

$$(i) \quad \overline{\rho} = \sum_{i=1}^{N} x_i \rho_i \qquad (ii) \quad \frac{1}{\overline{\rho}} = \sum_{i=1}^{N} \frac{x_i}{\rho_i}$$

Determine whether (*i*) or (*ii*) is the correct formula (show your proof), and then use the correct formula to estimate the density (g/cm^3) of a liquid mixture containing 60.0 wt% acetone, 25.0 wt% acetic acid, and 15.0 wt% carbon tetrachloride.

Equipment Encyclopedia
gas chromatography

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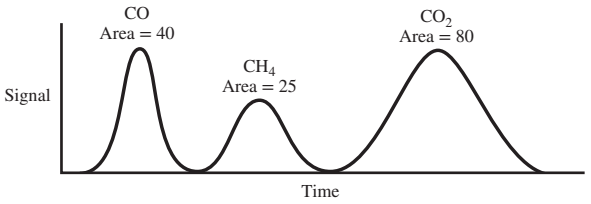
3.35. A gaseous mixture of CO, CO_2, CH_4, and N_2 is analyzed with a gas chromatograph (see Problem 3.36). The output appears on a computer monitor, as shown here.

[9] This is an approximation for most liquids, unlike the exact statement that the mass of the mixture is the sum of the component masses.



For each of the three species, the area under the peak is approximately proportional to the number of moles of the indicated substance in the sample. From other information, it is known that the molar ratio of methane (CH_4) to nitrogen is 0.200.

(a) What are the mole fractions of the four species in the gas?

(b) What is the average molecular weight of the gas?

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3.36. A *gas chromatograph* (GC) is a device used to separate, identify, and quantify components of gas mixtures. It consists of a column of solid particles that adsorb the gas components to different extents. A sample of a mixture is injected into a steadily flowing carrier gas and passed through the column, and a detector at the outlet measures a variable (such as electrical conductivity) proportional to the concentration of each species in the gas emerging from the column. The greater the extent to which a species is adsorbed on the solid particles, the more slowly it is released and so the longer it takes to emerge from the column.

The detector signal is often mapped as a series of peaks on a recorder, such as the plot in Problem 3.35. Each peak corresponds to a specific component, and the area under the peak is proportional to the amount of that component in the sample [$n_i(\text{mol}) = k_i A_i$, where A_i is the area of the peak corresponding to the ith species]. The proportionality constants (k_i) are determined in separate calibration experiments in which known amounts of the components are injected into the GC sample port and the corresponding peak areas are measured. Prepare a spreadsheet to calculate the composition of a mixture from a set of peak areas obtained from a chromatograph. The spreadsheet should appear as follows:

Sample	Species	MW	k	Peak Area	Mole Fraction	Mass Fraction
1	CH4	16.04	0.150	3.6	—	—
	C2H6	30.07	0.287	2.8	—	—
	C3H8	—	0.467	2.4	—	0.353
	C4H10	—	0.583	1.7	—	—
2	CH4	16.04	0.150	7.8	—	—
	C2H6	—	—	2.4	—	—
⋮	⋮	⋮	⋮	⋮	⋮	⋮

You may use additional columns to store intermediate quantities in the calculation of the mass and mole fractions. In the actual spreadsheet, replace the dashes (—) with numbers.

Test your program on data for five mixtures of methane, ethane, propane, and *n*-butane. The *k* values for these species are those given in the above table, and the measured peaks are given below. For example, the area of the methane peak for the first mixture is 3.6, the area of the ethane peak for the same mixture is 2.8, and so on.

Sample	A_1	A_2	A_3	A_4
1	3.6	2.8	2.4	1.7
2	7.8	2.4	5.6	0.4
3	3.4	4.5	2.6	0.8
4	4.8	2.5	1.3	0.2
5	6.4	7.9	4.8	2.3

ENVIRONMENTAL

3.37. Concerns regarding emissions of CO_2 into the atmosphere have increased substantially since an article on combustion of forests and grasslands was published in 1990.[10] Data in the table below show global emissions of carbon-containing compounds released to the atmosphere from biomass combustion and from all combustion sources in 1990.

Compound	Metric Tons C, All Sources	Metric Tons C, % from Biomass
CO_2	8700	40
CO	1100	26
CH_4	380	10

The numbers in the middle column reflect annual quantities of carbon released to the atmosphere in the indicated compounds; for example, 8700 metric tons of carbon (8.7×10^6 kg C) was released in carbon dioxide.

(a) Determine the combined annual release (in metric tons) of all three species resulting from biomass combustion and the average molecular weight of the combined gases.

(b) Find a reference on atmospheric pollution and list the environmental hazards associated with CO and CO_2 release. What other elements might be released in environmentally hazardous forms if biomass is burned?

(c) From recent data, estimate the percentage change in total CO_2 emissions since 1990.

3.38. A 5.00-wt% aqueous sulfuric acid solution ($\rho = 1.03$ g/ml) flows through a 45-m long pipe with a 6.0 cm diameter at a rate of 82 L/min.

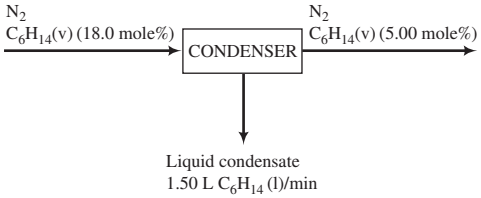
(a) What is the molarity of sulfuric acid in the solution?

(b) How long (in seconds) would it take to fill a 55-gallon drum, and how much sulfuric acid (lb_m) would the drum contain? (You should arrive at your answers with two dimensional equations.)

(c) The mean velocity of a fluid in a pipe equals the volumetric flow rate divided by the cross-sectional area normal to the direction of flow. Use this information to estimate how long (in seconds) it takes the solution to flow from the pipe inlet to the outlet.

3.39. You notice that the water in your friend's swimming pool is cloudy and that the pool walls are discolored at the water line. A quick analysis reveals that the pH of the water is 8.0 when it should be 7.2. The pool is 5 m wide, 12 m long, and has an average depth of 2 m. What volume (mL) of 5.00 wt% sulfuric acid (SG = 1.03) should be added to return the pool to the desired pH?

3.40. A gas stream contains 18.0 mole% hexane and the remainder nitrogen. The stream flows to a condenser, where its temperature is reduced and some of the hexane is liquefied. The hexane mole fraction in the gas stream leaving the condenser is 0.0500. Liquid hexane condensate is recovered at a rate of 1.50 L/min.



(a) What is the flow rate of the gas stream leaving the condenser in mol/min? (*Hint:* First calculate the molar flow rate of the condensate and note that the rates at which C_6H_{14} and N_2 enter the unit must equal the total rates at which they leave in the two exit streams.)

(b) What percentage of the hexane entering the condenser is recovered as a liquid?

(c) Suggest a change you could make in the process operating conditions to increase the percentage recovery of hexane. What would be the downside?

3.41. The little-known rare earth element nauseum (atomic weight = 172) has the interesting property of being completely insoluble in everything but 25-year-old single-malt Scotch. This curious fact was discovered in

[10] *Chemical & Engineering News*, **68**, 4 (March 26, 1990).

the laboratory of Professor Ludwig von Schlimazel, the eminent German chemist whose invention of the bathtub ring won him the Nobel Prize. Having unsuccessfully tried to dissolve nauseum in 7642 different solvents over a 10-year period, Schlimazel finally came to the 30 mL of The Macsporran that was the only remaining liquid in his laboratory. Always willing to suffer personal loss in the name of science, Schlimazel calculated the amount of nauseum needed to make up a 0.03 molar solution, put the Macsporran bottle on the desk of his faithful technician Edgar P. Settera, weighed out the calculated amount of nauseum and put it next to the bottle, and then wrote the message that has become part of history:

"Ed Settera. Add nauseum!"

How many grams of nauseum did he weigh out? (Neglect the change in liquid volume resulting from the nauseum addition.)

ENVIRONMENTAL

3.42. The *half-life* ($t_{1/2}$) of a radioactive species is the time it takes for half of the species to emit radiation and decay (turn into a different species). If a quantity N_0 of the species is present at time $t = 0$, the amount present at a later time t is given by the expression

$$N = N_0\left(\frac{1}{2}\right)^{t/t_{1/2}}$$

Each decay event involves the emission of radiation. A unit of the intensity of radioactivity is a *curie* (Ci), defined as 3.7×10^{10} decay events per second.

A 300,000-gallon tank has been storing aqueous radioactive waste since 1945. The waste contains the radioactive isotope cesium-137 (^{137}Cs), which has a half-life of 30.1 years and a specific radioactivity of 86.58 Ci/g. The isotope undergoes beta decay to radioactive barium-137, which in turn emits gamma rays and decays to stable (nonradioactive) barium with a half-life of 2.5 minutes. The concentration of ^{137}Cs in 2013 was 2.50×10^{-3} g/L.

(a) What fraction of the ^{137}Cs would have to decay for the level of cesium-related radioactivity of the contents to be 1.00×10^{-3} Ci/L? What total mass of cesium (kg) would that loss represent? In what year would that level be reached?

(b) What was the concentration of ^{137}Cs in the tank (g/L) when the waste was first stored?

(c) Explain why the radioactive cesium in the tank poses a significant environmental threat while the radioactive barium does not.

3.43. The reaction A → B is carried out in a laboratory reactor. According to a published article the concentration of A should vary with time as follows:

$$C_A = C_{A0}\exp(-kt)$$

where C_{A0} is the initial concentration of A in the reactor and k is a constant.

(a) If C_A and C_{A0} are in lb-moles/ft^3 and t is in minutes, what are the units of k?

(b) The following data are taken for $C_A(t)$:

t(min)	C_A(lb-mole/ft^3)
0.5	1.02
1.0	0.84
1.5	0.69
2.0	0.56
3.0	0.38
5.0	0.17
10.0	0.02

Verify the proposed rate law graphically (first determine what plot should yield a straight line), and calculate C_{A0} and k.

(c) Convert the formula with the calculated constants included to an expression for the molarity of A in the reaction mixture in terms of t (seconds). Calculate the molarity at $t = 265$ s.

3.44. Perform the following pressure conversions, assuming when necessary that atmospheric pressure is 1 atm. Unless otherwise stated, the given pressures are absolute.

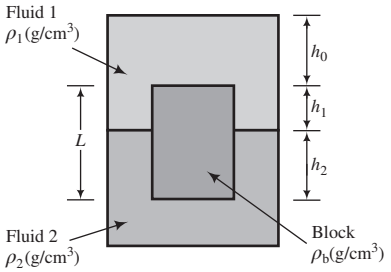
(a) 2600 mm Hg to psi
(b) 275 ft H_2O to kPa
(c) 3.00 atm to N/cm^2
(d) 280 cm Hg to $dyne/m^2$
(e) 20 cm Hg of vacuum to atm (absolute)
(f) 25.0 psig to mm Hg (gauge)
(g) 25.0 psig to mm Hg (absolute)
(h) 325 mm Hg to mm Hg gauge
(i) 45.0 psi to cm of carbon tetrachloride

3.45. A storage tank containing oil (SG = 0.92) is 10.0 meters high and 16.0 meters in diameter. The tank is closed, but the amount of oil it contains can be determined from the gauge pressure at the bottom.

(a) A pressure gauge connected to the bottom of the tank was calibrated with the top of the tank open to the atmosphere. The calibration curve is a plot of height of oil, h(m), versus P_{gauge}(kPa). Sketch the expected shape of this plot. What height of oil would lead to a gauge reading of 68 kPa? What would be the mass (kg) of oil in the tank corresponding to this height?

(b) An operator observes that the pressure gauge reading is 68 kPa and notes the corresponding liquid height from the calibration curve. What he did not know was that the absolute pressure above the liquid surface in the tank was 115 kPa when he read the gauge. What is the actual height of the oil? (Assume atmospheric pressure is 101 kPa.)

3.46. A rectangular block of height L and horizontal cross-sectional area A floats at the interface between two immiscible liquids, as shown below.



(a) Derive a formula for the block density, ρ_b, in terms of the fluid densities ρ_1 and ρ_2, the heights h_0, h_1, and h_2, and the cross-sectional area A. (It is not necessary that all of these variables appear in the final result.)

(b) Force balances on the block can be calculated in two ways: (i) in terms of the weight of the block and the hydrostatic forces on the upper and lower block surfaces; and (ii) in terms of the weight of the block and the buoyant force on the block as expressed by Archimedes' principle. Prove that these two approaches are equivalent.

SAFETY

*3.47. In the movie, *Willy Wonka and the Chocolate Factory*, Augustus Gloop leans over the chocolate river to get a drink and falls in. He is sucked through the pipe leading to the fudge room where he is saved by the Oompa Loompa workers. Unfortunately, real-life accidents do not always have such happy endings, even when they involve chocolate. In a tragic 2009 accident, a worker suffered fatal injuries after falling into a cylindrical mixing vat that had an 8-ft diameter and was 8 ft tall. At the time of the accident, the vat was full of molten chocolate.

(a) What was the total weight (lb_f) of chocolate in the vat? The specific gravity of chocolate is approximately 1.24.

(b) Determine the pressure (psig) at the bottom of the tank.

(c) Speculate on whether a person would float or sink in the vat and list two possible causes of the worker's death.

* Adapted from a problem contributed by Paul Blowers of the University of Arizona.

3.48. The viewing window in a diving suit has an area of roughly 65 cm^2.

(a) If an attempt were made to maintain the pressure on the inside of the suit at 1 atm, what force (N and lb_f) would the window have to withstand if the diver descended to a depth of 150 m. Take the specific gravity of the water to be 1.05.

(b) Repeat the calculation of Part (a) for the deepest Guiness-verified SCUBA dive.

SAFETY

3.49. The great Boston molasses flood occurred on January 15, 1919. In it, 2.3 million gallons of crude molasses flowed from a 30-foot-high storage tank that ruptured, killing 21 people and injuring 150. The estimated specific gravity of crude molasses is 1.4. What were the mass of molasses in the tank in lb_m and the pressure at the bottom of the tank in lb_f/in^2? Give at least two possible causes of the tragedy.

SAFETY

3.50. The chemical reactor shown below has a cover that is held in place by a series of bolts. The cover is made of stainless steel (SG = 8.0), is 3 inches thick, has a diameter of 24 inches, and covers and seals an opening 20 inches in diameter. During *turnaround*, when the reactor is taken out of service for cleaning and repair, the cover was removed by an operator who thought the reactor had been depressurized using a standard venting procedure. However, the pressure gauge had been damaged in an earlier process upset (the reactor pressure had exceeded the upper limit of the gauge), and instead of being depressurized completely, the vessel was under a gauge pressure of 30 psi.

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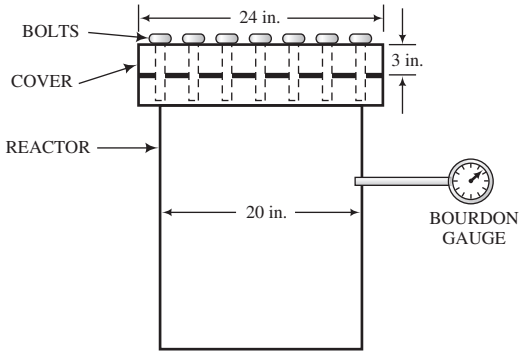

(a) What force (lb_f) were the bolts exerting on the cover before they were removed? (*Hint:* Don't forget that a pressure is exerted on the top of the cover by the atmosphere.) What happened when the last bolt was removed by the operator? Justify your prediction by estimating the initial acceleration of the cover upon removal of the last bolt.

(b) Propose an alteration in the turnaround procedure to prevent recurrence of an incident of this kind.

3.51. In the movie *The Drowning Pool*, private detective Lew Harper (played by Paul Newman) is trapped by the bad guy in a room containing a swimming pool. The room may be considered rectangular, 5 meters wide by 15 meters long, with an open skylight window 10 meters above the floor. There is a single entry to the room, reached by a stairway: a locked 2-m high by 1-m wide door, whose bottom is 1 meter above the floor. Harper knows that his enemy will return in eight hours and decides he can escape by filling the room with water and floating up to the skylight. He plugs the drain with his clothes, turns on the water valves, and puts his plan into action.

Assume that water enters the room at about 10 times the rate at which it enters an average bathtub and that the door can withstand a maximum force of 4500 newtons. Estimate (i) whether the door will break before the room fills and (ii) whether Harper has time to escape if the door holds. State any assumptions you make.

3.52. A housing development is served by a water tower with the water level maintained between 20 and 30 meters above the ground, depending on demand and water availability. Responding to a resident's complaint about the low flow rate of water at his kitchen sink, a representative of the developer measured the water pressure at the tap above the kitchen sink and at the junction between the water main (a pipe connected to the bottom of the water tower) and the feed pipe to the house. The junction is 5 m below the level of the kitchen tap. All water valves in the house were turned off.

(a) If the water level in the tower was 25 m above tap level, what should be the gauge pressures (kPa) at the tap and junction?

(b) Suppose the pressure measurement at the tap was lower than your estimate in Part (a), but the measurement at the junction was as predicted. State a possible explanation.

(c) If pressure measurements corresponded to the predictions in Part (a), what else could be responsible for the low water flow to the sink?

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manometer
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3.53. Two mercury manometers, one open-end and the other sealed-end, are attached to an air duct. The reading on the open-end manometer is 25 mm and that on the sealed-end manometer is 800 mm. Determine the absolute pressure in the duct, the gauge pressure in the duct, and the atmospheric pressure, all in mm Hg.

3.54. A student goes to the laboratory supply room and obtains five feet of clear plastic tubing with an outer diameter of 1/2 inch and a wall thickness of 1/16 inch. She bends the tube into a U shape with the open ends pointing up and uses a funnel to pour 75 mL of water into the tube. By blowing air into one end of the tube, she generates a 6-inch difference in the water levels on each side.

(a) What was the pressure (atm) she exerted with her lungs on the water in the tube? State all assumptions you make.

(b) If the fluid had been ethanol instead of water, what would the difference in the liquid levels have been?

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manometer
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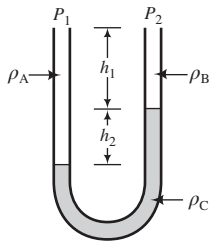
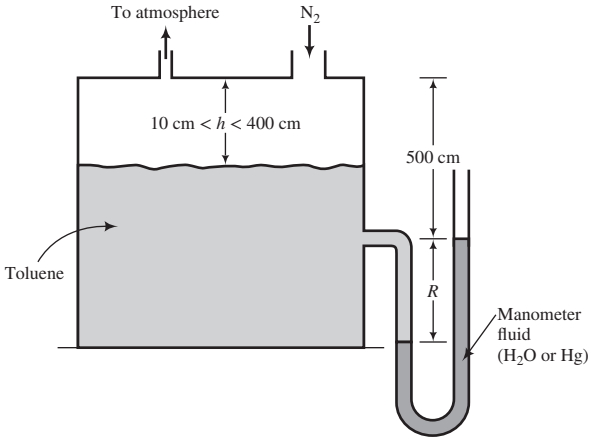
3.55. Three different liquids are used in the manometer shown here.



(a) Derive an expression for $P_1 - P_2$ in terms of ρ_A, ρ_B, ρ_C, h_1, and h_2.

(b) Suppose fluid A is methanol, B is water, and C is a manometer fluid with a specific gravity of 1.37; pressure $P_2 = 121.0$ kPa; $h_1 = 30.0$ cm; and $h_2 = 24.0$ cm. Calculate P_1 (kPa).

3.56. The level of toluene (a flammable hydrocarbon) in a storage tank may fluctuate between 10 and 400 cm from the top of the tank. Since it is impossible to see inside the tank, an open-end manometer with water or mercury as the manometer fluid is to be used to determine the toluene level. One leg of the manometer is attached to the tank 500 cm from the top. A nitrogen blanket at atmospheric pressure is maintained over the tank contents.



(a) When the toluene level in the tank is 150 cm below the top ($h = 150$ cm), the manometer fluid level in the open arm is at the height of the point where the manometer connects to the tank. What manometer reading, R (cm), would be observed if the manometer fluid is (i) mercury, (ii) water? Which manometer fluid would you use, and why?

(b) Briefly describe how the system would work if the manometer were simply filled with toluene. Give several advantages of using the fluid you chose in Part (a) over using toluene.

(c) What is the purpose of the nitrogen blanket?

3.57. The liquid level in a tank is determined by measuring the pressure at the bottom of the tank. A calibration curve is prepared by filling the tank to several known levels, reading the bottom pressure from a Bourdon gauge, and drawing a plot of level (m) vs. pressure (Pa).

(a) Would you expect the calibration curve to be a straight line? Explain your answer.

(b) The calibration experiment was done using a liquid with a specific gravity of 0.900, but the tank is used to store a liquid with specific gravity of 0.800. Will the liquid level determined from the calibration curve be too high, too low, or correct? Explain.

(c) If the actual liquid level is 8.0 meters, what value will be read from the calibration curve? If the tank has a height of 10.0 m, what value will be read from the curve when the tank overflows?

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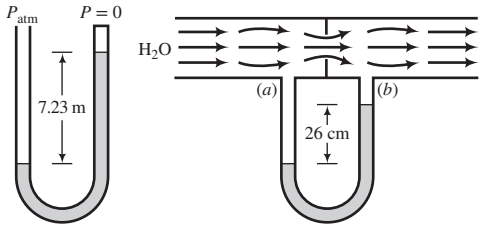
3.58. A fluid of unknown density is used in two manometers—one sealed-end, the other across an orifice in a water pipeline. The readings shown here are obtained on a day when barometric pressure is 756 mm Hg.



What is the pressure drop (mm Hg) from point (*a*) to point (*b*)*?*

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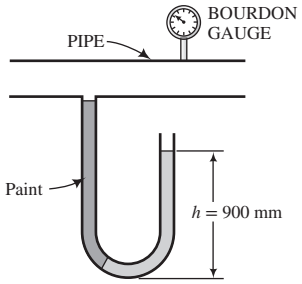
3.59. An open-end mercury manometer is connected to a low-pressure pipeline that supplies a gas to a laboratory. Because paint was spilled on the arm connected to the line during a laboratory renovation, it is impossible to see the level of the manometer fluid in this arm. During a period when the gas supply is connected to the line but there is no gas flow, a Bourdon gauge connected to the line downstream from the manometer gives a reading of 7.5 psig. The level of mercury in the open arm is 900 mm above the lowest part of the manometer.



(a) When the gas is not flowing, the pressure is the same everywhere in the pipe. How high above the bottom of the manometer would the mercury be in the arm connected to the pipe?

(b) When gas is flowing, the mercury level in the visible arm drops by 25 mm. What is the gas pressure (psig) at this moment?

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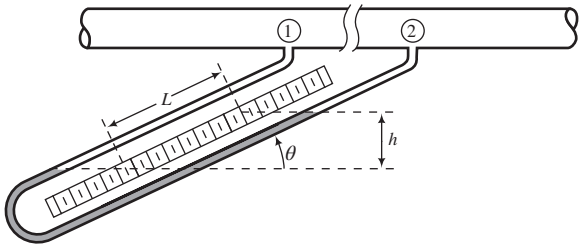
3.60. An **inclined manometer** is a useful device for measuring small pressure differences.



The formula given in Section 3.4 for the pressure difference in terms of the liquid-level difference h remains valid, but while h would be small and difficult to read for a small pressure drop if the manometer were vertical, L can be made quite large for the same pressure drop by making the angle of the inclination, θ, small.

(a) Derive a formula for h in terms of L and θ.

(b) Suppose the manometer fluid is water, the process fluid is a gas, the inclination of the manometer is $\theta = 15°$, and a reading $L = 8.7$ cm is obtained. What is the pressure difference between points ① and ②?

(c) The formula you derived in Part (a) would not work if the process fluid were a liquid instead of a gas. Give one definite reason and another possible reason.

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3.61. An open-end mercury manometer is to be used to measure the pressure in an apparatus containing a vapor that reacts with mercury. A 10-cm layer of silicon oil (SG = 0.92) is placed on top of the mercury in the arm attached to the apparatus. Atmospheric pressure is 765 mm Hg.

(a) If the level of mercury in the open end is 365 mm below the mercury level in the other arm, what is the pressure (mm Hg) in the apparatus?

(b) When the instrumentation specialist was deciding on a liquid to put in the manometer, she listed several properties the fluid should have and eventually selected silicon oil. What might the listed properties have been?

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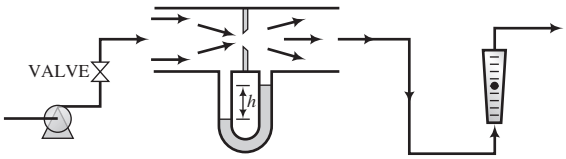
3.62. An orifice meter (see Figure 3.2-1) is to be calibrated for the measurement of the flow rate of a stream of liquid acetone. The differential manometer fluid has a specific gravity of 1.10.



The calibration is accomplished by connecting the orifice meter in series with a rotameter that has previously been calibrated for acetone, adjusting a valve to set the flow rate, and recording the flow rate (determined from the rotameter reading and the rotameter calibration curve) and the differential manometer reading, h. The procedure is repeated for several valve settings to generate an orifice meter calibration curve of flow rate versus h. The following data are taken.

Manometer Reading h(mm)	Flow Rate $\dot{V}$(mL/s)
0	0
5	62
10	87
15	107
20	123
25	138
30	151

(a) For each of the given readings, calculate the pressure drop across the orifice, ΔP(mm Hg).

(b) The flow rate through an orifice should be related to the pressure drop across the orifice by the formula

$$\dot{V} = K(\Delta P)^n$$

Verify graphically that the given orifice calibration data are correlated by this relationship, and determine the values of K and n that best fit the data.

(c) Suppose the orifice meter is mounted in a process line containing acetone and a reading $h = 23$ mm is obtained. Determine the volumetric, mass, and molar flow rates of acetone in the line.

3.63. Convert the temperatures in Parts (a) and (b) and temperature intervals in Parts (c) and (d):

(a) $T = 85$°F to °R, °C, K

(b) $T = -10$°C to K, °F, °R

(c) $\Delta T = 85°C$ to K, °F, °R
(d) $\Delta T = 150°R$ to °F, °C, K

3.64. A temperature scale that never quite caught on was formulated by the Austrian chemist Johann Sebastian Farblunget. The reference points on this scale were 0°FB, the temperature below which Farblunget's postnasal drip began to bother him, and 1000°FB, the boiling point of beer. Conversions between °C and °FB can be accomplished with the expression

$$T(°C) = 0.0940T(°FB) + 4.00$$

Louis Louis, Farblunget's French nephew, attempted to follow in his uncle's footsteps by formulating his own temperature scale. He defined the degree Louie using as reference conditions the optimum serving temperature of marinated snails (100°L corresponding to 15°C) and the temperature at which the elastic in his briefs began to relax (1000°L corresponding to 43°C).
(a) At what temperature in °F does beer boil?
(b) What is the temperature interval of 10.0 Farblunget degrees equivalent to in °C, K, °F, and °R?
(c) Derive equations for T(°C) in terms of T(°L) (see Example 3.5-1) and T(°L) in terms of T(°FB).
(d) What is the boiling point of ethane at 1 atm (Table B.1) in °F, K, °R, °FB, and °L?
(e) What is a temperature interval of 50.0 Louie degrees equivalent to in Celsius degrees, Kelvin degrees, Fahrenheit degrees, Rankine degrees, and Farblunget degrees?

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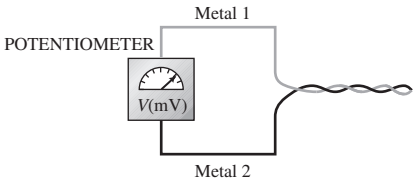
3.65. A **thermocouple** is a temperature-measurement device that consists of two dissimilar metal wires joined at one end. An oversimplified diagram follows.



A voltage generated at the metal junction is read on a potentiometer or millivoltmeter. When certain metals are used, the voltage varies linearly with the temperature at the junction of the two metals:

$$V(\text{mV}) = aT(°C) + b$$

An iron-constantan thermocouple (constantan is an alloy of copper and nickel) is calibrated by inserting its junction in boiling water and measuring a voltage $V = 5.27$ mV, and then inserting the junction in silver chloride at its melting point and measuring $V = 24.88$ mV.
(a) Derive the linear equation for V(mV) in terms of T(°C). Then convert it to an equation for T in terms of V.
(b) If the thermocouple is mounted in a chemical reactor and the voltage is observed to go from 10.0 mV to 13.6 mV in 20 s, what is the average value of the rate of change of temperature, dT/dt, during the measurement period?
(c) State the principal benefits and disadvantages of thermocouples.

3.66. A thermostat control with dial markings from 0 to 100 is used to regulate the temperature of an oil bath. A calibration plot on logarithmic coordinates of the temperature, T(°F), versus the dial setting, R, is a straight line that passes through the points ($R_1 = 20.0$, $T_1 = 110.0$°F) and ($R_2 = 40.0$, $T_2 = 250.0$°F).
(a) Derive an equation for T(°F) in terms of R.
(b) Estimate the thermostat setting needed to obtain a temperature of 320°F.
(c) Suppose you set the thermostat to the value of R calculated in Part (b), and the reading of a thermocouple mounted in the bath equilibrates at 295°F instead of 320°F. Suggest several possible explanations.

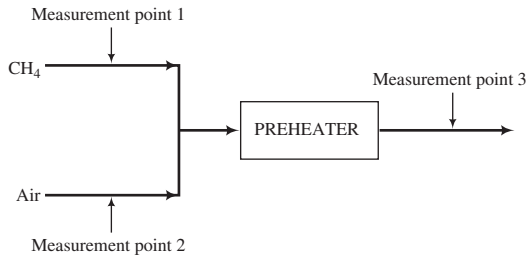
3.67. As will be discussed in detail in Chapter 5, the **ideal-gas equation of state** relates absolute pressure, P(atm); gas volume, V(liters); number of moles of gas, n(mol); and absolute temperature, T(K):

$$PV = 0.08206nT$$

(a) Convert the equation to one relating P(psig), $V(\text{ft}^3)$, n(lb-mole), and T(°F).
(b) A 30.0 mole% CO and 70.0 mole% N_2 gas mixture is stored in a cylinder with a volume of 3.5 ft^3 at a temperature of 85°F. The reading on a Bourdon gauge attached to the cylinder is 500 psi. Calculate the total amount of gas (lb-mole) and the mass of CO (lb_m) in the tank.

(c) Approximately to what temperature (°F) would the cylinder have to be heated to increase the gas pressure to 3000 psig, the rated safety limit of the cylinder? (The estimate would only be approximate because the ideal gas equation of state would not be accurate at pressures this high.)

3.68. Streams of methane and air (79 mole% N_2, the balance O_2) are combined at the inlet of a combustion furnace preheater. The pressures of each stream are measured with open-end mercury manometers, the temperatures are measured with resistance thermometers, and the volumetric flow rates are measured with orifice meters.



Data:
Flowmeter 1: $V_1 = 947\ \text{m}^3/\text{h}$
Flowmeter 2: $V_2 = 195\ \text{m}^3/\text{min}$
Manometer 1: $h_1 = 232\ \text{mm}$
Manometer 2: $h_2 = 156\ \text{mm}$
Manometer 3: $h_3 = 74\ \text{mm}$
Resistance thermometer 1: $r_1 = 26.159$ ohms
Resistance thermometer 2: $r_2 = 26.157$ ohms
Resistance thermometer 3: $r_3 = 44.789$ ohms
Atmospheric pressure: A sealed-end mercury manometer reads $h = 29.76$ inches

The resistance thermometers were calibrated by measuring their resistances at the freezing and boiling points of water, with the following results:

$T = 0°\text{C}$: $r = 23.624$ ohms
$T = 100°\text{C}$: $r = 33.028$ ohms

A straight-line relationship between T and r may be assumed.

The relationship between the total molar flow rate of a gas and its volumetric flow rate is, to a good approximation, given by a form of the ideal gas equation of state:

$$\dot{n}\left(\frac{\text{kmol}}{\text{s}}\right) = \frac{12.186P(\text{atm})\dot{V}(\text{m}^3/\text{s})}{T(\text{K})}$$

where P is the *absolute* pressure of the gas.

(a) Derive the resistance thermometer calibration formula for $T(°\text{C})$ in terms of $r(\text{ohm})$.
(b) Convert the given gas law expression to an expression for $\dot{n}(\text{kmol/min})$ in terms of $P(\text{mm Hg})$, $T(°\text{C})$, and $\dot{V}(\text{m}^3/\text{min})$.
(c) Calculate the temperatures and pressures at points 1, 2, and 3.
(d) Calculate the molar flow rate of the combined gas stream.
(e) Calculate the reading of flowmeter 3 in m^3/min.
(f) Calculate the total mass flow rate and the mass fraction of the methane at point 3.

3.69. You are part of a team working on the development of a process in which a mineral species (labeled A for proprietary reasons) undergoes a reaction to form a new pigment to be used in house paints. In a series of experiments in a large well-mixed stirred tank reactor, you fill a tank with a known quantity of an inert liquid, bring the liquid up to a specified temperature, add a known quantity of A, and measure the concentration of A in the tank as a function of time. The reaction gives off heat as it progresses, but

cooling water circulating in a jacket around the reactor keeps the temperature of the reacting mixture constant. The following data are recorded.

	Concentration of A, C_A(mol A/L)			
t(min)	$T = 94$°C	$T = 110$°C	$T = 127$°C	$T = 142$°C
10	9.30×10^{-2}	5.19×10^{-2}	2.10×10^{-2}	9.87×10^{-3}
20	6.17×10^{-2}	2.35×10^{-2}	1.33×10^{-2}	5.55×10^{-3}
30	4.41×10^{-2}	1.91×10^{-2}	8.15×10^{-3}	3.97×10^{-3}
40	3.12×10^{-2}	1.45×10^{-2}	5.92×10^{-3}	2.45×10^{-3}
50	2.58×10^{-2}	1.01×10^{-2}	4.48×10^{-3}	2.27×10^{-3}
60	9.30×10^{-2}	9.50×10^{-3}	4.36×10^{-3}	1.83×10^{-3}

A research article indicates that concentration of A should vary with time according to the following expression:

$$C_{\mathrm{A}}(t) = \frac{1}{\dfrac{1}{C_{\mathrm{A0}}} + kt} \tag{1}$$

where C_{A0} (mol/L) is the initial concentration of A in the reactor [$C_{\mathrm{A}}(t = 0)$] and k is called the *reaction rate constant*. Despite being called a constant, k is a strong function of the absolute temperature in the reactor:

$$k(T) = k_0 \exp\left(-\frac{E_{\mathrm{a}}}{RT(\mathrm{K})}\right) \tag{2}$$

In this equation (known as the *Arrhenius equation* after the Swedish chemist who proposed it), k_0 is a constant, E_{a}(J/mol) is the reaction *activation energy*, and $R = 8.314$ J/(mol·K) is the *universal gas constant*. Your task will be to verify that the expressions for $C_{\mathrm{A}}(t)$ and $k(T)$ fit the data, and if they do, to determine the parameters C_{A0} and k at each temperature and then the constants k_0 and E_{a}.

(a) What are the units of k, k_0, and E_{a} if C_{A} is in mol/L and t is in min?

(b) Transform Equation 1 into an equation of the form $y = at + b$, so that if Equation 1 is valid, a plot of y vs. t would be a straight line. How would you determine C_{A0} and k from the slope and intercept of the line?

(c) Create an Excel spreadsheet with the structure shown as Rows 1–10 in the figure at the end of this problem statement, and fill in the data table in Columns A–I. Then create the four scatterplots shown in Rows 15–21. In the "Trendline" options of each plot, check the boxes for "Display equation on chart" and "Display R-squared value on chart" but not the one for "Set intercept." R^2 is the *coefficient of determination* (it has several other names as well), and provides a measure of how well a straight line fits a set of data: the closer it is to 1, the better the fit. What can you conclude about Equation 1 from the four plots?

(d) From the four trendline equations, calculate the values of k and C_{A0} for each of the four experimental temperatures and fill in Columns B–I in Rows 12 and 13 of the spreadsheet.

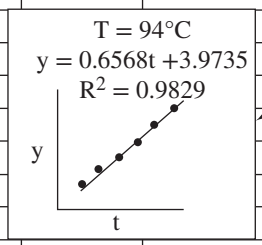
(e) Enough A was initially added to the tank to make the initial concentration $C_{\mathrm{A0}} = 0.25$ mol/L, yet you calculated four different values of C_{A0} in Part (d). How do you explain this result?

(f) Next, transform Equation 2 so that a straight-line plot ($y = ax + b$) would enable you to calculate the parameters k_0 and E_{a}. Below the four charts of Part (c), insert the information shown in Rows 23–27, Columns A–D, filling in the k values from the results of Part (d). Create the appropriate plot, show the trendline equation and R^2 value, use the equation to determine k_0 and E_{a}, and fill in Columns A and B in Rows 29–31. What can you conclude about the temperature dependence of the reaction rate constant?

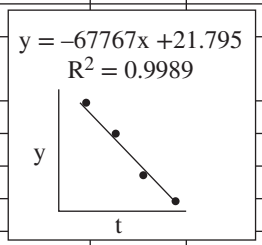
(g) In running this set of experiments, it is essential that the reactor temperature be carefully controlled and the reactor contents be very well mixed. Speculate on the probable reasons for both requirements.

(h) Finally, create and fill in Rows 1–3 and 12 of Columns J and K. Use Equation 2 to calculate k at 120°C and 160°C and insert them in Cells J13 and K13, respectively. Then fill in Rows 5–10 of Columns J and K using Equation 1 and assuming an initial concentration $C_{A0} = 0.25$ mol/L. In which of the two sets of estimated concentrations would you have more confidence? Explain your answer.

	A	B	C	D	E	F	G	H	I	J	K
1											
2										C_{A0} = 0.25	C_{A0} = 0.25
3		T(°C) = 94	T(°C) = 110	T(°C) = 127	T(°C) = 142	T(°C) = 120	T(°C) = 160				
4	t(min)	C_A	y	C_A	y	C_A	y	C_A	y	C_A	C_A
5	10	9.30E–02	10.75	...	...	...	...	...	...	3.03E–02	4.99E–03
6	20	6.17E–02	16.21	...	...	...	...	...	...	...	...
7	30	...	...	...	...	...	...	...	...	...	...
8	40	...	...	...	...	...	...	...	...	...	...
9	50	...	...	...	...	...	...	...	...	...	...
10	60	...	41.32	...	...	...	...	...	...	5.63E–03	...
11											
12		C_{A0} =	0.252	C_{A0} =	0.336	C_{A0} =	...	C_{A0} =	...	k	k
13		k =	0.657	k =	1.760	k =	...	k =	...	2.895	...
14											
15											
16											
17											
18											
19											
20											
21											
22											
23	T(°C)	k	1/8.314T(K)	ln k							
24	94	0.6568	3.276E–04	–0.4201							
25	110	...	...	...							
26	127	...	...	...							
27	142	...	...	...							
28											
29	ln k_0 =	21.795									
30	k_0 =	...									
31	E_a =	6.777E04									



+ similar plots for 110°C, 127°C, & 142°C



PART 2

Material Balances

CHAPTER 4

Fundamentals of Material Balances

Certain restrictions imposed by nature must be taken into account when designing a new process or analyzing an existing one. You cannot, for example, specify an input to a reactor of 1000 g of lead and an output of 2000 g of lead or gold or anything else. Similarly, if you know that 1500 lb_m of sulfur is contained in the coal burned each day in a power plant boiler, you do not have to analyze the ash and stack gases to know that on average 1500 lb_m of sulfur per day leaves the furnace in one form or another.

The basis for both of these observations is the *law of conservation of mass*, which states that mass can neither be created nor destroyed. (We will not be concerned in this book with the almost infinitesimal conversions between mass and energy associated with chemical reactions nor with the conversion of mass into energy associated with nuclear reactions.) Statements based on the law of conservation of mass such as "total mass of input = total mass of output" or "$(lb_m \text{ sulfur/day})_{in} = (lb_m \text{ sulfur/day})_{out}$" are examples of **mass balances** or **material balances**. The design of a new process or analysis of an existing one is not complete until it is established that the inputs and outputs of the entire process and of each individual unit satisfy balance equations.

The next three chapters outline procedures for writing material balances on individual process units and multiple-unit processes. This chapter presents methods for organizing known information about process variables, setting up material balance equations, and solving these equations for unknown variables. In Chapters 5 and 6 we introduce various physical properties and laws that govern the behavior of process materials and indicate how these properties and laws are taken into account (as they must be) in formulating material balances.

4.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- Briefly and clearly explain in your own words the meaning of the following terms: (a) *batch, semibatch, continuous, transient*, and *steady-state* processes; (b) *recycle* (and its purposes); (c) *purge* (and its purpose); (d) *degrees of freedom*; (e) *fractional conversion* of a limiting reactant; (f) *percentage excess* of a reactant; (g) *yield* and *selectivity*; (h) *dry-basis composition* of a mixture containing water; and (i) *theoretical air* and *percent excess air* in a combustion reaction.
- Given a process description, (a) draw and fully label a flowchart; (b) choose a convenient basis of calculation; (c) for a multiple-unit process, identify the subsystems for which balances might be written; (d) perform the degree-of-freedom analysis for the overall system and each possible subsystem; (e) write the equations you would use to calculate specified process variables; and (f) perform the calculations. You should be able to do these computations for single-unit and multiple-unit processes and for processes involving recycle, bypass, or purge streams. If the system involves reactions, you should be able to use molecular species balances, atomic species balances, or extents of reaction for both the degree-of-freedom analysis and the process calculations.

- Given a combustion reactor and information about the fuel composition and feed rate, calculate the feed rate of air from a given percent excess or vice versa. Given additional information about the conversion of the fuel and the absence or presence of partially oxidized species such as CO in the product gas, calculate the flow rate and composition of the product gas.

4.1 PROCESS CLASSIFICATION

Chemical processes may be classified as **batch, continuous,** or **semibatch** and as either **steady-state** or **transient**. Before writing material balances for a process system, you must know into which of these categories the process falls.

1. ***Batch process.*** The feed is charged (fed) to a vessel at the beginning of the process and the vessel contents are removed sometime later. No mass crosses the system boundaries between the time the feed is charged and the time the product is removed. *Example:* Add reactants to a tank and remove the products and unconsumed reactants sometime later when the system has come to equilibrium. Neglect any reactions that occur during charging and discharging.

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distillation column

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2. ***Continuous process.*** The inputs and outputs flow continuously throughout the duration of the process. *Example:* Pump a mixture of liquids into a distillation column at a constant rate and steadily withdraw product streams from the top and bottom of the column.

3. ***Semibatch process.*** Any process that is neither batch nor continuous. *Examples:* Allow the contents of a pressurized gas container to escape to the atmosphere; slowly blend several liquids in a tank from which nothing is being withdrawn.

If the values of all the variables in a process (i.e., all temperatures, pressures, volumes, flow rates) do not change with time, except possibly for minor fluctuations about constant mean values, the process is said to be operating at **steady state**. If any of the process variables change with time, **transient** or **unsteady-state** operation is said to exist. By their nature, batch and semibatch processes are unsteady-state operations (why?), whereas continuous processes may be either steady-state or transient.

Batch processing is commonly used when relatively small quantities of a product are to be produced, while continuous processing generally is better suited to large production rates. Continuous processes are usually run as close to steady state as possible; unsteady-state (transient) conditions exist during the start-up of a process and following changes—intentional or otherwise—in process operation conditions.

Test Yourself

(Answers, p. 655)

Classify the following processes as batch, continuous, or semibatch, and transient or steady-state.

1. A balloon is filled with air at a steady rate of 2 g/min.
2. A bottle of milk is taken from the refrigerator and left on the kitchen table.
3. Water is boiled in an open flask.
4. Carbon monoxide and steam are fed into a tubular reactor at a steady rate and react to form carbon dioxide and hydrogen. Products and unused reactants are withdrawn at the other end. The reactor contains air when the process is started up. The temperature of the reactor is constant, and the composition and flow rate of the entering reactant stream are also independent of time. Classify the process (a) initially and (b) after a long period of time has elapsed.

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4.2 BALANCES

4.2a The General Balance Equation

Suppose methane is a component of both the input and output streams of a continuous process unit, and that in an effort to determine whether the unit is performing as designed, the mass flow rates of methane in both streams are measured and found to be different ($\dot{m}_{in} \neq \dot{m}_{out}$).[1]

There are several possible explanations for the observed difference between the measured flow rates:

1. Methane is being consumed as a reactant or generated as a product within the unit.

2. Methane is accumulating in the unit—possibly adsorbing on the walls or other surfaces in the vessel.

3. Methane is leaking from the unit.

4. The measurements are wrong.

If the measurements are correct and there are no leaks, the other possibilities—generation or consumption in a reaction and accumulation within the process unit—are all that can account for a difference between the input and output flow rates.

A **balance** on a conserved quantity (total mass, mass of a particular species, energy, momentum) in a system (a single process unit, a collection of units, or an entire process) may be written in the following general way:

input (enters through system boundaries)	+	*generation* (produced within system)	−	*output* (leaves through system boundaries)	−	*consumption* (consumed within system)	=	*accumulation* (buildup within system)

(4.2-1)

The meaning of each term of the equation is illustrated in the following example.

Example 4.2-1 The General Balance Equation

Each year 50,000 people move into a city, 75,000 people move out, 22,000 are born, and 19,000 die. Write a balance on the population of the city.

Solution Let P denote people:

$$\text{input} + \text{generation} - \text{output} - \text{consumption} = \text{accumulation}$$

$$50{,}000\frac{P}{\text{yr}} + 22{,}000\frac{P}{\text{yr}} - 75{,}000\frac{P}{\text{yr}} - 19{,}000\frac{P}{\text{yr}} = A\left(\frac{P}{\text{yr}}\right)$$

$$\Downarrow$$

$$A = -22{,}000\frac{P}{\text{yr}}$$

In other words, each year the city's population decreases by 22,000 people.

[1] We will generally use the symbol m to denote a mass, $\dot{m}$ a mass flow rate, n a number of moles, and $\dot{n}$ a molar flow rate.

Two types of balances may be written:

1. ***Differential balances*** indicate what is happening with a system at an instant in time. Each term of the balance equation is a **rate** (rate of input, rate of generation, etc.) and has units of the balanced quantity unit divided by a time unit (people/yr, g SO_2/s, barrels/day). This is the type of balance usually applied to a continuous process. (See Example 4.2-1.)
2. ***Integral balances*** describe what happens between two instants of time. Each term of the equation is an **amount** of the balanced quantity and has the corresponding unit (people, g SO_2, barrels). This type of balance is usually applied to a batch process, with the two instants of time being the moment after the input takes place and the moment before the product is withdrawn.

We are concerned in this text primarily with differential balances applied to continuous steady-state systems and integral balances applied to batch and semibatch systems between their initial and final states. In Chapter 10, we consider general balances on unsteady-state systems and show how integral and differential balances are related—in fact, how each can be derived from the other.

The following rules may be used to simplify the material balance:

- *If the balanced quantity is total mass*, *set generation* = 0 *and consumption* = 0. Except in nuclear reactions, mass can neither be created nor destroyed.
- *If the balanced substance is a nonreactive species (neither a reactant nor a product), set generation* = 0 *and consumption* = 0.
- *If a system is at steady state*, *set accumulation* = 0, *regardless of what is being balanced*. By definition, in a steady-state system nothing can change with time, including the amount of the balanced quantity.

4.2b Balances on Continuous Steady-State Processes

For continuous processes at steady-state, the accumulation term in the general balance equation, Equation 4.2-1, equals zero, and the equation simplifies to

$$\boxed{\text{input} + \text{generation} = \text{output} + \text{consumption}} \qquad \textbf{(4.2-2)}$$

If the balance is on a nonreactive species or on total mass, the generation and consumption terms equal zero and the equation reduces to *input* = *output*.

Example 4.2-2 Material Balances on a Continuous Distillation Process

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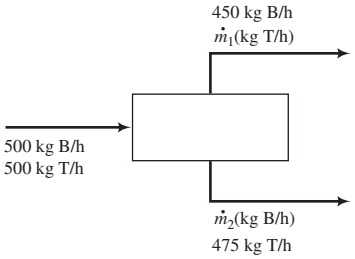
One thousand kilograms per hour of a mixture of benzene (B) and toluene (T) containing 50% benzene by mass is separated by distillation into two fractions. The mass flow rate of benzene in the top stream is 450 kg B/h and that of toluene in the bottom stream is 475 kg T/h. The operation is at steady state. Write balances on benzene and toluene to calculate the unknown component flow rates in the output streams.

Solution The process can be depicted schematically as follows:



Since the process is at steady state there can be no buildup of anything in the system, so the accumulation term equals zero in all material balances. In addition, since no chemical reactions occur, there can be no nonzero generation or consumption terms. For all balances, Equation 4.2-2 therefore takes the simple form *input* = *output*.

Benzene Balance:

$$500 \text{ kg B/h} = 450 \text{ kg B/h} + \dot{m}_2$$

$$\Downarrow$$

$$\boxed{\dot{m}_2 = 50 \text{ kg B/h}}$$

Toluene Balance:

$$500 \text{ kg T/h} = \dot{m}_1 + 475 \text{ kg T/h}$$

$$\Downarrow$$

$$\boxed{\dot{m}_1 = 25 \text{ kg T/h}}$$

Check the calculation.

Total Mass Balance:

$$1000 \text{ kg/h} = 450 + \dot{m}_1 + \dot{m}_2 + 475 \quad \text{(all kg/h)}$$

$$\Downarrow \dot{m}_1 = 25 \text{ kg/h}, \ \dot{m}_2 = 50 \text{ kg/h}$$

$$1000 \text{ kg/h} = 1000 \text{ kg/h} \quad \checkmark$$

4.2c Integral Balances on Batch Processes

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Ammonia is produced from nitrogen and hydrogen in a batch reactor. At time $t = 0$ there are n_0 mol of NH_3 in the reactor, and at a later time t_f the reaction terminates and the contents of the reactor, which include n_f mol of ammonia, are withdrawn. Between t_0 and t_f no ammonia enters or leaves through the reactor boundaries, and ammonia is not consumed in a reaction. The general balance equation (Equation 4.2-1) is simply *generation* = *accumulation*. Moreover, the quantity of ammonia that builds up (accumulates) in the reactor between t_0 and t_f is simply $n_f - n_0$, the final amount minus the initial amount.

The same reasoning may be applied to any substance participating in a batch process to obtain

$$\begin{aligned} \text{accumulation} &= \text{final output} - \text{initial input} \quad \text{(by definition)} \\ &= \text{generation} - \text{consumption} \quad \text{(from Equation 4.2-1)} \end{aligned}$$

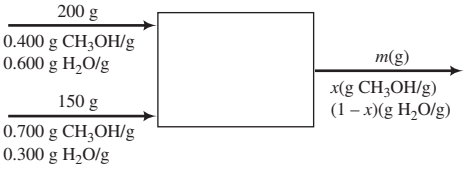
Equating these two expressions for the accumulation yields

$$\boxed{\text{initial input} + \text{generation} = \text{final output} + \text{consumption}} \tag{4.2-3}$$

This equation is identical to Equation 4.2-2 for continuous steady-state processes, except that in this case the input and output terms denote the initial and final amounts of the balanced substance rather than flow rates of the balanced substance in continuous feed and product streams. The words "initial" and "final" may be left out for brevity, as long as you don't lose sight of what "input" and "output" mean in the context of batch processes.

Example 4.2-3 Balances on a Batch Mixing Process

Two methanol–water mixtures are contained in separate flasks. The first mixture contains 40.0 wt% methanol, and the second contains 70.0 wt% methanol. If 200 g of the first mixture is combined with 150 g of the second, what are the mass and composition of the product?



Solution Observe that the input and output "streams" shown on the chart denote the initial and final states for this batch process. Since no reactions are involved, the generation and consumption terms of Equation 4.2-3 may be omitted so that all balances have the simple form *"input = output."*

Total Mass Balance:

$$200\text{ g} + 150\text{ g} = m$$

$$\Downarrow$$

$$\boxed{m = 350\text{ g}}$$

Methanol Balance:

$$\frac{200\text{ g}}{}\left|\frac{0.400\text{ g CH}_3\text{OH}}{\text{g}}\right. + \frac{150\text{ g}}{}\left|\frac{0.700\text{ g CH}_3\text{OH}}{\text{g}}\right. = \frac{m\text{(g)}}{}\left|\frac{x\text{(g CH}_3\text{OH)}}{\text{(g)}}\right.$$

$$\Downarrow m = 350\text{ g}$$

$$\boxed{x = 0.529\text{ g CH}_3\text{OH/g}}$$

We now know everything about the product, including the mass fraction of water. (What is it?). A water balance serves to check the solution.

Water Balance: (Verify that each additive term has the unit g H_2O.)

$$\text{input} = \text{output}$$

$$(200)(0.600) + (150)(0.300) = (350)(1 - 0.529) \quad (\textit{Verify!})$$

$$\Downarrow$$

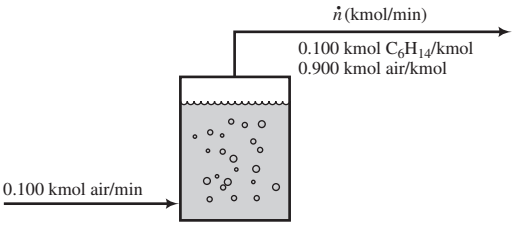
$$165\text{ g H}_2\text{O} = 165\text{ g H}_2\text{O} \quad \checkmark$$

4.2d Integral Balances on Semibatch Processes

Integral balances can also be written for semibatch and continuous processes. The procedure is to write a differential balance on the system and then to integrate it between two instants of time. (A general discussion of the procedure is presented in Chapter 10.) In most cases the required calculations are more complex than those we have seen so far; however, some problems of this type are relatively straightforward, such as the one in the next example.

Example 4.2-4 Integral Balance on a Semibatch Process

Air is bubbled through a tank of liquid hexane at a rate of 0.100 kmol/min. The gas stream leaving the tank contains 10.0 mole% hexane vapor. Air may be considered insoluble in liquid hexane. Use an integral balance to estimate the time required to vaporize 10.0 m^3 of the liquid.



Solution We begin with a differential balance on air. Since we assume that air neither dissolves in the liquid (*accumulation* = 0) nor reacts with hexane in the process unit (*generation* = *consumption* = 0), the balance reduces to *input* = *output*:

$$0.100\ \frac{\text{kmol air}}{\text{min}} = \frac{0.900\ \text{kmol air}}{\text{kmol}} \left| \frac{\dot{n}(\text{kmol})}{(\text{min})} \right. \Longrightarrow \dot{n} = 0.111\ \text{kmol/min}$$

We next write an integral hexane balance, proceeding from time $t = 0$ to $t = t_f(\text{min})$, the time we seek to calculate. The balance has the form *accumulation* = −*output* (*verify*). The accumulation term, which is the total change in the moles of liquid hexane in the system during time t_f, must be negative since hexane is being lost from the system. Since the total number of moles of hexane evaporated occupied a liquid volume of 10.0 cubic meters and (from Table B.1) the specific gravity of liquid hexane is 0.659, the accumulation term equals

$$\Delta n = \frac{-10.0\ \text{m}^3}{} \left| \frac{0.659\ \text{kg}}{\text{L}} \right| \frac{10^3\ \text{L}}{\text{m}^3} \left| \frac{1\ \text{kmol}}{86.2\ \text{kg}} \right. = -76.45\ \text{kmol}\ C_6H_{14}$$

The output term in the balance is the rate at which hexane is leaving the system [$0.100\dot{n}$ (kmol C_6H_{14}/min)] times the total process time, t_f(min). The balance (*accumulation* = −*output*) is therefore

$$-76.45\ \text{kmol}\ C_6H_{14} = -0.100\dot{n}t_f$$

$$\Downarrow \dot{n} = 0.111\ \text{kmol/min}$$

$$\boxed{t_f = 6880\ \text{min}}$$

Test Yourself

(Answers, p. 655)

Balances are to be written for each of the quantities listed below for a continuous process. For each case, state the conditions under which the balance equation takes the simple form "input = output." (The solutions to the first two parts are given as illustrations.)

1. Total mass. (Steady state)
2. Mass of species A. (Steady state, A is nonreactive)
3. Total moles.
4. Moles of species A.
5. Volume. (The answer provides an indication of why volumes should be converted to masses or moles before balances are written.)

CREATIVITY EXERCISE

Equipment Encyclopedia
rotameter, gas chromatograph
@
www.wiley.com/college/felder

Sulfur dioxide is contained in the feed and effluent streams of a chemical reactor, but it is neither a reactant nor a product. The volumetric flow rates of both streams (L/min) are measured with rotameters, and the concentrations of SO_2 in both streams (mol/L) are determined with a gas chromatograph. The molar flow rate of SO_2 in the reactor effluent (determined as the product of volumetric flow rate and concentration) is 20% lower than the molar flow rate of SO_2 in the feed. Think of as many possible explanations for the discrepancy as you can.

4.3 MATERIAL BALANCE CALCULATIONS

All material balance problems are variations on a single theme: given values of some input and output stream variables, derive and solve equations for other variables. Solving the equations is usually a matter of simple algebra, but deriving them from a description of a process and a

collection of process data may present considerable difficulties. It may not be obvious from the problem statement just what is known and what is required, for example, and it is not uncommon to find students (particularly on tests) scratching their heads and staring vacantly for an hour at a problem that should take ten minutes to solve.

In this section we outline a procedure for reducing a description of a process to a set of equations that can be solved for unknown process variables. The approach to be outlined is not the only way to attack material balance problems, but it always works and it keeps the time spent on vacant staring and head scratching to a minimum.

4.3a Flowcharts

Equipment Encyclopedia
packed-bed reactor, absorber stripper distillation column
@
www.wiley.com/college/felder

In this book and in years to come, you will be confronted with prose of the following type.

> *The catalytic dehydrogenation of propane is carried out in a continuous packed-bed reactor. One thousand pounds per hour of pure propane is preheated to a temperature of 670°C before it passes into the reactor. The reactor effluent gas, which includes propane, propylene, methane, and hydrogen, is cooled from 800°C to 110°C and fed to an absorption tower, where the propane and propylene are dissolved in oil. The oil then goes to a stripping tower in which it is heated, releasing the dissolved gases; these gases are recompressed and sent to a distillation column in which the propane and propylene are separated. The propane stream is recycled to join the feed to the reactor preheater. The product stream from the distillation column contains 98% propylene, and the recycle stream is 97% propane. The stripped oil is recycled to the absorption tower.*

When you are given process information like this and asked to determine something about the process, it is essential to organize the information in a way that is convenient for subsequent analysis and calculations. The best way to do this is to draw a **flowchart** of the process, using boxes or other symbols to represent process units (reactors, mixers, separation units, etc.) and lines with arrows to represent inputs and outputs.[2]

For example, suppose a gas containing N_2 and O_2 is combined with propane in a batch combustion chamber in which some (but not all) of the O_2 and C_3H_8 react to form CO_2 and H_2O, and the product is then cooled, condensing the water. The flowchart of this two-unit process might appear as shown in Figure 4.3-1.

Used properly, the flowchart of a process can help get material balance calculations started and keep them moving. To do so, the chart must be fully *labeled* when it is first drawn, with values of known process variables and symbols for unknown variables being written for each input and output stream. Thereafter, the chart functions as a scoreboard for the problem solution: as each unknown variable is determined its value is filled in, so that the chart provides a continuous record of where the solution stands and what must still be done.

Equipment Encyclopedia
condenser
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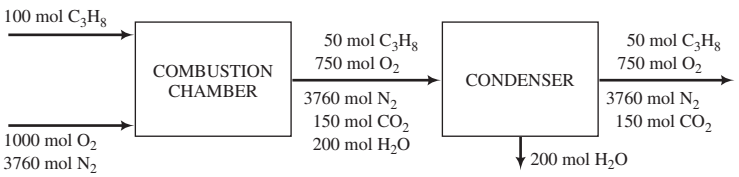


FIGURE 4.3-1 Flowchart of a combustion-condensation process.

[2] In professionally drawn flowcharts, special symbols are used to denote different types of process units such as distillation columns and heat exchangers. We will not generally use these symbols in this text, since our main purpose is to show you how to perform material and energy balance calculations. Simple boxes are perfectly adequate to represent process units on the flowcharts you draw for these calculations.

Several suggestions follow for labeling a flowchart to get the greatest possible benefit from it in material balance calculations.

1. ***Write the values and units of all known stream variables at the locations of the streams on the chart***. For example, a stream containing 21 mole% O_2 and 79% N_2 at 320°C and 1.4 atm flowing at a rate of 400 mol/h might be labeled

   400 mol/h
   $\longrightarrow$
   0.21 mol O_2/mol
   0.79 mol N_2/mol
   T = 320°C, P = 1.4 atm

   When you have done this for every stream on the chart, you have a summary of the known information about the process, each item being conveniently associated with the part of the process to which it relates.

   The stream variables of primary interest in material balance problems are those that indicate how much of each component is present in the stream (for a batch process) or the flow rate of each component (for a continuous process). This information can be given in two ways: as the total amount or flow rate of the stream and the fractions of each component, or directly as the amount or flow rate of each component.

   $\longrightarrow$ $\Longleftrightarrow$ 100 kmol/min $\longrightarrow$
   60 kmol N_2/min
   40 kmol O_2/min
   0.6 kmol N_2/kmol
   0.4 kmol O_2/kmol

   $\longrightarrow$ $\Longleftrightarrow$ 10 lb_m mixture $\longrightarrow$
   3.0 lb_m CH_4
   4.0 lb_m C_2H_4
   3.0 lb_m C_2H_6
   0.30 lb_m CH_4 /lb_m
   0.40 lb_m C_2H_4 /lb_m
   0.30 lb_m C_2H_6 /lb_m

   Once you have labeled a stream one way, it is easy to calculate the quantities that correspond to the alternative way of labeling. (Verify this for the two examples just given.)

2. ***Assign algebraic symbols to unknown stream variables*** [such as $\dot{m}$(kg solution/min),[3] x(lb_m N_2/lb_m), and n(kmol C_3H_8)] ***and write these variable names and their associated units on the chart***. For example, if you did not know the flow rate of the stream described in the first illustration of step 1, you might label the stream

   $\dot{n}$(mol/h)
   $\longrightarrow$
   0.21 mol O_2/mol
   0.79 mol N_2/mol
   T = 320°C, P = 1.4 atm

   while if the flow rate were known and the mole fractions were not, the stream might be labeled

   400 mol/h
   $\longrightarrow$
   y(mol O_2/mol)
   (1 – y)(mol N_2/mol)
   T = 320°C, P = 1.4 atm

[3] By convention we will show the units of labeled variables in parentheses and omit the parentheses for numerical values (e.g., 2 kg/s).

You may ultimately have to derive and solve an equation for each unknown that appears on the chart, so it is to your advantage to keep the number of labeled unknowns to a minimum. When labeling component mass or mole fractions of a stream, for example, variable names need only be assigned to all but one fraction, since the last one must be 1 minus the sum of the others. If you are given that the mass of stream 1 is half that of stream 2, label the masses of these streams m and $2m$ rather than m_1 and m_2; if you know that there is three times as much nitrogen (by mass) in a stream as oxygen, label the mass fractions of O_2 and N_2 y(g O_2/g) and $3y$(g N_2/g) rather than y_1 and y_2.

If a volumetric flow rate of a stream is given, it is generally useful to label the mass or molar flow rate of this stream or to calculate it directly, since balances are not normally written on volumetric qualities.

Note on Notation: Although any symbol may be used to represent any variable, having a consistent notation can aid understanding. In this text, we will generally use m for mass, $\dot{m}$ for mass flow rate, n for moles, $\dot{n}$ for molar flow rate, V for volume, and $\dot{V}$ for volumetric flow rate. Also, we will use x for component fractions (mass or mole) in liquid streams and y for fractions in gas streams.

Example 4.3-1 Flowchart of an Air Humidification and Oxygenation Process

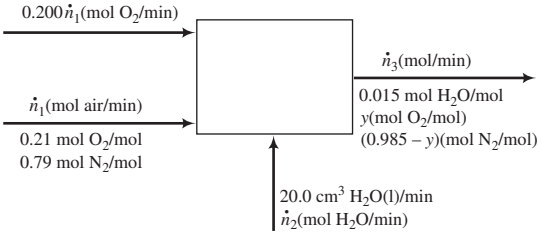
Equipment Encyclopedia
evaporators
www.wiley.com/college/felder
BIOENGINEERING

An experiment on the growth rate of certain organisms (e.g., yeasts, bacteria, or viruses) requires an environment of humid air enriched in oxygen. Three input streams are fed into an evaporation chamber to produce an output stream with the desired composition.

A: Liquid water, fed at a rate of 20.0 cm^3/min
B: Air (21 mole% O_2, the balance N_2)
C: Pure oxygen, with a molar flow rate one-fifth of the molar flow rate of stream B

The output gas is analyzed and is found to contain 1.5 mole% water. Draw and label a flowchart of the process, and calculate all unknown stream variables.

Solution



Notes on the Labeling:

1. Since the one known flow rate (20 cm^3 H_2O/min) is given on a per minute basis, it is most convenient to label all stream flow rates on this basis.
2. Once the variable name ($\dot{n}_1$) is chosen for the air flow rate, the given information about the ratio of the air and O_2 flow rates may be used to label the O_2 flow rate 0.200 $\dot{n}_1$.
3. The mole fractions of the components of any stream must add up to 1. Since the mole fraction of H_2O in the outlet stream is known to be 0.015, once the mole fraction of O_2 is labeled y, that of N_2 must be $1 - (y + 0.015) = (0.985 - y)$ (mol N_2/mol).

The quantity $\dot{n}_2$ may be calculated from the given volumetric flow rate and the density of liquid water:

$$\dot{n}_2 = \frac{20.0\ \text{cm}^3\ \text{H}_2\text{O}}{\text{min}} \left| \frac{1.00\ \text{g H}_2\text{O}}{\text{cm}^3} \right| \frac{1\ \text{mol}}{18.02\ \text{g}} \Longrightarrow \boxed{\dot{n}_2 = 1.11 \frac{\text{mol H}_2\text{O}}{\text{min}}}$$

The three remaining unknowns ($\dot{n}_1$, $\dot{n}_3$, and y) may be determined from balances, all of which have the simple form *input* = *output* for this nonreactive steady-state process. The balances are easily written by referring to the flowchart.

H_2O Balance:

$$\dot{n}_2\left(\frac{\text{mol } H_2O}{\text{min}}\right) = \frac{\dot{n}_3(\text{mol/min}) \mid 0.015 \text{ mol } H_2O}{\text{mol}}$$

$$\Downarrow \dot{n}_2 = 1.11 \text{ mol/min}$$

$$\boxed{\dot{n}_3 = 74 \frac{\text{mol}}{\text{min}}} \quad \text{(rounded down from 74.1)}$$

Total Mole Balance:

$$0.200\dot{n}_1 + \dot{n}_1 + \dot{n}_2 = \dot{n}_3$$

$$\Downarrow \dot{n}_2 = 1.11 \text{ mol/min}, \quad \dot{n}_3 = 74.1 \text{ mol/min}$$

$$\boxed{\dot{n}_1 = 60 \frac{\text{mol}}{\text{min}}} \quad \text{(rounded down from 60.8)}$$

N_2 Balance:

$$\frac{\dot{n}_1(\text{mol/min}) \mid 0.79 \text{ mol } N_2}{\text{mol}} = \frac{\dot{n}_3(\text{mol/min}) \mid (0.985 - y)(\text{mol } N_2)}{(\text{mol})}$$

$$\Downarrow$$

$$0.79\dot{n}_1 = \dot{n}_3(0.985 - y)$$

$$\Downarrow \dot{n}_1 = 60.8 \text{ mol/min}, \quad \dot{n}_3 = 74.1 \text{ mol/min}$$

$$\boxed{y = 0.34 \text{ mol } O_2/\text{mol}} \quad \text{(rounded down from 0.337)}$$

Test Yourself

(Answers, p. 655)

Several labeled process streams are shown below. Calculate the indicated quantities in terms of the labeled stream variables. The solution of the first problem is given as an illustration.

1. 100 lb-mole[4]

0.300 lb-mole CH_4/lb-mole
0.400 lb-mole C_2H_4/lb-mole
0.300 lb-mole C_2H_6/lb-mole

→ Calculate n (lb-mole CH_4)
m (lb_m C_2H_4)

Solution

$$n = (0.300)(100) \text{ lb-mole } CH_4 = 30.0 \text{ lb-mole } CH_4$$

$$m = \frac{(0.400)(100) \text{ lb-mole } C_2H_4 \mid 28.0 \text{ lb}_m \text{ } C_2H_4}{\text{lb-mole } C_2H_4} = 1120 \text{ lb}_m \text{ } C_2H_4$$

[4] Whenever we give a round quantity like 100 lb-moles, assume that it is a basis of calculation and exact, so that it has an infinite number of significant figures.

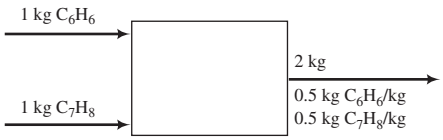
2. 250 kg/h
x(kg C_6H_6/kg)
$(1 - x)$(kg C_7H_8/kg)
→ Calculate $\dot{m}_T$ (kg C_7H_8/min) in terms of x

3. 75 ml CCl_4 (liquid) → Calculate n (mol CCl_4)

4. 50 kg H_2O/s
$\dot{m}_{dg}$ kg dry gas/s
0.25 kg CO/kg dry gas
0.75 kg CO_2/kg dry gas
→ Calculate $\dot{m}$ (kg total/s), $\dot{m}_{CO}$ (kg CO/s), and y (kg CO_2/kg total) in terms of $\dot{m}_{dg}$

4.3b Flowchart Scaling and Basis of Calculation

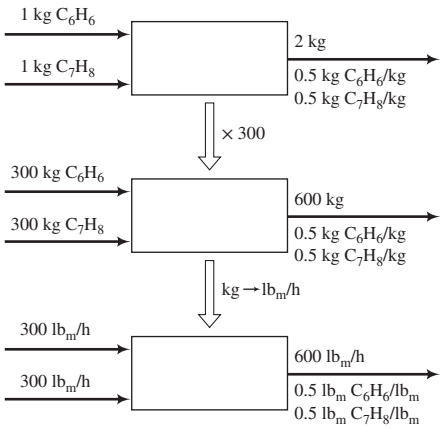
Suppose a kilogram of benzene is mixed with a kilogram of toluene. The output from this simple process is obviously 2 kg of a mixture that is 50% benzene by mass.



The process depicted by this flowchart is said to be **balanced**, since material balances on both system components—C_6H_6 and C_7H_8—are satisfied. [1 kg in = (2×0.5) kg out in both cases.]

Observe now that the masses *(but not the mass fractions)* of all streams could be multiplied by a common factor and the process would remain balanced; moreover, the stream masses could be changed to mass flow rates, and the mass units of all stream variables (including the mass fractions) could be changed from kg to g or lb_m or any other mass unit, and the process would still be balanced.

The procedure of changing the values of all stream amounts or flow rates by a proportional amount while leaving the stream compositions unchanged is referred to as **scaling** the flowchart—**scaling up** if the final stream quantities are larger than the original quantities, **scaling down** if they are smaller.



Suppose you have balanced a process and the amount or flow rate of one of the process streams is n_1. You can scale the flowchart to make the amount or flow rate of this stream n_2 by

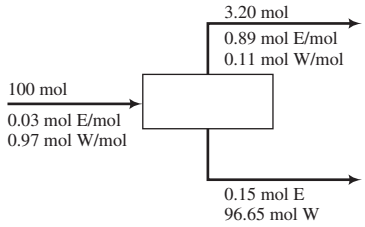
multiplying all stream amounts or flow rates by the ratio n_2/n_1. You cannot, however, scale masses or mass flow rates to molar quantities or vice versa by simple multiplication; conversions of this type must be carried out using the methods of Section 3.3b.

Example 4.3-2 Scale-up of a Separation Process Flowchart

BIOENGINEERING

Conversion of biomass into ethanol has been stimulated by the quest for a liquid fuel to replace gasoline. While technologies to convert corn and other starch crops into ethanol are widely used, great effort is being made to develop economical processes for utilizing lignocellulosics, such as wood and grasses, for that purpose.

In the conversion of biomass into ethanol, which can be used as a fuel or in the synthesis of other chemicals, the synthesized ethanol leaves a fermentation reactor in an aqueous solution containing approximately 3.0 mole% ethanol with (for purposes of this illustration) the remainder water. One hundred gram-moles of the mixture is fed to a distillation column in which it is separated into two streams: the *distillate*, which contains most of the ethanol (E) in the feed, and a reject stream containing mostly water (W). A flowchart of the process is shown here.



The same separation is desired for a process with a continuous production of 100.0 lb-moles/h of distillate. After confirming that the balances on ethanol and water close, scale the flowchart accordingly.

Solution We may easily confirm that 3.0 mol of ethanol and 97 mol of water enter and leave the system. The scale factor is

$$\frac{100.0 \text{ lb-moles/h}}{3.20 \text{ mol}} = 31.25 \frac{\text{lb-moles/h}}{\text{mol}}$$

The masses of all streams in the batch process are converted to flow rates as follows:

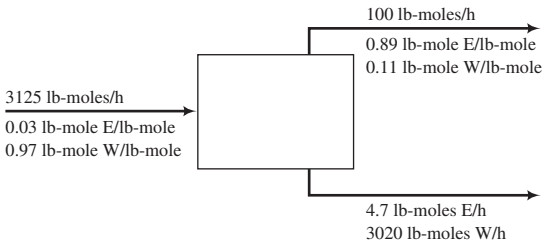
$$\textit{Feed}: \quad \left.\begin{array}{l|l} 100 \text{ mol} & 31.25 \text{ lb-moles/h} \\ & \text{mol} \end{array}\right| = 3125 \frac{\text{lb-moles}}{\text{h}}$$

$$\textit{Top product stream}: \quad (3.20)(31.25) = 100 \text{ lb-moles/h} \quad \text{(as specified)}$$

$$\textit{Bottom product stream}: \quad (0.15)(31.25) = 4.69 \text{ lb-moles E/h}$$

$$(96.65)(31.25) = 3020.3 \text{ lb-moles W/h}$$

The units of the mole fractions in the top product stream may be changed from mol/mol to lb-mole/lb-mole, but their values remain the same. The flowchart for the scaled-up process follows.



Since a balanced process can always be scaled, material balance calculations can be performed on the basis of any convenient set of stream amounts or flow rates and the results can afterward be scaled to any desired extent. A **basis of calculation** is an amount (mass or moles) or flow rate (mass or molar) of one stream or stream component in a process. Often the first step in

balancing a process is to choose a basis of calculation; all unknown variables are then determined to be consistent with this basis.

If a stream amount or flow rate is given in a problem statement, it is usually most convenient to use this quantity as a basis of calculation. If no stream amounts or flow rates are known, assume one, preferably that of a stream with a known composition. If mass fractions are known, choose a total mass or mass flow rate of that stream (e.g., 100 kg or 100 kg/h) as a basis; if mole fractions are known, choose a total number of moles or a molar flow rate.

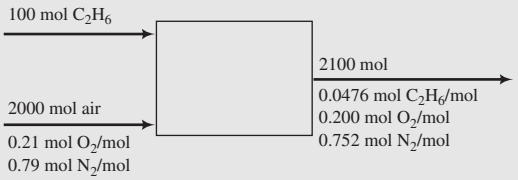
Test Yourself

(Answers, p. 655)

1. What is a balanced process? How do you scale a flowchart? What is a basis of calculation?

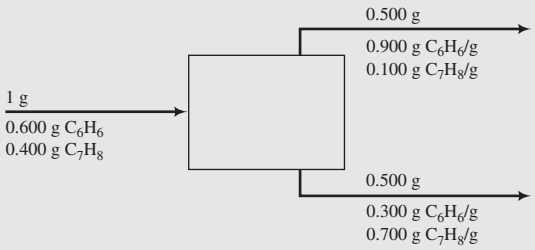
2. The processes shown below were balanced using the indicated bases of calculation. Scale as directed, and draw flowcharts for the scaled processes.

(a) Mix C_2H_6 with air. *Basis of calculation: 100 mol C_2H_6.*



Scale up to a feed of 1000 kmol C_2H_6/h.

(b) Distill a benzene–toluene mixture. *Basis: 1 g feed.*



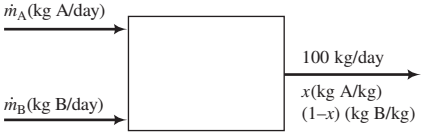
Scale up to a flow rate of 100 lb_m/min of the upper product stream.

4.3c Balancing a Process

BIOENGINEERING

Nonsteroidal anti-inflammatory drugs (NSAIDS), such as that described in the illustration, vary in their utility and how they are eliminated from the body. Aspirin is an especially important NSAID that has been on the market since 1915 and has gained in popularity as a preventative of strokes and heart attacks.

The pain remedy Aleve-D™ (http://aleved.com/faqs/) is made by combining naproxen sodium (A), also known as sodium naproxen, and pseudoephedrine (B) in a mass ratio of 220 mg A/120 mg B. The process shown below is used to produce 100 kg/day of the required blend. After the blending step shown, other ingredients are added to facilitate formulation of the final product.



There are three unknown quantities—$\dot{m}_A, \dot{m}_B$ and x—associated with the process, so three equations are needed to calculate their values. One of them is given by the specified ratio of A to B: 220 mg A/120 mg B; i.e. $\dot{m}_A/\dot{m}_B = 220$ kg A/120 kg B or $\dot{m}_A = 1.83\dot{m}_B$.

Material balances for this nonreactive process all have the simple form: flow rate in = flow rate out. Three possible balances can be written—on total mass, on naproxen sodium (A), and on pseudoephedrine (B)—any two of which are independent and can be combined with the given ratio of A to B to provide the equations needed to determine the unknowns. For example,

Total Mass Balance: $\dot{m}_A + \dot{m}_B = 1.83\dot{m}_B + \dot{m}_B = 100\ \text{kg/day} \Longrightarrow \boxed{\dot{m}_B = 35.3\ \text{kg B/day}}$

$$\Downarrow$$

$$\boxed{\dot{m}_A = 64.7\ \text{kg A/day}}$$

Naproxen Sodium Balance: $\dot{m}_A(\text{kg A/day}) = 100\ \text{kg/day} \times x \Longrightarrow \boxed{x = 0.647\ \text{kg A/kg}}$

A logical question to ask at this point is how far can you go with this procedure? If the product flow rate had also been unknown, for example, could another balance (on pseudoephedrine) have been written to solve for it? Other points to consider are which balances to use when a choice exists and the order in which these balances should be written.

The answers to these questions are not at all obvious when chemical reactions are involved in the process, and we will temporarily postpone consideration of that subject. The following rules apply to nonreactive processes.

1. ***The maximum number of independent equations that can be derived by writing balances on a nonreactive system equals the number of chemical species in the input and output streams.***

   In the given example, two substances—sodium naproxen (A) and pseudoephedrine (B)—make up the input and output streams of the process; you can write mass or mole balances on A and B and a total mass or mole balance, but only two of these three equations are independent—writing the third accomplishes nothing. (If you wrote all three equations in an effort to determine three unknown variables, you would probably go through an elaborate algebraic exercise to prove that 1 = 1 or something equally uninformative.)

2. ***Write balances first that involve the fewest unknown variables.***

   In the example, a total mass balance involves only one unknown, $\dot{m}$, while A and B balances each involve both $\dot{m}$ and x. By writing first a total balance and then a A balance, we were able to solve first one equation in one unknown, then a second equation, also in one unknown. If we had instead written A and B balances, we would have had to solve two simultaneous equations in two unknowns; the same answers would have been obtained, but with greater effort if we are doing it manually. (If we are using software to solve the equations, which two we choose makes no difference.)

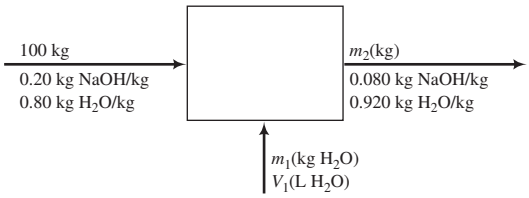
Example 4.3-3 Balances on a Mixing Unit

An aqueous solution of sodium hydroxide contains 20.0% NaOH by mass. It is desired to produce an 8.0% NaOH solution by diluting a stream of the 20% solution with a stream of pure water. Calculate the ratios (liters H_2O/kg feed solution) and (kg product solution/kg feed solution).

Solution

- **Choose a basis of calculation**—an amount or flow rate of one of the feed or product streams—**and then draw and label the flowchart**.

  We will arbitrarily choose a basis of 100 kg of the 20% feed solution. (We could also have chosen a flow rate of 100 lb_m/min of the 8% product solution or 10 tons of diluent water. The final results do not depend on the basis chosen since we are only asked to find ratios of stream amounts.) The flowchart appears as follows:



- **Express what the problem asks you to determine in terms of the labeled variables on the flowchart**.
  The desired quantities are $V_1/100$ (liters H_2O/kg feed solution) and $m_2/100$ (kg product solution/kg feed solution). Our task is therefore to calculate the variables V_1 and m_2.
- **Count unknown variables and equations relating them**.
  If the number of unknowns equals the number of independent equations relating them, you will be able to solve the problem; otherwise, either you have forgotten some relations or the problem is not well defined. In the latter case, there is no point wasting your time by jumping into time-consuming calculations.
  (a) Unknowns. Examining the flowchart, we see three unknown variables—m_1, m_2, and V_1.
  (b) Equations. *For a nonreactive process that involves N species, up to N independent material balance equations may be written*. Since there are two species in our process (sodium hydroxide and water), we can write two balances. We could write them on sodium hydroxide, water, total mass, atomic sodium, atomic hydrogen, and so on; the point is that once we have written any two, we can obtain no new information by writing a third one.
  Since we may only write two material balances, we will need a third equation to solve for our three unknowns (m_1, m_2, and V). Fortunately, we have one: the mass and volume of the diluent water, m_1 and V_1, are related by the density of liquid water, which we know. We thus have three equations in three unknowns and therefore a solvable problem.
- **Outline the solution procedure**.
  All balances for this system have the form *input = output*. For example, a total mass balance is $100\text{ kg} + m_1 = m_2$. Looking at the flowchart, we can see that balances on total mass and water each involve two unknowns (m_1 and m_2), a sodium hydroxide balance only involves one unknown (m_2), and the water density relationship involves two unknowns (m_1 and V_1). We would therefore begin the solution by writing and solving the NaOH balance for m_2, then writing and solving a total mass or water balance for m_1, and finally determining V_1 from m_1 and the density.
- **NaOH balance** (input = output).

$$(0.20\text{ kg NaOH/kg})(100\text{ kg}) = (0.080\text{ kg NaOH/kg})m_2 \Longrightarrow m_2 = 250\text{ kg NaOH}$$

  It is a good practice to write calculated variable values on the flowchart as soon as they are known for ease of use in later calculations. At this point, 250 would therefore be written in place of m_2 on the chart.
- **Total mass balance** (input = output).

$$100\text{ kg} + m_1 = m_2 \xrightarrow{m_2=250\text{ kg}} m_1 = 150\text{ kg H}_2\text{O}$$

- **Diluent water volume**. Although we are not given the temperature or pressure at which the mixing is done, the density of liquid water is approximately constant at 1.00 kg/liter (see Equation 3.1-2). We may therefore calculate

$$V_1 = \frac{150\text{ kg}}{\left|\dfrac{1.00\text{ liter}}{\text{kg}}\right.} = 150\text{ liters}$$

- **Ratios requested in problem statement**.

$$\frac{V_1}{100\text{ kg}} = \boxed{1.50\text{ liters H}_2\text{O/kg feed solution}}$$

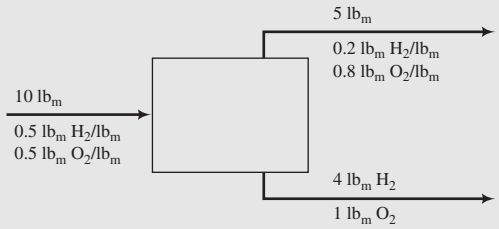
$$\frac{m_2}{100\text{ kg}} = \boxed{2.50\text{ kg product solution/kg feed solution}}$$

Exercise: Prove to yourself that you would get the same results for a different basis of calculation.

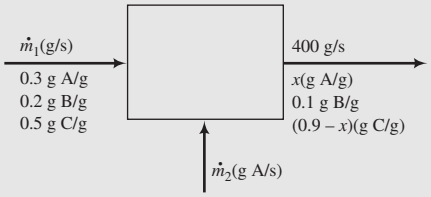
Test Yourself

(Answers, p. 655)

1. Prove that the following flowchart depicts a balanced process by writing three balances.



2. Indicate the balances you would write and the order in which you would write them to solve efficiently for the unknown stream variables in the following process:



4.3d Degree-of-Freedom Analysis

Everyone who has done material balance calculations has had the frustrating experience of spending a long time deriving and attempting to solve equations for unknown process variables, only to discover that not enough information is available. Before you do any lengthy calculations, you can use a properly drawn and labeled flowchart to determine whether you have enough information to solve a given problem. The procedure for doing so is referred to as **degree-of-freedom analysis**.

To perform a degree-of-freedom analysis, draw and *completely* label a flowchart, count the unknown variables on the chart, then count the *independent* equations relating them,[5] and subtract the second number from the first. The result is the number of *degrees of freedom* of the process, $n_{df}(= n_{unknowns} - n_{indep\ eqns})$. There are three possibilities:

1. If $n_{df} = 0$, there are n independent equations in n unknowns and the problem can in principle be solved.

2. If $n_{df} > 0$, there are more unknowns than independent equations relating them, and at least n_{df} additional variable values must be specified before all of the remaining variable values can be determined. Either relations have been overlooked or the problem is *underspecified* and has infinitely many solutions; in either case, plunging into calculations is likely to be a waste of time.[6]

3. If $n_{df} < 0$, there are more independent equations than unknowns. Either the flowchart is incompletely labeled or the problem is *overspecified* with redundant and possibly inconsistent

[5] Equations are independent if you cannot derive one by adding and subtracting combinations of the others. For example, only two of the three equations $x = 3$, $y = 2$, and $x + y = 5$ are independent; any one of them can be obtained from the other two by addition or subtraction.

[6] When a proposed process has a positive number of degrees of freedom, n_{df}, it is possible to perform a *process optimization*. The engineer chooses n_{df} *design variables* and assigns values to them, calculates values of the remaining system variables from the system equations, and calculates the value of an *objective function* from the full set of system variable values. The objective function may be a cost, a profit, or a rate of return on investment. The goal is to find the set of design variable values that yields the maximum or minimum value of the objective function.

relations. Again there is little point wasting time trying to solve it until the equations and unknowns are brought into balance.

Sources of equations relating unknown process stream variables include the following:

1. ***Material balances***. For a nonreactive process, no more than n_{ms} independent material balances may be written, where n_{ms} is the number of molecular species (e.g., CH_4, O_2) involved in the process. For example, if benzene and toluene are the species in the streams entering and leaving a distillation column, you could write balances on benzene, toluene, total mass, atomic carbon, atomic hydrogen, and so on, but at most two of those balances would be independent. If additional balances are written, they will not be independent of the first ones and so will provide no new information.

   For a reactive process, the procedure becomes more complicated. We will defer further discussion of this point to Section 4.7.

2. ***An energy balance*** (Chapters 7 through 9). If the amount of energy exchanged between the system and its surroundings is specified or if it is one of the unknown process variables, an energy balance provides a relationship between inlet and outlet material flows and temperatures.

3. ***Process specifications***. The problem statement may specify how several process variables are related. For example, you may be told that of the acetone fed to a condenser [flow rate = $\dot{m}_1$ (kg acetone/s)], 40% appears in a condensate stream [flow rate = $\dot{m}_2$ (kg acetone/s)]. A system equation would then be $\dot{m}_2 = 0.40\,\dot{m}_1$.

4. ***Physical properties and laws***. Two of the unknown variables may be the mass and volume of a stream material, in which case a tabulated specific gravity for liquids and solids or an equation of state for gases (Chapter 5) would provide an equation relating the variables. In other instances, saturation or equilibrium conditions for one or more of the process streams (Chapter 6) may provide needed relations.

5. ***Physical constraints***. For example, if the mole fractions of the three components of a stream are labeled x_A, x_B, and x_C, then a relation among these variables is $x_A + x_B + x_C = 1$. (If instead of x_C you label the last fraction $1 - x_A - x_B$, then you will have one less variable and one less equation to worry about.)

6. ***Stoichiometric relations***. If chemical reactions occur in a system, the stoichiometric equations of the reactions (e.g., $2H_2 + O_2 \rightarrow 2H_2O$) provide relationships between the quantities of the reactants consumed and of the products generated. We will consider how to incorporate these relationships into a degree-of-freedom analysis in Section 4.7.

Example 4.3-4 Degree-of-Freedom Analysis

Equipment Encyclopedia
condenser

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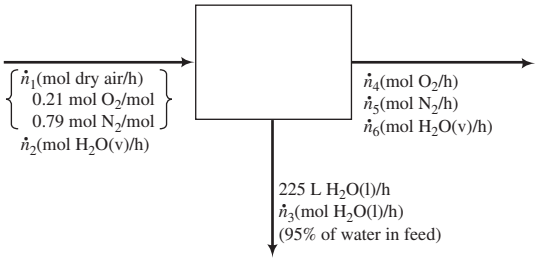
A stream of humid air enters a condenser in which 95% of the water vapor in the air is condensed. The flow rate of the condensate (the liquid leaving the condenser) is measured and found to be 225 L/h. Dry air may be taken to contain 21 mole% oxygen, with the balance nitrogen. Calculate the flow rate of the gas stream leaving the condenser and the mole fractions of oxygen, nitrogen, and water in this stream.

Solution

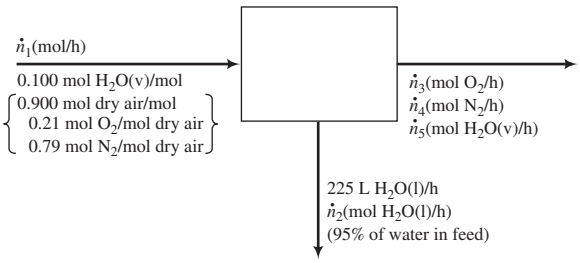
Basis: 225 L/h Condensate



We first do the degree-of-freedom analysis. There are six unknowns on the chart—$\dot{n}_1$ through $\dot{n}_6$. We are allowed up to three material balances—one for each species. We must therefore find three additional relations to solve for all unknowns. One is the relationship between the volumetric and molar flow rates of the condensate: we can determine $\dot{n}_3$ from the given volumetric flow rate and the known specific gravity and molecular weight of liquid water. A second is the given fact that 95% of the water is condensed. This specification provides a relationship between $\dot{n}_3$ and $\dot{n}_2$ ($\dot{n}_3 = 0.95\dot{n}_2$).

However, no information in the problem statement provides a basis for establishing a sixth relation, so there is one degree of freedom. The problem is therefore underspecified, and there is no point in attempting to solve it. Without the flowchart, it would have been difficult to see this and a great deal of time would have been wasted in a futile effort.

Suppose now that we had been given an additional piece of information—for example, that the entering air contains 10.0 mole% water. The flowchart would then appear as follows:



The degree-of-freedom analysis tells us that there are five unknowns and that we have five equations to solve for them [three mole balances, the density relationship between $\dot{V}_2$(= 225 L/h) and $\dot{n}_2$, and the fractional condensation], hence zero degrees of freedom. The problem is therefore solvable in principle. We may now lay out the solution—still before proceeding to any algebraic or numerical calculations—by writing out the equations in an efficient solution order (equations involving only one unknown first, then simultaneous pairs of equations, etc.) and circling the variables for which we would solve each equation or set of simultaneous equations. In this problem, a solution procedure can be found that does not involve simultaneous equations. (Verify that the units are correct in each equation.)

- ***Density relationship.***

$$\textcircled{\dot{n}_2}\left(\frac{\text{mol } H_2O(l)}{\text{h}}\right) = \frac{225 \text{ L } H_2O(l)}{\text{h}} \left| \frac{1.00 \text{ kg } H_2O(l)}{\text{L}} \right| \frac{1 \text{ mol } H_2O}{18.0 \times 10^{-3} \text{ kg}}$$

- ***95% Condensation.*** $\dot{n}_2 = 0.95\,(0.100\,\textcircled{\dot{n}_1})$
- ***O_2 Balance.*** $\dot{n}_1(0.900)(0.21) = \textcircled{\dot{n}_3}$
- ***N_2 Balance.*** $\dot{n}_1(0.900)(0.79) = \textcircled{\dot{n}_4}$
- ***H_2O Balance.*** $\dot{n}_1(0.100) = \dot{n}_2 + \textcircled{\dot{n}_5}$
- ***Total outlet gas flow rate.*** $\textcircled{\dot{n}_{\text{total}}} = \dot{n}_3 + \dot{n}_4 + \dot{n}_5$
- ***Outlet gas composition.*** $\textcircled{y_{O_2}} = \dot{n}_3/\dot{n}_{\text{total}}$, $\textcircled{y_{N_2}} = \dot{n}_4/\dot{n}_{\text{total}}$, $\textcircled{y_{H_2O}} = \dot{n}_5/\dot{n}_{\text{total}}$

The algebra and arithmetic are left as an exercise.

4.3e General Procedure for Single-Unit Process Material Balance Calculations

The problem-solving approach introduced in the previous sections and several additional procedural suggestions are summarized below. Given a description of a process, the values of several process variables, and a list of quantities to be determined:

1. ***Choose as a basis of calculation an amount or flow rate of one of the process streams.***

- If an amount or flow rate of a stream is given in the problem statement, it is usually convenient to use it as the basis of calculation. Subsequently calculated quantities will then be correctly scaled.
- If several stream amounts or flow rates are given, always use them collectively as the basis.
- If no stream amount or flow rate is specified in the problem statement, take as a basis an arbitrary amount or flow rate of a stream with a known composition (e.g., 100 kg or 100 kg/h if all mass fractions are known, or 100 mol or 100 mol/h if all mole fractions are known).

2. ***Draw a flowchart and fill in all known variable values, including the basis of calculation. Then label unknown stream variables on the chart.***
   - *The flowchart is completely labeled if you can express the mass or mass flow rate (or moles or molar flow rate) of each component of each stream in terms of labeled quantities.* Labeled variables for each process stream should therefore include *either*
     (a) the total mass [e.g., m_1(kg)] or mass flow rate [$\dot{m}_1$(kg/s)] and the mass fractions of all stream components [e.g., y_{CH_4}(kg CH_4/kg)], *or*
     (b) the total moles [e.g., n_1(kmol)] or molar flow rate [$\dot{n}_1$(kmol/s)] and the mole fractions of all stream components [e.g., y_{CH_4}(kmol CH_4/kmol)], *or*
     (c) for each stream component, the mass [e.g., m_{H_2}(kg H_2)], mass flow rate [$\dot{m}_{H_2}$(kg H_2/s)], moles [n_{CO}(kmol CO)], or molar flow rate [$\dot{n}_{CO}$(kmol CO/s)].
   - If you are given (or you can easily determine) either the amount or flow rate or any of the component fractions for a stream, label the total stream quantity or flow rate and the component fractions (categories (a) and (b) in the preceding list). If you only know the species present but have no quantitative information, label component quantities or flow rates (category (c) in the preceding list). Any labeling system will work for any stream, but the algebra tends to be simpler if you follow these guidelines.
   - Try to incorporate given relationships between unknown quantities in the labeling. For example, if you know that the molar flow rate of Stream 2 is double that of Stream 1, label the flow rates $\dot{n}_1$ and $2\dot{n}_1$ rather than $\dot{n}_1$ and $\dot{n}_2$.
   - *Label volumetric quantities only if they are given in the problem statement or you are asked to calculate them.* You will write mass or mole balances, but not volume balances. (Can you think of why that might be?)

3. ***Express what the problem statement asks you to determine in terms of the labeled variables.*** You will then know which unknowns you have to determine in order to solve the problem. We will refer to the equations relating the unknown labeled variables on the flowchart as "system equations" and these expressions as "additional equations."

4. ***If you are given mixed mass and mole units for a stream*** (such as a total mass flow rate and component mole fractions or vice versa), ***convert all quantities to one basis or the other using the methods of Section 3.3.***

5. ***Do the degree-of-freedom analysis.*** Count unknowns and identify the system equations that relate them. The equations may be any of the six types listed in Section 4.3d: material balances, an energy balance, process specifications, physical property relationships and laws, physical constraints, and stoichiometric relations. If you count more unknown variables than equations or vice versa, figure out what's wrong (e.g., the flowchart is not completely labeled, or an additional relation exists that was not counted, or one or more of your equations are not independent of the others, or the problem is underspecified or overspecified). If the number of unknowns does not equal the number of equations, there is

no point wasting time trying to solve the problem. If there are zero degrees of freedom, go to the next step.

6. **(a)** ***If the system equations are to be solved manually, write them in an efficient order (minimizing simultaneous equations) and circle the variables for which you will solve*** (as in Example 4.3-4). Start with equations that only involve one unknown variable, then pairs of simultaneous equations containing two unknown variables, and so on. Then do the necessary algebra to solve the equations.

   (b) ***If equation-solving software will be used, write the system equations in any order and solve them.***

7. ***Check your solution by substituting the calculated variable values into any balance equations you did not use***. For example, if you used only component balances when obtaining the solution, substitute the variable values into the overall balance and make sure the left-hand and right-hand sides are equal.

8. ***Solve the additional equations for quantities requested in the problem statement***.

9. ***If a stream quantity n_g or flow rate $\dot{n}_g$ was given in the problem statement and another value n_c (or $\dot{n}_c$) was either chosen as a basis or calculated for this stream, scale the balanced process by the ratio of the given value to the basis or calculated value to obtain the final result***.

The following example illustrates this procedure.

Example 4.3-5 Material Balances on a Distillation Column

Equipment Encyclopedia
distillation column
@
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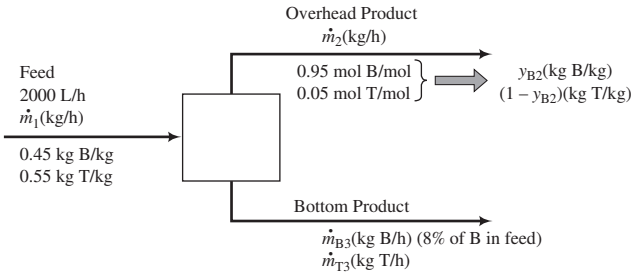
A liquid mixture containing 45.0% benzene (B) and 55.0% toluene (T) by mass is fed to a distillation column. A product stream leaving the top of the column (the *overhead product*) contains 95.0 mole% B, and a bottom product stream contains 8.0% of the benzene fed to the column (meaning that 92% of the benzene leaves with the overhead product). The volumetric flow rate of the feed stream is 2000 L/h and the specific gravity of the feed mixture is 0.872. Determine the mass flow rate of the overhead product stream and the mass flow rate and composition (mass fractions) of the bottom product stream (a) solving the equations manually, and (b) using an equation-solving program.

Solution

We will explicitly illustrate the implementation of the steps of the procedure just outlined. The first five steps of the procedure are the same regardless of whether the system equations are to be solved manually or with equation-solving software.

1. ***Choose a basis***. Having no reason to do otherwise, we choose the given feed stream flow rate (2000 L/h) as the basis of calculation.
2. ***Draw and label the flowchart.***



Note several points about the flowchart labeling:

- A volumetric flow rate is given for the feed stream, but mass flow rates and fractions will be needed for balances. The mass flow rate of the stream should therefore be considered an unknown

process variable and labeled as such on the chart. Its value will be determined from the known volumetric flow rate and density of the feed stream.

- Since mass balances will be written, the given component mole fractions in the overhead product stream will have to be converted to mass fractions. The mass fractions are accordingly labeled as unknowns.
- We could have labeled the mass flow rate and mass fractions of the bottom stream as we did the overhead. However, since we have no information about either the flow rate or composition of this stream, we have instead labeled the component flow rates (following the guideline given in Step 2 of the general procedure).
- Every component mass flow rate in every process stream can be expressed in terms of labeled quantities and variables. (Verify this statement.) For example, the flow rates of toluene (kg T/h) in the feed, overhead, and bottom streams are, respectively, $0.55\dot{m}_1$, $\dot{m}_2(1 - y_{B2})$, and $\dot{m}_{T3}$. The flowchart is therefore labeled completely.
- The 8%–92% benzene split between the product streams is not a stream flow rate or composition variable; nevertheless, we write it on the chart to remind ourselves that it is an additional relation among the stream variables and so should be included in the degree-of-freedom analysis.

3. ***Write expressions for the quantities requested in the problem statement.*** In terms of the quantities labeled on the flowchart, the quantities to be determined are $\dot{m}_2$ (the overhead product mass flow rate), $\dot{m}_3 = \dot{m}_{B3} + \dot{m}_{T3}$ (the bottom product mass flow rate), $x_B = \dot{m}_{B3}/\dot{m}_3$ (the benzene mass fraction in the bottom product), and $x_T = 1 - x_B$ (the toluene mass fraction). Once we determine $\dot{m}_2$, $\dot{m}_{B3}$, and $\dot{m}_{T3}$, the problem is essentially solved.

4. ***Convert mixed units in overhead product stream*** (see procedure preceding Example 3.3-3).

Basis: 100 kmol overhead $\Longrightarrow$ 95.0 kmol B, 5.00 kmol T

$\Longrightarrow$ (95.0 kmol B) × (78.11 kg B/kmol B) = 7420 kg B, (5.00 × 92.13) = 461 kg T

$\Longrightarrow$ (7420 kg B) + (461 kg T) = 7881 kg mixture

$\Longrightarrow y_{B2}$ = (7420 kg B)/(7881 kg mixture) = 0.942 kg B/kg (write on chart)

The molecular weights of benzene (78.11) and toluene (92.13) were looked up in Table B.1.

5. ***Perform degree-of-freedom analysis.***

4 unknowns	($\dot{m}_1, \dot{m}_2, \dot{m}_{B3}, \dot{m}_{T3}$)
−2 material balances	(since there are two molecular species in this nonreactive process)
−1 density relationship	(relating the mass flow rate to the given volumetric flow rate of the feed)
−1 specified benzene split	(8% in bottom − 92% in overhead)
0 degrees of freedom	

The problem is therefore solvable.

(a) Manual solution

6. ***Write and solve system equations.*** No simultaneous solutions to equations are required.

Conversion of volumetric flow rate. $$\textcircled{\dot{m}_1} = \left(2000\ \frac{\text{L}}{\text{h}}\right)\left(0.872 \times 1.00\ \frac{\text{kg}}{\text{L}}\right)$$

Benzene split fraction. The benzene in the bottom product stream is 8% of the benzene in the feed stream. This statement translates directly into the equation

$$\textcircled{\dot{m}_{B3}} = 0.08(0.45\dot{m}_1)$$

There are two unknowns remaining on the flowchart ($\dot{m}_2$ and $\dot{m}_{T3}$) and we are allowed to write two balances. Balances on total mass and toluene each involve both unknowns, but a benzene balance only involves $\dot{m}_2$ (convince yourself, remembering that $\dot{m}_{B3}$ is now known), so we begin with that one.

Benzene balance: $0.45\dot{m}_1 = \textcircled{\dot{m}_2} y_{B2} + \dot{m}_{B3}$

Toluene balance: $0.55\dot{m}_1 = (1 - y_{B2})\dot{m}_2 + \textcircled{\dot{m}_{T3}}$

The solutions of these four equations are

$$\dot{m}_1 = 1744 \text{ kg/h},\ \dot{m}_{B3} = 62.8 \text{ kg B/h},\ \boxed{\dot{m}_2 = 766 \text{ kg/h}},\ \dot{m}_{T3} = 915 \text{ kg T/h}$$

7. ***Check the solution.*** A total mass balance (the sum of the benzene and toluene balances) may be written as a check on the solution.

$$\dot{m}_1 = \dot{m}_2 + \dot{m}_{B3} + \dot{m}_{T3} \Longrightarrow 1744 \text{ kg/h} = (766 + 62.8 + 915) \text{ kg/h} = 1744 \text{ kg/h} \quad \checkmark$$

8. ***Solve the additional equations.***

Mass flow rate of bottom product stream

$$\textcircled{\dot{m}_3} = \dot{m}_{B3} + \dot{m}_{T3} \boxed{= 978 \text{ kg/h}}$$

Composition of bottom product stream

$$\textcircled{y_{B3}} = \frac{\dot{m}_{B3}}{\dot{m}_3} \boxed{= 0.064} \qquad \textcircled{y_{T3}} = 1 - y_{B3} \boxed{= 0.936}$$

If we had chosen a basis of calculation other than an actual stream amount or flow rate, we would now scale the process from the calculated base value to the actual value of this variable. Since in this case our basis was the actual feed stream flow rate, the solution is complete.

(b) Computer solution

9. ***Write and solve the system equations.*** The four system equations (two material balances, feed density relationship, and benzene split equation) may be written in that (or any other) order.

Mass balance: $$\dot{m}_1 = \dot{m}_2 + \dot{m}_{B3} + \dot{m}_{T3} \quad \textbf{(1)}$$

Benzene balance: $$0.45\dot{m}_1 = 0.942\dot{m}_2 + \dot{m}_{B3} \quad \textbf{(2)}$$

Conversion of volumetric flow rate: $$\dot{m}_1 = \left(2000 \frac{\text{L}}{\text{h}}\right)\left(0.872 \times 1.00 \frac{\text{kg}}{\text{L}}\right) \quad \textbf{(3)}$$

Benzene split: $$\dot{m}_{B3} = 0.08(0.45\dot{m}_1) \quad \textbf{(4)}$$

The equations can be solved with Excel's Solver or any other equation-solving program.

10. ***Check the solution.*** The left-hand and right-hand sides of the toluene balance would be calculated and checked to make sure they are equal.
11. ***Solve the additional equations.*** The three additional requested variables would be calculated from the variable values determined in Step 6.

The following Excel spreadsheet illustrates the complete problem solution. The solution procedure is summarized below the spreadsheet.

	A	B	C	D	E	F
1	**Solution to Example 4.3-5**					
2						
3		**Variable**	**m1**	**m2**	**mB3**	**mT3**
4		Value	1744	766.47	62.78	914.75
5						
6	**System equations**		**LHS**	**RHS**	**(LHS–RHS)^2**	
7	(1) Mass balance	m1 = m2 + mB3 + mT3	1744	1744	0	
8	(2) Benzene balance	0.45*m1 = 0.942*m2 + mB3	784.8	784.8	0	
9	(3) Volumetric flow rate	m1 = 2000*0.872	1744	1744	5.17E–26	
10	(4) Benzene split	mB3 = 0.08*(0.45*m1)	62.78	62.78	8.53E–27	
11				**SUM**	6.02E–26	
12						
13	**Check: Toluene balance**	0.55*m1 = 0.05*m2 + mT3	**LHS**	**RHS**		
14			959.2	959.2	Checks	
15						
16	**Additional equations**					
17	(5) Bottom prod. flow rate	m3 = mB3 + mT3 =	978			
18	(6) Bottom prod. benz. fract.	yB3 = mB3/m3 =	0.064			
19	(7) Bottom prod. tol. fract.	yT3 = 1 – yB3 =	0.936			

- Type the text entries in [A1:A19], [B3:B18], [C3:F3], [C6:E6], and [D11] as shown.
- Enter initial guesses of the four unknown variables (say, 100, 100, 50, 50) into [C4:F4].
- Enter the following formulas in [C7:E10].

[C7] = C4	[D7] = D4 + E4 + F4	[E7] = (C7 – D7)^2
[C8] = 0.45*C4	[D8] = 0.942*D4 + E4	[E8] = (C8 – D8)^2
[C9] = C4	[D9] = 2000*0.872	[E9] = (C9 – D9)^2
[C10] = E4	[D10] = 0.08*0.45*C4	[E10] = (C10 – D10)^2

- Call *Solver* to minimize the value in Cell [E11] by adjusting the values in [C4:F4]. Solver converges to the values shown in [C4:F4], and the negligible value in [E11] indicates that those four values are virtually the exact solution of the four equations.
- Enter the left-hand and right-hand sides of the toluene balance in [C14] and [D14], respectively. The equality of the two values confirms the correctness of the system equation solutions. The word "checks" is entered in [E14].
- Enter

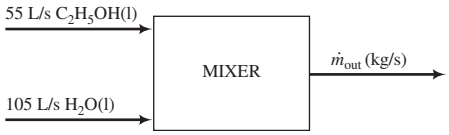
[C17] = E4 + F4 [C18] = E4/C17 [C19] = 1 – C18

Note: This example illustrates the direct use of Solver. An alternative would be to enter the four system equations into the Equation Solving Wizard of APEx, which would then generate the block of cells [B3:F11] on the spreadsheet with the contents shown above and then call on Solver to obtain the solution.

4.3f In Textbooks, Balances Usually Close; In Real Chemical Processes, Not So Much.

The procedure outlined in the preceding section will enable you to solve most of the problems in Chapters 4–6 and (once you've learned about energy balances) in Chapters 7–9 as well. You should be aware, however, that those problems were created based on three conditions that may be unrealistic for real process systems: (1) just enough variables are known to allow calculation of all unknown values; (2) given variable values (which in a real system would all have been measured using instruments like those described in Chapter 3) are all accurately known; (3) material balances on all species always close—that is, for batch and steady-state continuous processes, input + generation always equals output + consumption, and if a species is nonreactive, input always equals output. Real systems seldom function that neatly: in fact, if a balance ever closes exactly it is only because of a coincidental cancellation of errors. In practice, unless the species is either exceptionally valuable or exceptionally dangerous, a balance that comes close to closing is usually good enough.

Consider the following trivial system in which continuous streams of liquid ethanol and liquid water are mixed, and you are asked to calculate the mass flow rate of the mixture.



The task of calculating $\dot{m}_{out}$ appears straightforward. Letting E and W stand for ethanol and water and using specific gravities from Table B.1, we obtain

$$\dot{m}_{in} = \frac{55\ \text{L E}}{\text{s}} \left| \frac{0.789\ \text{kg}}{1\ \text{L E}} + \frac{105\ \text{L W}}{\text{s}} \right| \frac{1.000\ \text{kg}}{1\ \text{L W}} = 148\ \frac{\text{kg}}{\text{s}} \Longrightarrow \dot{m}_{out} = \dot{m}_{in} = 148\ \frac{\text{kg}}{\text{s}}$$

Now suppose a technician comes in and informs the process engineer (that would be you) that the volumetric flow rate at the outlet was measured and converted to a mass flow rate of 144 kg/s. There is no longer anything to calculate, and your job is now to explain why the mass balance on the system is not closing (148 kg/s in $\neq$ 144 kg/s out).

The first question to consider is whether the difference between the predicted value of 148 kg/s and the measured value of 144 kg/s (a difference of about 3%) is real or simply a result of the fact that the measured variable values—the three volumetric flow rates—may all fluctuate. If you take repeated measurements using the three flowmeters and calculate the standard deviation of the results, straightforward analysis will tell you whether the 4 kg/s difference is statistically significant or if it falls in the range of normal measurement error. In the latter case, you would carry out several more measurements to lower the margin of error. If the difference is significant, however, then you are still faced with the need to explain the discrepancy.

Cover the table that follows, take a moment and think about possible explanations, and then uncover the table and see how many you got and whether you thought of others not on the list.

Possible reasons for input ≠ output

- Steady state had not been attained when the measurements were made.
- The flow measurements of any of the three streams could have been faulty due to either instrument or human error.
- The densities of the fluid streams could be different from those in Table B.1 (for example, because of temperature variations), leading to errors in the conversion of volumetric to mass flow rates.
- There could be a slight leak in the tank.

In more complex processes the list of possibilities may be considerably longer, including such things as impurities in feed materials, temperature and pressure fluctuations, chemical reactions among process species that have not been taken into account, unjustified assumptions of ideal behavior, and so on.

In a number of chapter-end problems in this text, you will be asked to generate similar lists of possible reasons for discrepancies between what you calculate and what would actually be measured for a process, or reasons for failures of balances to close. You may not see such textbook problems again for the remainder of your studies. You are almost certain to encounter deviations from predictions and balances that don't close in your laboratory courses, however, and if you go to work in industry or academic research you are guaranteed to encounter them routinely. We hope the exercises in this book help prepare you for those occasions.

4.4 BALANCES ON MULTIPLE-UNIT PROCESSES

In the preceding sections, we referred rather loosely to "the system," as in the statement "At steady state the rate at which benzene enters the system equals the rate at which it leaves." Not much was said about what "the system" was. Up to now, however, not much needed to be said, since we have considered only processes involving a single unit—a mixer, or a distillation column, or a reactor—and that unit necessarily constituted the system.

Industrial chemical processes rarely involve just one process unit. One or more chemical reactors are often present, as are units for mixing reactants, blending products, heating and cooling process streams, separating products from each other and from unconsumed reactants, and removing potentially hazardous pollutants from streams prior to discharging the streams to the plant environment. Before we analyze such processes, we must take a closer look at what we mean by a system.

In general terms, a "system" is any portion of a process that can be enclosed within a hypothetical box (boundary). It may be the entire process, an interconnected combination of some of the process units, a single unit, or a point at which two or more process streams come together or one stream splits into branches. The inputs and outputs to a system are the process streams that intersect the system boundary.

A flowchart for a two-unit process is shown in Figure 4.4-1. Five boundaries drawn about portions of the process define systems on which balances may be written.

Boundary Ⓐ encloses the entire process; the system defined by this boundary has as inputs Feed Streams 1, 2, and 3 and Product Streams 1, 2, and 3. (Convince yourself.) Balances on this system are referred to as **overall balances**. The stream that connects Units 1 and 2 is internal to this system and so would not enter into overall system balances.

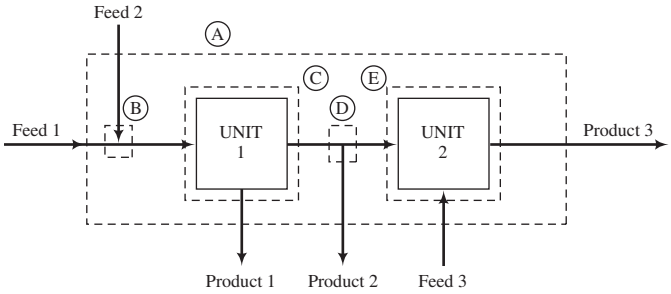


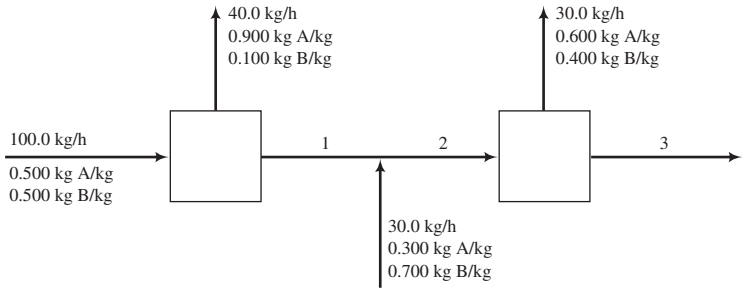
FIGURE 4.4-1 Flowchart of a two-unit process. Dashed lines denote boundaries of systems about which balances can be written.

Boundary Ⓑ encloses a feed stream mixing point. Feed Streams 1 and 2 are inputs to this system and the stream flowing to Unit 1 is an output. Boundary Ⓒ encloses Unit 1 (one input stream and two output streams), Boundary Ⓓ encloses a stream splitting point (one input stream and two output streams), and Boundary Ⓔ encloses Unit 2 (two input streams and one output stream).

The procedure for material balance calculations on multiple-unit processes is nearly the same as that outlined in Section 4.3. The difference is that with multiple-unit processes you may have to isolate and write balances on several subsystems of the process to obtain enough equations to determine all unknown stream variables. When analyzing multiple-unit processes, carry out degree-of-freedom analyses on the overall process and on each subsystem, taking into account only the streams that intersect the boundary of the system under consideration. Do not begin to write and solve equations for a subsystem until you have verified that it has zero degrees of freedom.

Example 4.4-1 Two-Unit Process

A labeled flowchart of a continuous steady-state two-unit process is shown below. Each stream contains two components, A and B, in different proportions. Three streams whose flow rates and/or compositions are not known are labeled 1, 2, and 3.

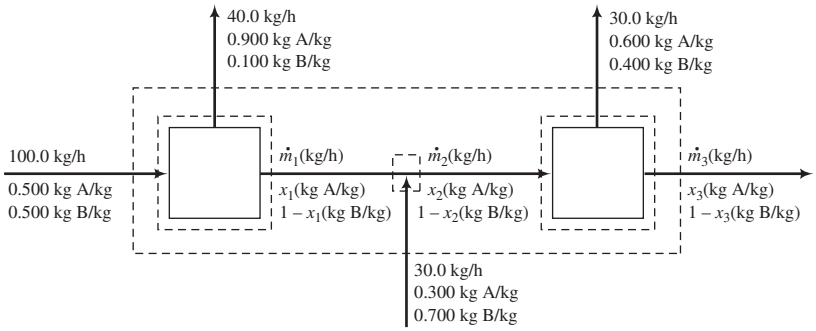


Calculate the unknown flow rates and compositions of streams 1, 2, and 3.

Solution

Basis—Given Flow Rates

The systems about which balances might be written are shown on the following representation of the flowchart:



The outer boundary encompasses the entire process and has as input and output streams all of the streams that enter and leave the process. Two of the interior boundaries surround individual process units, and the third encloses a stream junction point.

Degree-of-Freedom Analysis

We first outline the solution procedure by performing degree-of-freedom analyses on different systems. Remember that only variables associated with streams intersecting a system boundary are counted in the analysis of that system.

Overall system (outer dashed boundary):

$$2 \text{ unknowns } (\dot{m}_3,\ x_3) - 2 \text{ balances (2 species)} = 0 \text{ degrees of freedom}$$

$$\Longrightarrow \underline{\text{Determine } \dot{m}_3 \text{ and } x_3}$$

In subsequent analyses, we may consider these two variables as known. Suppose we decide to consider the intermediate stream mixing point as the next system.

Mixing point:

$$4 \text{ unknowns } (\dot{m}_1, x_1, \dot{m}_2, x_2) - 2 \text{ balances (2 species)} = 2 \text{ degrees of freedom}$$

We have too many unknowns for the number of available equations. Let's try Unit 1.

Unit 1:

$$2 \text{ unknowns } (\dot{m}_1,\ x_1) - 2 \text{ balances (2 species)} = 0 \text{ degrees of freedom}$$

$$\Longrightarrow \underline{\text{Determine } \dot{m}_1 \text{ and } x_1}$$

We may now analyze either the mixing point or Unit 2, each of which has two unknown variables associated with it.

Mixing point:

$$2 \text{ unknowns } (\dot{m}_2,\ x_2) - 2 \text{ balances (2 species)} = 0 \text{ degrees of freedom}$$

$$\Longrightarrow \underline{\text{Determine } \dot{m}_2 \text{ and } x_2}$$

The procedure will therefore be to write overall system balances to determine $\dot{m}_3$ and x_3, then balances on Unit 1 to determine $\dot{m}_1$ and x_1, and finally balances on the intermediate mixing point to determine $\dot{m}_2$ and x_2.

The calculations are straightforward. Note that all balances on this steady-state nonreactive process have the form *input* = *output*, and also note that the balances are written in an order that does not require solution of simultaneous equations (each equation involves only one unknown variable).

Calculations

Overall Mass Balance:

$$(100.0 + 30.0)\ \frac{\text{kg}}{\text{h}} = (40.0 + 30.0)\ \frac{\text{kg}}{\text{h}} + \dot{m}_3 \Longrightarrow \boxed{\dot{m}_3 = 60.0 \text{ kg/h}}$$

Overall Balance on A: (Verify that each additive term has the units kg A/h.)

$$(0.500)(100.0) + (0.300)(30.0) = (0.900)(40.0) + (0.600)(30.0) + x_3(60.0)$$

$$\Longrightarrow \boxed{x_3 = 0.0833 \text{ kg A/kg}}$$

Mass Balance on Unit 1: (Each term has the units kg/h.)

$$100 = 40 + \dot{m}_1 \Longrightarrow \boxed{\dot{m}_1 = 60.0 \text{ kg/h}}$$

A Balance on Unit 1: (Each additive term has the units kg A/h.)

$$(0.500)(100.0) = (0.900)(40.0) + x_1(60.0) \Longrightarrow \boxed{x_1 = 0.233 \text{ kg A/kg}}$$

Mass Balance on Stream Mixing Point: (Each term has the units kg/h.)

$$\dot{m}_1 + 30.0 = \dot{m}_2 \xrightarrow{\dot{m}_1 = 60.0 \text{ kg/h}} \boxed{\dot{m}_2 = 90.0 \text{ kg/h}}$$

A Balance on Stream Mixing Point: (Each additive term has the units kg A/h.)

$$x_1\dot{m}_1 + (0.300)(30.0) = x_2\dot{m}_2$$

$$\Downarrow \begin{array}{l} \dot{m}_1 = 60.0\ \text{kg/h} \\ x_1 = 0.233\ \text{kg A/kg} \\ \dot{m}_2 = 90.0\ \text{kg/h} \end{array}$$

$$\boxed{x_2 = 0.255\ \text{kg A/kg}}$$

The situation becomes still more complicated when three or more process units are involved. In such cases, balances may be written not only for the overall process and individual process units, but also for combinations of units. Finding the right combinations can lead to a considerable gain in computational efficiency.

Solvent extraction is used frequently to separate components of a liquid mixture (let's call them A and B) that are almost equally volatile, so they cannot be easily separated by methods such as evaporation or distillation. Here is how it works. Mix the solution of A and B with a third species, C, that has a strong affinity for B but is immiscible or nearly immiscible with A. Upon settling, the combined mixture separates into two phases. One is rich in A and may contain small amounts of B and C; the other is rich in C and contains most of the B in the original mixture and possibly a small amount of A. The C-rich phase is then fed to another operation that separates B and C, with B recovered as product and C recycled to the extractor.

Another common reason for choosing extraction is that Species A and/or B are *thermally labile:* that is, they may react or degrade when exposed to high temperatures, such as those normally found in evaporation and distillation. Such systems are especially common among complex compounds often found in biological or pharmaceutical processes.[7] The following example illustrates another important application of extraction and provides an example of formulating and solving multi-unit mass balances.

Example 4.4-2 An Extraction–Distillation Process

Equipment Encyclopedia
extractors (mixer-settler), distillation column
@
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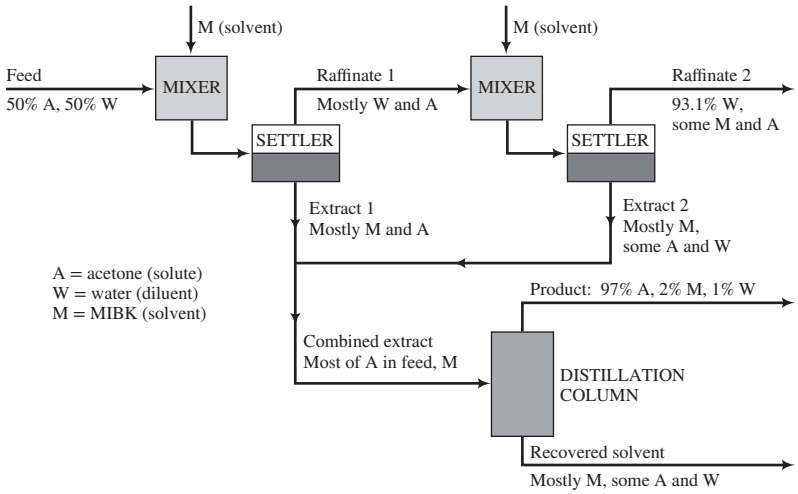
A mixture containing 50.0 wt% acetone (A) and 50.0 wt% water (W) is to be separated into two streams—one rich in acetone and the other in water. The separation process consists of extraction of the acetone from the water into methyl isobutyl ketone (MIBK or M), which has a much higher affinity for acetone than it does for water. The process is shown schematically below.



BIOENGINEERING

[7] For example, a solvent extraction process was a key development in the large-scale production of penicillin in the 1940s. (R. I. Mateles, Ed., *Penicillin: A Paradigm for Biotechnology*, Candida Corporation, Chicago, IL, 1998.)

The acetone (**solute**)–water (**diluent**) mixture is first contacted with the MIBK (**solvent**) in a mixer that provides good contact between the two liquid phases. A portion of the acetone in the feed transfers from the aqueous (water) phase to the organic (MIBK) phase in this step. The mixture passes into a settling tank, where the phases separate and are separately withdrawn. The phase rich in the diluent (water, in this process) is referred to as the **raffinate**, and the phase rich in the solvent (MIBK) is the **extract**. The mixer–settler combination is the first **stage** of this separation process.

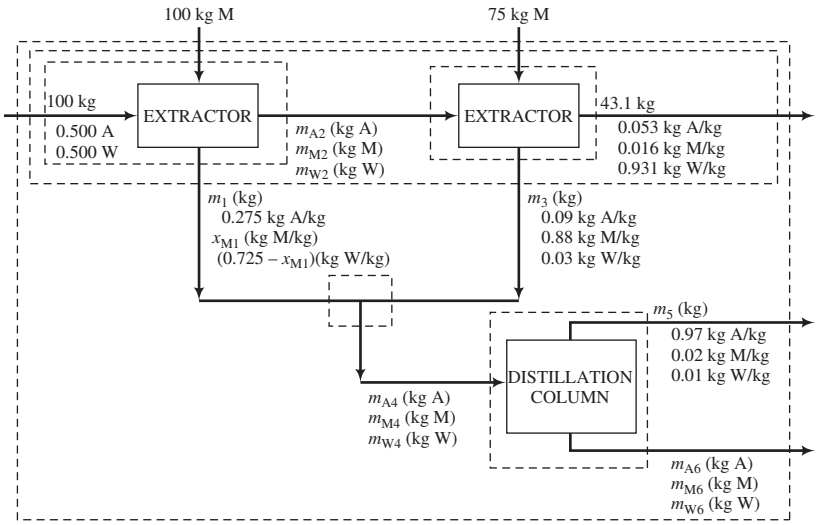
The raffinate passes to a second extraction stage where it is contacted with a second stream of pure MIBK, leading to the transfer of more acetone. The two phases are allowed to separate in a second settler, and the raffinate from this stage is sent to a waste-treatment operation. The extracts from the two mixer–settler stages are combined and fed to a distillation column. The overhead effluent is rich in acetone and is the process product. The bottom effluent is rich in MIBK and in a real process would be treated further and recycled back to the first extraction stage, but we will not consider recycle in this example.

In a pilot–plant study, for every 100 kg of acetone–water fed to the first extraction stage, 100 kg of MIBK is fed to the first stage and 75 kg is fed to the second stage. The extract from the first stage is found to contain 27.5 wt% acetone. (All percentages in the remainder of this paragraph are weight percents.) The second-stage raffinate has a mass of 43.1 kg and contains 5.3% acetone, 1.6% MIBK, and 93.1% water, and the second-stage extract contains 9.0% acetone, 88.0% MIBK, and 3.0% water. The overhead product from the distillation column contains 2.0% MIBK, 1.0% water, and the balance acetone.

Taking a basis of calculation of 100 kg acetone–water feed, calculate the masses and compositions (component weight percentages) of the Stage 1 raffinate and extract, the Stage 2 extract, the combined extract, and the distillation overhead and bottoms products.

Solution This is a "trick" problem in that there is not enough information to calculate all of the requested quantities. We will show how degree-of-freedom analysis allows a fairly quick determination of which variables can be determined and how to determine them efficiently, and also helps avoid wasting a great deal of time trying to solve a problem with insufficient information.

As always, we begin by drawing and labeling the flowchart. For simplicity, we will treat each mixer–settler combination as a single "extractor" unit.



Balances may be written for any of the systems shown on the chart, including the overall process, the individual extractors, the two-extractor combination, the point where the two extract streams combine, and the distillation column. A degree-of-freedom analysis for the overall process indicates that there are four unknown variables (m_5, m_{A6}, m_{M6}, m_{W6}) and only three equations that relate them (one material balance for

each of the three independent species involved in the process), leaving one degree of freedom. Similarly, the first extractor has two degrees of freedom, the second extractor has one, the extract mixing point has three, and the distillation column has four. (Verify these figures.) However, the system composed of the two extraction units involves only three unknowns (m_1, x_{M1}, m_3) and three balances relating them, hence zero degrees of freedom. The solution procedure is as follows:

- ***Analyze two-extractor subsystem.*** Write a total mass balance and an acetone balance; solve simultaneously to determine m_1 and m_3. Write an MIBK balance to determine x_{M1}.
- ***Analyze extract mixing point.*** Write acetone, MIBK, and water balances; solve to determine m_{A4}, m_{M4}, and m_{W4}, respectively.
- ***Analyze first (or second) extractor.*** Write acetone, MIBK, and water balances; solve to determine m_{A2}, m_{M2}, and m_{W2}.

At this point, we may quickly determine that we can go no farther. There are four remaining unknowns—m_5, m_{A6}, m_{M6}, and m_{w6}. Whether we choose the overall process or the distillation column as our system, we will only have three independent equations and hence one degree of freedom, and so we will be unable to solve the problem. Moreover, since acetone, MIBK, and water all appear in both outlet streams, we cannot solve for any one of the individual unknowns. (If there were no water in the overhead product from the distillation column, for example, we could deduce that $m_{W6} = m_{W4}$). The problem is thus underspecified; unless another piece of information is furnished, the amounts and compositions of the distillation column products are indeterminate.

The calculations that can be performed are shown below. All balances have the form *input* = *output* (why?), and every additive term of each balance has units of kilograms of the balanced species.

Balances Around Two-Extractor Subsystem:

$$\textit{Total mass: } (100 + 100 + 75)\,\text{kg} = 43.1\,\text{kg} + m_1 + m_3$$

$$\text{A: } 100(0.500)\,\text{kg A} = (43.1)(0.053)\,\text{kg A} + m_1(0.275) + m_3(0.09)$$

$$\Downarrow \text{Solve simultaneously}$$

$$\boxed{m_1 = 145\,\text{kg},\ m_3 = 86.8\,\text{kg}}$$

$$\text{M: } (100 + 75)\,\text{kg M} = (43.1)(0.016)\,\text{kg M} + m_1 x_{M1} + m_3(0.88)$$

$$\Downarrow m_1 = 145\,\text{kg}, m_3 = 86.8\,\text{kg}$$

$$\boxed{x_{M1} = 0.675\,\text{kg MIBK/kg}}$$

Balances Around Extract Mixing Point:

$$\text{A: } m_1(0.275) + m_3(0.09) = m_{A4}$$

$$\Downarrow m_1 = 145\,\text{kg},\ m_3 = 86.8\,\text{kg}$$

$$\boxed{m_{A4} = 47.7\,\text{kg acetone}}$$

$$\text{M: } m_1 x_{M1} + m_3(0.88) = m_{M4}$$

$$\Downarrow m_1 = 145\,\text{kg},\ m_3 = 87\,\text{kg}, x_{M1} = 0.675\,\text{kg M/kg}$$

$$\boxed{m_{M4} = 174\,\text{kg MIBK}}$$

$$\text{W: } m_1(0.725 - x_{M1}) + m_3(0.03) = m_{W4}$$

$$\Downarrow m_1 = 145\,\text{kg},\ m_3 = 86.8\,\text{kg}, x_{M1} = 0.675\,\text{kg W/kg}$$

$$\boxed{m_{W4} = 9.9\,\text{kg water}}$$

Balances Around First Extractor:

$$\text{A: } 100(0.500)\text{ kg A} = m_{A2} + m_1(0.275)$$

$$\Downarrow m_1 = 145\text{ kg}$$

$$\boxed{m_{A2} = 10.1\text{ kg acetone}}$$

$$\text{M: } 100\text{ kg M} = m_{M2} + m_1 x_{M1}$$

$$\Downarrow m_1 = 145\text{ kg},\ x_{M1} = 0.675\text{ kg M/kg}$$

$$\boxed{m_{M2} = 2.3\text{ kg MIBK}}$$

$$\text{W: } (100)(0.500) = m_{W2} + m_1(0.725 - x_{M1})$$

$$\Downarrow m_1 = 145\text{ kg},\ x_{M1} = 0.675\text{ kg M/kg}$$

$$\boxed{m_{W2} = 42.6\text{ kg water}}$$

If we knew (or could independently determine) any one of the variables m_5, m_{A6}, m_{M6}, or m_{W6}, we could calculate the remaining three. Since we don't, we must terminate the calculations at this point.

4.5 RECYCLE AND BYPASS

It is rare that a chemical reaction A → B proceeds to completion in a reactor. No matter how little A is present in the feed or how long the reaction mixture remains in the reactor, some A is normally found in the product.

Unfortunately, you have to pay for *all* the reactant fed to a process, not just the fraction that reacts, and any A that leaves with the product therefore represents wasted resources. Suppose, however, you could find a way to separate most or all of the unconsumed reactant from the product stream. You could then sell the resulting relatively pure product and **recycle** the unconsumed reactant back to the reactor. You would, of course, have to pay for the separation and recycle equipment, but you would compensate for this cost by having to purchase less fresh reactant and being able to sell the purified product at a higher price.

A labeled flowchart of a chemical process involving reaction, product separation, and recycle is shown in Figure 4.5-1. Note the distinction between the *fresh feed* to the process and the feed to the reactor, which is the sum of the fresh feed and recycle stream. If some of the stream variables

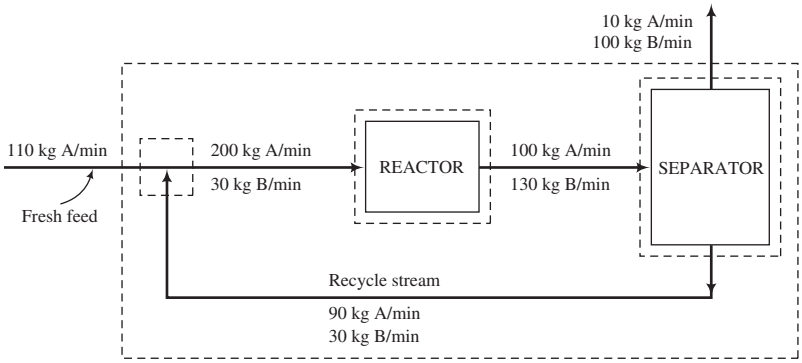


FIGURE 4.5-1 Flowchart of a reactor with separation and recycle of unconsumed reactant.

shown in Figure 4.5-1 were unknown, you could determine them by writing balances on the overall process and about the reactor, separator, and mixing point.

Students frequently have difficulty when they first encounter the concept of recycle because they find it hard to understand that material can circulate in a system without an accumulation of mass. If you have this difficulty, you might find it helpful to refer back to the flowchart of Figure 4.5-1. Observe that even though there is material circulating within the system, there is no net accumulation: 110 kg of material enters the system each minute, and the same mass leaves each minute. Within the system there is a net circulation rate of 120 kg/min, but the circulation has no effect on the overall process material balance.

The next example illustrates two approaches to solving material balance problems on systems with recycle. The first one should be used if a manual solution is sought, and involves identifying the overall system and subsystems for which balances may be written and using a degree-of-freedom analysis to determine an efficient order in which to perform the analysis. The second approach is to count unknown system variables, subtract the number of equations that can be written for each subsystem (but not the overall system), and verify that there are zero degrees of freedom. If there are, then write the subsystem equations and solve them with an equation-solving program.

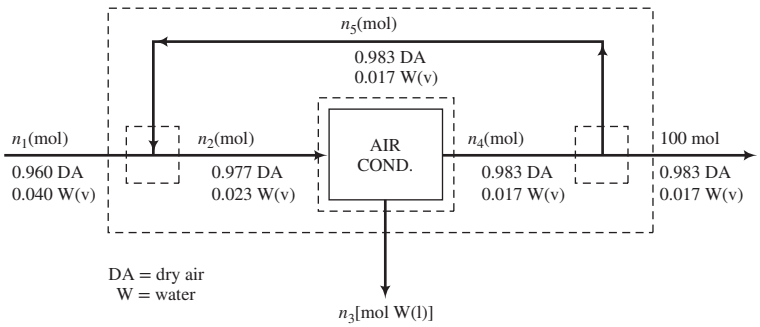
Example 4.5-1 Material and Energy Balances on an Air Conditioner

Equipment Encyclopedia
reactor, condenser
@
www.wiley.com/college/felder

Fresh air containing 4.00 mole% water vapor is to be cooled and dehumidified to a water content of 1.70 mole% H_2O. A stream of fresh air is combined with a recycle stream of previously dehumidified air and passed through the cooler. The blended stream entering the unit contains 2.30 mole% H_2O. In the air conditioner, some of the water in the feed stream is condensed and removed as liquid. A fraction of the dehumidified air leaving the cooler is recycled and the remainder is delivered to a room. Taking 100 mol of dehumidified air delivered to the room as a basis of calculation, calculate the moles of fresh feed, moles of water condensed, and moles of dehumidified air recycled (a) manually, and (b) using Excel's Solver.

Solution

The labeled flowchart for this process, including the assumed basis of calculation, is shown below. Dashed lines depict the four subsystems about which balances might be written—the overall process, the recycle–fresh feed mixing point, the air conditioner, and the recycle–product gas splitting point. The quantities to be determined are n_1, n_3, and n_5.



(a) Manual solution. Students first attempting recycle problems are tempted to jump in and start writing balances immediately, and when they do they find themselves spending a *long* time on the problems, often failing to get solutions. If you first take a few minutes to go through a degree-of-freedom analysis you should be able to work out an efficient solution method before doing any calculations, ultimately saving yourself much more time than it took to do the analysis. Observe the procedure.

Overall System:

2 variables (n_1, n_3)	(Only consider streams that intersect the system boundary.)
− 2 balance equations	(Two species—dry air and water—are in the streams.)
0 degrees of freedom	

We can therefore determine n_1 and n_3 from overall system balances. We would write a dry air balance first since it only involves one unknown (n_1), while total mole and water balances involve both unknowns. Once n_1 has been determined, the second balance yields n_3. No more can be done with the overall system, so we move on to other subsystems.

Mixing Point:	***Cooler:***	***Splitting Point:***
2 variables (n_2, n_5)	2 variables (n_2, n_4)	2 variables (n_4, n_5)
− 2 balances	− 2 balances	− 1 balance (see below)
0 degrees of freedom	0 degrees of freedom	1 degree of freedom

Only one independent balance can be written for the splitting point because the streams entering and leaving this subsystem are labeled as having identical compositions, so that the dry air/water mixture in all three streams behaves like a single species. (Convince yourself: write a total mole balance and a dry air or water balance around the splitting point and observe that you get the same equation each time.)

At this point we could either write balances around the mixing point to determine n_2 and n_5 or around the cooler to determine n_2 and n_4 (but not around the splitting point, which has one degree of freedom). The mixing point is the logical subsystem to attack, since the problem statement asks for n_5 but not n_4. Writing and solving balances around the mixing point will therefore complete the solution.

Now, finally, we do the calculations. All balances have the form *input* = *output*, and each additive term in each equation has the units (mol of the balanced quantity).

Overall dry air balance: $0.960n_1 = 0.983(100\text{ mol}) \Longrightarrow$ $\boxed{n_1 = 102.4\text{ mol fresh feed}}$

Overall mole balance: $n_1 = n_3 + 100\text{ mol} \xrightarrow{n_1 = 102.4\text{ mol}}$ $\boxed{n_3 = 2.4\text{ mol } H_2O\text{ condensed}}$

Mole balance on mixing point: $n_1 + n_5 = n_2$

Water balance on mixing point: $0.04n_1 + 0.017n_5 = 0.023n_2$

$\Downarrow$ $n_1 = 102.4\text{ mol}$, Solve simultaneously

$n_2 = 392.5\text{ mol}$

$\boxed{n_5 = 290\text{ mol recycled}}$

Almost three moles are recycled for every mole of air delivered to the room.

(b) Computer solution. There are five unknown variables on the flowchart ($n_1 - n_5$), and we can write two material balances for the mixing point, two more for the air conditioner, and one for the stream splitting point, for a total of five equations. We therefore have zero degrees of freedom, so the problem is solvable. The Excel spreadsheet will appear as follows for initial guesses of 100 mol for each of the five unknown variables. Overall balances are written for each subsystem, and water balances are written for the first two subsystems.

	A	B	C	D	E	F
1	**Solution to Example 4.5-1**					
2						
3	**Variable**	n_1	n_2	n_3	n_4	n_5
4	**Value**	100	100	100	100	100
5						
6	**Equation**	**LHS**	**RHS**	**(LHS–RHS)^2**		
7	$n_1 + n_5 = n_2$	200	100	1.00E + 04		
8	$0.04^*n_1 + 0.017^*n_5 = 0.023^*n_2$	5.7	2.3	1.16E + 01		
9	$n_2 = n_3 + n_4$	100	200	1.00E + 04		
10	$0.023^*n_2 = n_3 + 0.017^*n_4$	2.3	101.7	9.88E + 03		
11	$n_4 = n_5 + 100$	100	200	1.00E + 04		
12			SUM	3.99E + 04		

[B7] = B4 + F4
[B8] = 0.04*B4 + 0.017*F4
[B9] = C4
[B10] = 0.023*C4
[B11] = E4

[C7] = C4
[C8] = 0.023*C4
[C9] = D4 + E4
[C10] = D4 + 0.017*E4
[C11] = F4 + 100

[D7] = (B7–C7)^2
[D8] = (B8–C8)^2
[D9] = (B9–C9)^2
[D10] = (B10–C10)^2
[D11] = (B11–C11)^2
[D12] = SUM(D7:D11)

Once the values and formulas are entered, have *Solver* minimize the value in Cell D12 by adjusting the values in Cells B4 through F4. The solutions reported in Part (a) immediately appear in Row 4.

There are several reasons for using recycle in a chemical process besides the one given previously (recovering and reusing unconsumed reactants), including the following:

1. ***Recovery of catalyst.*** Many reactors use catalysts to increase the rate of the reaction. Catalysts are usually expensive, and the processes generally include provisions for recovering them from the product stream and recycling them to the reactor. They may be recovered with the unconsumed reactants or recovered separately in special facilities designed for this purpose.

Equipment Encyclopedia
filter
@
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2. ***Dilution of a process stream.*** Suppose a slurry (a suspension of solids in a liquid) is fed to a filter. If the concentration of solids in the slurry is too high, the slurry is difficult to handle and the filter will not operate properly. Rather than diluting the feed with fresh liquid, a portion of the filtrate can be recycled to dilute the feed to the desired solids concentration.

3. ***Control of a process variable.*** Suppose a reaction releases an extremely large amount of heat, making the reactor difficult and expensive to control. The rate of heat generation can be reduced by lowering the reactant concentration, which can in turn be accomplished by recycling a portion of the reactor effluent to the inlet. In addition to acting as a diluent for the reactants, the recycled material also serves as a capacitance for the heat released: the greater the mass of the reaction mixture, the lower the temperature to which that mass will be raised by a fixed amount of heat.

4. ***Circulation of a working fluid.*** The most common example of this application is the refrigeration cycle used in household refrigerators and air conditioners. In these devices, a single material is reused indefinitely, with only small makeup quantities occasionally being added to the system to replenish fluid that may be lost through leaks.

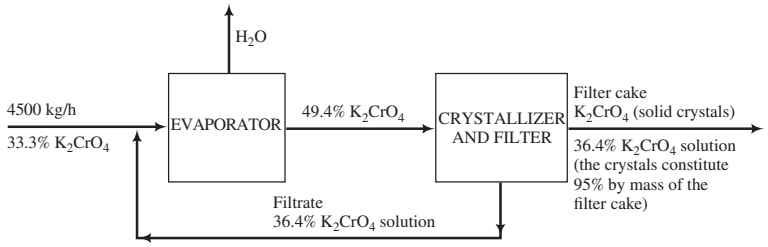
Part 1 of the next example presents a detailed material balance calculation for a separation process that involves recycle. Part 2 of the problem shows what would happen if the recycle were omitted and, in doing so, illustrates one of the reasons for recycling.

Example 4.5-2 An Evaporative Crystallization Process

Equipment Encyclopedia
evaporator, crystallizer, filter

www.wiley.com/college/felder

The flowchart of a steady-state process to recover crystalline potassium chromate (K_2CrO_4) from an aqueous solution of this salt is shown below.



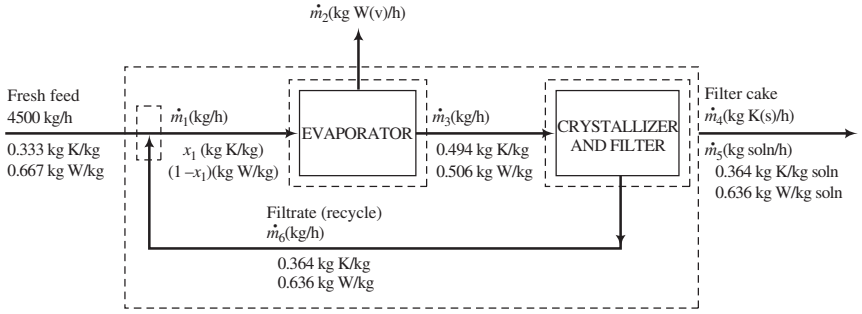
Forty-five hundred kilograms per hour of a solution that is one-third K_2CrO_4 by mass is joined by a recycle stream containing 36.4% K_2CrO_4, and the combined stream is fed to an evaporator. The concentrated stream leaving the evaporator contains 49.4% K_2CrO_4; this stream is fed into a crystallizer in which it is cooled (causing crystals of K_2CrO_4 to come out of solution) and then filtered. The wet filter cake consists of K_2CrO_4 crystals and solution that contains 36.4% K_2CrO_4 by mass. The crystals account for 95% of the total mass of the filter cake. The solution that passes through the filter, also 36.4% K_2CrO_4, is the recycle stream.

1. Calculate the rate of evaporation, the rate of production of crystalline K_2CrO_4, the feed rates that the evaporator and the crystallizer must be designed to handle, and the *recycle ratio* (mass of recycle)/(mass of fresh feed).
2. Suppose that the filtrate were discarded instead of being recycled. Calculate the production rate of crystals. What are the benefits and costs of the recycling?

Solution

1. Basis: 4500 kg/h Fresh Feed.

Let K denote K_2CrO_4 and W denote water. The flowchart is shown below; included on it are dashed boxes denoting the overall system and subsystems about which balances may be written.



In terms of labeled variables, the quantities requested in the problem statement are $\dot{m}_2$ (kg W evaporated/h), $\dot{m}_4$ [kg K(s)/h], $\dot{m}_1$ (kg/h fed to evaporator), $\dot{m}_3$ (kg/h fed to crystallizer), and ($\dot{m}_6$/4500 kg/h) (kg recycle/kg fresh feed).

Notice how the product stream is labeled to take maximum advantage of what we know about its composition. The filter cake is a mixture of solid K crystals and liquid solution with known K and W mass fractions. Instead of labeling as usual the mass flow rate and component mass fractions or the individual mass flow rates of K and W, we label the flow rates of the crystals and the solution, along with the solution component mass fractions. To confirm that the stream is fully labeled, we must verify that all component flow rates may be expressed in terms of labeled quantities. In this case, the total flow rate of potassium chromate is $\dot{m}_4 + 0.364\dot{m}_5$ (kg K/h) and the flow rate of water is $0.636\dot{m}_5$ (kg W/h), so that the labeling is complete.

Degree-of-Freedom Analysis

The degree-of-freedom analysis begins with the overall system and proceeds as follows:

- ***Overall system***

  3 unknown variables ($\dot{m}_2, \dot{m}_4, \dot{m}_5$)
  −2 balances (2 species involved)
  −1 additional relation ($\dot{m}_4 = 95\%$ of the total filter cake mass)
  0 degrees of freedom

  We will therefore be able to determine $\dot{m}_2$, $\dot{m}_4$, and $\dot{m}_5$ by analyzing the overall system.

- ***Recycle-fresh feed mixing point***

  3 unknown variables ($\dot{m}_6, \dot{m}_1, x_1$)
  −2 balances
  1 degree of freedom

  Since we do not have enough equations to solve for the unknowns associated with this subsystem, we proceed to the next one.

- ***Evaporator***

  3 unknown variables ($\dot{m}_1, x_1, \dot{m}_3$)
  −2 balances
  1 degree of freedom

  Again, no luck. We have one last hope.

- ***Crystallizer/filter***

  2 unknown variables ($\dot{m}_3, \dot{m}_6$)
  −2 balances
  0 degree of freedom

  We can therefore determine $\dot{m}_3$ and $\dot{m}_6$ by writing and solving balances on the crystallizer/filter and then analyze either the mixing point or the evaporator to determine the two remaining unknowns ($\dot{m}_1$ and x_1), thereby completing the solution. (*Suggestion:* Try to reproduce this analysis on your own before reading any farther.) The calculations follow, beginning with the analysis of the overall system.

  Since the solids constitute 95% by mass of the filter cake:

$$\dot{m}_4 = 0.95(\dot{m}_4 + \dot{m}_5)$$
$$\Downarrow \qquad (1)$$
$$\dot{m}_5 = 0.05263\,\dot{m}_4$$

We next write the two allowed overall system balances. The questions are, which ones and in what order?

- A total mass balance involves all three system variables—$\dot{m}_2$, $\dot{m}_4$, and $\dot{m}_5$.
- A K balance involves $\dot{m}_4$ and $\dot{m}_5$—the same two variables that occur in Equation 1.
- A W balance involves $\dot{m}_2$ and $\dot{m}_5$.

The procedure is therefore to write a K_2CrO_4 balance, solve it simultaneously with Equation 1 to determine $\dot{m}_4$ and $\dot{m}_5$, and then write a total mass balance to determine $\dot{m}_2$. The additive terms in each equation have units of kg/h of the balanced species.

Overall K_2CrO_4 Balance:

$$(0.333)(4500)\ \text{kg K/h} = \dot{m}_4 + 0.364\dot{m}_5$$
$$\Downarrow \text{ Solve simultaneously with Equation 1}$$
$$\dot{m}_4 = \boxed{1470\ \text{kg } K_2CrO_4 \text{ crystals/h}}$$
$$\dot{m}_5 = 77.5\ \text{kg entrained solution/h}$$

Overall Total Mass Balance:

$$4500\ \text{kg/h} = \dot{m}_2 + \dot{m}_4 + \dot{m}_5$$

$$\Downarrow \dot{m}_4 = 1470\ \text{kg/h},\ \dot{m}_5 = 77.5\ \text{kg/h}$$

$$\dot{m}_2 = \boxed{2950\ \text{kg H}_2\text{O evaporated/h}}$$

Mass Balance Around Crystallizer:

$$\dot{m}_3 = \dot{m}_4 + \dot{m}_5 + \dot{m}_6$$

$$\Downarrow \dot{m}_4 = 1470\ \text{kg/h},\ \dot{m}_5 = 77.5\ \text{kg/h}$$

$$\dot{m}_3 = 1550\ \text{kg/h} + \dot{m}_6 \qquad \textbf{(2)}$$

Water Balance Around Crystallizer:

$$0.506\dot{m}_3 = 0.636\dot{m}_5 + 0.636\dot{m}_6$$

$$\Downarrow \dot{m}_5 = 77.5\ \text{kg/h}$$

$$\dot{m}_3 = 97.4\ \text{kg/h} + 1.257\dot{m}_6 \qquad \textbf{(3)}$$

Solving Equations 2 and 3 simultaneously yields

$$\boxed{\dot{m}_3 = 7200\ \text{kg/h fed to crystallizer}}$$

$$\dot{m}_6 = 5650\ \text{kg/h}$$

and hence

$$\frac{\dot{m}_6(\text{kg recycle/h})}{4500\ \text{kg fresh feed/h}} = \frac{5650}{4500} = \boxed{1.26\ \frac{\text{kg recycle}}{\text{kg fresh feed}}}$$

Mass Balance Around Recycle-Fresh Feed Mixing Point:

$$4500\ \text{kg/h} + \dot{m}_6 = \dot{m}_1$$

$$\Downarrow \dot{m}_6 = 5650\ \text{kg/h}$$

$$\boxed{\dot{m}_1 = 10{,}150\ \text{kg/h feed to evaporator}}$$

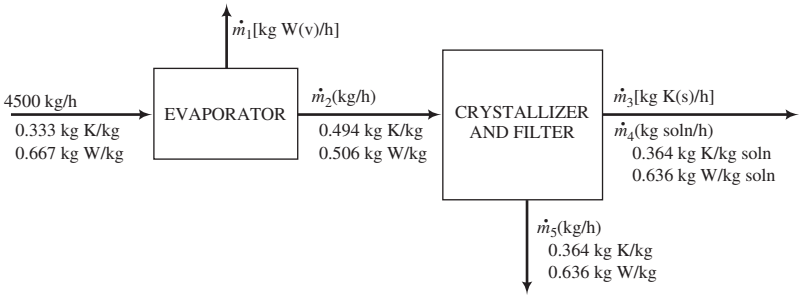
Check: A mass balance about the evaporator yields

$$\dot{m}_1 = \dot{m}_2 + \dot{m}_3$$

$\Longrightarrow$ 10,150 kg/h entering evaporator = (2950 + 7200) kg/h = 10,150 kg/h leaving evaporator. ✔

2. Basis: 4500 kg/h Fresh Feed.

The flowchart for the system without recycle appears as shown below.



We will not go through the detailed solution but will simply summarize. The degree-of-freedom analysis leads to the results that the overall system has one degree of freedom, the evaporator has zero, and the crystallizer-filter has one. (Verify these statements.) The strategy is therefore to begin with the evaporator and solve the balance equations for $\dot{m}_1$ and $\dot{m}_2$. Once $\dot{m}_2$ is known, the crystallizer has zero degrees of freedom and its three equations may be solved for $\dot{m}_3$, $\dot{m}_4$, and $\dot{m}_5$. The rate of production of crystals is

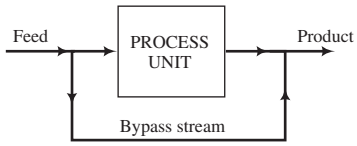
$$\boxed{\dot{m}_3 = 622\,\text{kg K(s)/h}}$$

With recycle it was 1470 kg/h, a dramatic difference. The mass flow rate of the filtrate is

$$\boxed{\dot{m}_5 = 2380\,\text{kg/h}}$$

The filtrate (which is discarded) contains $0.364 \times 2380 = 866$ kg/h of potassium chromate, more than the filter cake contains. Recycling the filtrate enables us to recover most of this salt. The obvious benefit of recycling is the revenue from selling the additional potassium chromate. The costs include the purchase and installation costs for the recycle piping and pump and the cost of power consumed by the pump. It would probably not take long for the benefit to equal the cost, and thereafter the recycling would continue to increase the process profitability.

A procedure that has several features in common with recycle is **bypass**, in which a fraction of the feed to a process unit is diverted around the unit and combined with the output stream from the unit. (For examples of processes that uses bypass, see Problems 4.43 and 4.44 at the end of this chapter.) By varying the fraction of the feed that is bypassed, we can vary the composition and properties of the product.



Bypass and recycle calculations are approached in exactly the same manner: the flowchart is drawn and labeled, and overall balances and balances around the process unit or the stream mixing point following the process unit are used to determine unknown variables.

4.6 CHEMICAL REACTION STOICHIOMETRY

The occurrence of a chemical reaction in a process brings several complications into the material balance procedures described in the previous sections. The stoichiometric equation of the reaction imposes constraints on the relative amounts of reactants and products in the input and output streams (if A → B, for example, you cannot start with 1 mol of pure A and end with 2 mol of B). In addition, a material balance on a reactive substance does not have the simple form input = output, but must include a generation and/or consumption term.

In this section we review reaction terminology and outline procedures for carrying out material balance calculations on reactive systems.

4.6a Stoichiometry

The **stoichiometric equation** of a chemical reaction is a statement of the *relative* number of molecules of reactants and products that participate in the reaction. For example, the stoichiometric equation for the oxidation of sulfur dioxide

$$2SO_2 + O_2 \rightarrow 2SO_3$$

indicates that for every two molecules of SO_2 consumed, one molecule of O_2 is consumed and two molecules of SO_3 are produced. Since a gram-mole of a species contains a fixed number of

molecules (6.02×10^{23}), the chemical equation also can be taken to mean two gram-moles of SO_2 react with one gram-mole of O_2 to produce two gram-moles of SO_3. The numbers that precede the symbols for each species are the **stoichiometric coefficients** of the species. They are written without units in stoichiometric equations, but when they are used in mass balances, they typically take on units (mol, kmol, lb-mole, etc.) of the species with which they are associated.

A valid stoichiometric equation must be *balanced*; that is, the number of atoms of each atomic species must be the same on both sides of the equation, since atoms can neither be created nor destroyed in chemical reactions (as opposed to nuclear reactions). The equation

$$SO_2 + O_2 \rightarrow SO_3$$

cannot be valid, for example, since it indicates that three atoms of atomic oxygen (O) are produced for every four atoms that enter into the reaction, for a net loss of one atom, but

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3 \qquad \begin{pmatrix} 1S \rightarrow 1S \\ 3O \rightarrow 3O \end{pmatrix}$$

and

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad \begin{pmatrix} 2S \rightarrow 2S \\ 6O \rightarrow 6O \end{pmatrix}$$

are balanced.

The **stoichiometric ratio** of two molecular species participating in a reaction is the ratio of their stoichiometric coefficients in the balanced reaction equation. This ratio can be used as a conversion factor to calculate the amount of a particular reactant (or product) that was consumed (or produced), given a quantity of another reactant or product that participated in the reaction. For the reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

you can write the stoichiometric ratios

$$\frac{2 \text{ mol } SO_3 \text{ generated}}{1 \text{ mol } O_2 \text{ consumed}}, \quad \frac{2 \text{ lb-moles } SO_2 \text{ consumed}}{2 \text{ lb-moles } SO_3 \text{ generated}}$$

and so on. If you know, for example, that 1600 kg/h of SO_3 is to be produced, you can calculate the amount of oxygen required as

$$\frac{1600 \text{ kg } SO_3 \text{ generated}}{\text{h}} \left| \frac{1 \text{ kmol } SO_3}{80 \text{ kg } SO_3} \right| \frac{1 \text{ kmol } O_2 \text{ consumed}}{2 \text{ kmol } SO_3 \text{ generated}} = 10 \frac{\text{kmol } O_2}{\text{h}}$$

$$\Longrightarrow 10 \frac{\text{kmol } O_2}{\text{h}} \left| \frac{32 \text{ kg } O_2}{1 \text{ kmol } O_2} \right. = 320 \text{ kg } O_2/\text{h}$$

It is a good practice to include the terms "consumed" and "generated" when performing conversions of this sort: simply writing 1 mol O_2/2 mol SO_3 could be taken to mean that 2 mol of SO_3 contains 1 mol of O_2, which is not true.

Test Yourself

(Answers, p. 655)

Consider the reaction

$$C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$$

1. Is the stoichiometric equation balanced?
2. What is the stoichiometric coefficient of CO_2?
3. What is the stoichiometric ratio of H_2O to O_2? (Include units.)

4. How many lb-moles of O_2 react to form 400 lb-moles of CO_2? (Use a dimensional equation.)
5. One hundred mol/min of C_4H_8 is fed into a reactor, and 50% reacts. At what rate is water formed?

4.6b Limiting and Excess Reactants, Fractional Conversion, and Extent of Reaction

Two reactants, A and B, are said to be present in **stoichiometric proportion** if the ratio (moles A present)/(moles B present) equals the stoichiometric ratio obtained from the balanced reaction equation. For the reactants in the reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

to be present in stoichiometric proportion, there must be 2 moles of SO_2 for every mole of O_2 (so that $n_{SO_2}/n_{O_2} = 2{:}1$) present in the feed to the reactor.

If reactants are fed to a chemical reactor in stoichiometric proportion and the reaction proceeds to completion, all of the reactants are consumed. In the above reaction, for example, if 200 mol of SO_2 and 100 mol of O_2 are initially present and the reaction proceeds to completion, the SO_2 and O_2 would disappear at the same instant. It follows that if you start with 100 mol of O_2 and less than 200 mol of SO_2 (i.e., if the SO_2 is present in less than its stoichiometric proportion), the SO_2 would disappear first, while if more than 200 mol of SO_2 is initially present the O_2 would be completely consumed first.

The reactant that would be eliminated first if a reaction proceeded to completion is called the **limiting reactant**, and the other reactants are termed **excess reactants**. *A reactant is limiting if it is present in less than its stoichiometric proportion relative to every other reactant*. If all reactants are present in stoichiometric proportion, then no reactant is limiting (or they all are, depending on how you choose to look at it).

Suppose $(n_A)_{feed}$ is the number of moles of an excess reactant, A, present in the feed to a reactor and that $(n_A)_{stoich}$ is the **stoichiometric requirement** of A, or the amount needed to react completely with the limiting reactant. Then $(n_A)_{feed} - (n_A)_{stoich}$ is the amount by which the A in the feed exceeds the amount needed to react completely if the reaction goes to completion. The **fractional excess** of the reactant is the ratio of the excess to the stoichiometric requirement:

$$\text{fractional excess of A} = \frac{(n_A)_{feed} - (n_A)_{stoich}}{(n_A)_{stoich}} \qquad \textbf{(4.6-1)}$$

The **percentage excess of A** is 100 times the fractional excess.

Consider, for example, the hydrogenation of acetylene to form ethane:

$$C_2H_2 + 2H_2 \rightarrow C_2H_6$$

and suppose that 20.0 kmol/h of acetylene and 50.0 kmol/h of hydrogen are fed to a reactor. The stoichiometric ratio of hydrogen to acetylene is 2:1 (the ratio of coefficients in the stoichiometric equation), and since the ratio of H_2 to C_2H_2 in the feed is 2.5:1 (50:20), hydrogen is fed in a greater-than-stoichiometric proportion to acetylene. Acetylene is therefore the limiting reactant. (Convince yourself.) Since it would take 40.0 kmol H_2/h to react completely with all the acetylene fed to the reactor, $(n_{H_2})_{stoich} = 40.0$ kmol/h, and from Equation 4.6-1,

$$\text{fractional excess of } H_2 = \frac{(50.0 - 40.0)\text{kmol/h}}{40.0\ \text{kmol/h}} = 0.25$$

We say that there is *25% excess hydrogen* in the feed.

Chemical reactions do not take place instantaneously, and indeed may proceed rather slowly. In such cases, it is not practical to design a reactor for complete conversion of the limiting reactant; instead, the reactor effluent emerges with some of the limiting reactant still present and is then usually subjected to a separation process to remove the unconverted reactant from the product. The separated reactant is then recycled to the reactor inlet. The **fractional conversion** of a reactant is the ratio

$$f = \frac{\text{moles reacted}}{\text{moles fed}} \tag{4.6-2}$$

The fraction unreacted is accordingly $1 - f$. If 100 moles of a reactant are fed and 90 moles react, the fractional conversion is 0.90 (the **percentage conversion** is 90%) and the fraction unreacted is 0.10. If 20 mol/min of a reactant is fed and the percentage conversion is 80%, then (20 mol/min)(0.80) = 16 mol/min has reacted and (20 mol/min)(1 − 0.80) = 4 mol/min remains unreacted.

Considering the reaction discussed above ($C_2H_2 + 2H_2 \rightarrow C_2H_6$), suppose 20.0 kmol of acetylene, 50.0 kmol of hydrogen, and 50.0 kmol of ethane are charged into a batch reactor. Furthermore, suppose that after some time 30.0 kmol of hydrogen has reacted. How much of each species will be present in the reactor at that moment?

Clearly, if you start with 50.0 kmol of H_2 and 30.0 kmol reacts, you will be left with $\boxed{20.0 \text{ kmol } H_2}$. Also, if 30.0 kmol of H_2 reacts, 15.0 kmol of C_2H_2 also reacts (Why?), leaving $(20.0 - 15.0)$ kmol $C_2H_2 = \boxed{5.0 \text{ kmol } C_2H_2}$. Finally, the 30.0 kmol of H_2 that reacts forms 15.0 kmol of C_2H_6, which when added to the 50.0 kmol you started with gives $\boxed{65.0 \text{ kmol } C_2H_6}$.

We next define a variable called the *extent of reaction*, which—like fractional conversion—is a measure of how far a reaction has proceeded from its initial state (at time 0 for a batch reaction or at the inlet of a continuous reactor) to some later point (e.g., the endpoint of the batch reaction or the product at the reactor outlet). Using the extent of reaction makes it easy to keep track of the molar quantities or flow rates of reactants and products in feed and outlet streams. Although the explanation we are about to give may seem somewhat complex, the method itself is simple.

To begin with, we define ν_i (where ν is the Greek letter nu) to be the **stoichiometric coefficient** of the ith species in a chemical reaction. As part of the definition, we specify that ν_i *has units of moles of Species i and is negative for reactants and positive for products*. For example, in the acetylene hydrogenation reaction ($C_2H_2 + 2H_2 \rightarrow C_2H_6$), $\nu_{C_2H_2} = -1$ mol C_2H_2, $\nu_{H_2} = -2$ mol H_2, and $\nu_{C_2H_6} = +1$ mol C_2H_6. If the reactor is continuous, we similarly define $\dot{\nu}_i$ (moles species i/time) with the same sign convention.

Let us stay with the acetylene hydrogenation reaction, but for convenience abbreviate the stoichiometric reaction as $A + 2B \rightarrow C$, so that $\nu_A = -1$ mol A, $\nu_B = -2$ mol B, $\nu_C = 1$ mol C. Suppose we start with n_{A0}, n_{B0}, and n_{C0} moles of A, B, and C, and at some time later there are n_A, n_B, and n_C moles of the three species in the reactor. We define the **extent of reaction** ξ (the Greek letter xi, which is pronounced as *zai* and rhymes with *high*) as follows:

$$\xi = \frac{(n_i - n_{i0})(\text{moles } i)}{\nu_i(\text{moles } i)}$$

The extent of reaction is clearly dimensionless. Other key properties of ξ are that it starts at zero when the reaction commences, increases as the reaction proceeds, and has the same value for all species. Let's see why. For the reaction we are considering, $A + 2B \rightarrow C$, we get

$$\xi = \frac{(n_i - n_{i0})(\text{moles } i)}{\nu_i(\text{moles } i)} = \frac{(n_A - n_{A0})(\text{moles A})}{-1 \text{ mole A}} = \frac{(n_B - n_{B0})(\text{moles B})}{-2 \text{ moles B}} = \frac{(n_C - n_{C0})(\text{moles C})}{1 \text{ mole C}}$$

The numerators of each of those four expressions represent the moles of each species (i, A, B, C) involved in the reaction. When the reaction commences, $n_i = n_{i0}$ for every species, and so the initial value of ξ is zero. Thereafter, the numerators must be negative for reactant species (since $n_i < n_{i0}$) and positive for products (since $n_i > n_{i0}$). Since ν_i is also negative for reactants and positive for products, the value of ξ must start at zero and increase as the reaction proceeds.

Finally, the quantities of species that react are proportional to their stoichiometric coefficients. In the reaction $A + 2B \rightarrow C$, for example, 2 moles of B react for every mole of A that reacts and every mole of C that is formed. The three expressions for ξ on the right, which are the ratios of amounts reacting to stoichiometric coefficients of each species, must therefore have the same value, so that ξ does not require the subscript i. The same result is obtained for any batch reaction, and if dots are put above the symbols n and ν, for continuous steady-state reactors as well. In short,

$$\xi = \frac{(n_i - n_{i0})(\text{moles } i)}{\nu_i(\text{moles } i)} = \frac{(\dot{n}_i - \dot{n}_{i0})(\text{moles } i/\text{time})}{\dot{\nu}_i(\text{moles } i/\text{time})} \tag{4.6-3}$$

If we know the values of n_{i0} for all species in a system and the value of n_i for any one species, we can calculate ξ from Eq. (4.6-3) for that species and then calculate the remaining n_i values from

$$\boxed{n_i = n_{i0} + \nu_i \xi \quad (\text{or } \dot{n}_i = \dot{n}_{i0} + \dot{\nu}_i \xi)} \tag{4.6-4}$$

Equations 4.6-3 and 4.6-4 enable you to keep track of how much of each species exists at any point in a reaction. If, for example, you know all the feed quantities n_{i0} ($i = 1, 2, 3, \ldots$.) and just one of the outlet quantities, say n_1, you can write Equation 4.6-3 for that species, substitute the known values of n_{10}, n_1, and ν_1, and solve for ξ. You can then calculate the amounts of all other species (2, 3, ...) from Equation 4.6-4.

For example, consider the ammonia formation reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Suppose the feed to a continuous reactor consists of 100 mol/s of nitrogen, 300 mol/s of hydrogen, and 1 mol/s of argon (an inert gas). From Equation 4.6-4, we may write for the reactor outlet flow rates

$$\begin{aligned} \dot{n}_{N_2} &= 100 \text{ mol } N_2/\text{s} + (-1 \text{ mol } N_2/\text{s})\xi \\ \dot{n}_{H_2} &= 300 \text{ mol } H_2/\text{s} + (-3 \text{ mol } H_2/\text{s})\xi \\ \dot{n}_{NH_3} &= (2 \text{ mol } NH_3/\text{s})\xi \\ \dot{n}_{Ar} &= 1 \text{ mol Ar/s} \end{aligned}$$

If you know the exit flow rate of any component or the fractional conversion of nitrogen or hydrogen, you can calculate ξ and then the other two unknown outlet flow rates. *Try it:* for a fractional conversion of hydrogen of 0.60, calculate the outlet flow rate of hydrogen, the extent of reaction, and the outlet flow rates of nitrogen and ammonia. The last value should be 120 mol/s.

A brief word about units: We explicitly included the units of stoichiometric coefficients in the above equations to emphasize dimensional consistency. It is not uncommon, however, to see the balances written as

$$\begin{aligned} \dot{n}_{N_2} &= 100 \text{ mol } N_2/\text{s} - \xi \\ \dot{n}_{H_2} &= 300 \text{ mol } H_2/\text{s} - 3\xi \\ \dot{n}_{NH_3} &= 2\xi \\ \dot{n}_{Ar} &= 1 \text{ mol Ar/s} \end{aligned}$$

where the numerical values of the stoichiometric coefficients (−1, −3, and 2) are understood to have units of mol/s. We accept such practice as inevitable but urge caution in its use.

Test Yourself

(Answers, p. 655)

The oxidation of ethylene to produce ethylene oxide proceeds according to the equation

$$2C_2H_4 + O_2 \rightarrow 2C_2H_4O$$

The feed to a reactor contains 100 kmol C_2H_4 and 100 kmol O_2.

1. Which reactant is limiting?
2. What is the percentage excess of the other reactant?
3. If the reaction proceeds to completion, how much of the excess reactant will be left; how much C_2H_4O will be formed; and what is the extent of reaction?
4. If the reaction proceeds to a point where the fractional conversion of the limiting reactant is 50%, how much of each reactant and product is present at the end, and what is the extent of reaction?
5. If the reaction proceeds to a point where 60 kmol of O_2 is left, what is the fractional conversion of C_2H_4? The fractional conversion of O_2? The extent of reaction?

CREATIVITY EXERCISE

Equipment Encyclopedia
reactors-batch reactor
www.wiley.com/college/felder

A single chemical reaction A → 2B takes place in a batch reactor, with known initial quantities of A and B. Think of as many process variables as you can that might vary with the extent of reaction; then suggest means by which each of these variables might be measured in an experiment to determine the extent of reaction versus time. For example, the refractive index of the reaction mixture might vary with the mixture composition; the experiment would then be to pass a beam of light through the reaction vessel and measure the angle of refraction as a function of time.

Example 4.6-1 Reaction Stoichiometry

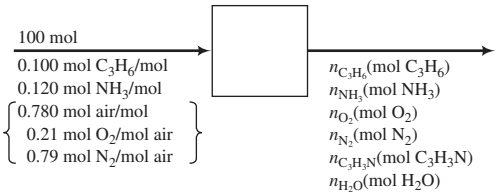
MATERIALS

Acrylonitrile is an intermediate used in the production of a number of polymers, including nylon (after conversion to hexamethylenediamine), acrylic fibers, and elastomers. It is used in the manufacture of many polymers including acrylonitrile butadiene styrene (ABS), a polymer used to make toys, pipes, musical instruments, and auto parts. The primary means of synthesizing acrylonitrile is ammoxidation of propylene:

$$C_3H_6 + NH_3 + \tfrac{3}{2}O_2 \rightarrow C_3H_3N + 3H_2O$$

The feed to a propylene ammoxidation process contains 10.0 mole% propylene, 12.0% ammonia, and 78.0% air. A fractional conversion of 30.0% of the limiting reactant is achieved. Taking 100 mol of feed as a basis, determine which reactant is limiting, the percentage by which each of the other reactants is in excess, and the molar amounts of all product gas constituents for a 30% conversion of the limiting reactant.

Solution **Basis: 100 mol Feed**



The feed to the reactor contains

$$(n_{C_3H_6})_0 = 10.0\ \text{mol}$$
$$(n_{NH_3})_0 = 12.0\ \text{mol}$$
$$(n_{O_2})_0 = \frac{78.0\ \text{mol air} \;\Big|\; 0.210\ \text{mol O}_2}{\text{mol air}} = 16.4\ \text{mol}$$

$$\Downarrow$$

$$\left.\begin{aligned}(n_{NH_3}/n_{C_3H_6})_0 &= 12.0/10.0 = 1.20\\ (n_{NH_3}/n_{C_3H_6})_{\text{stoich}} &= 1/1 = 1\end{aligned}\right\} \Longrightarrow \text{NH}_3 \text{ is in excess of } C_3H_6\ (1.20 > 1)$$

$$\left.\begin{aligned}(n_{O_2}/n_{C_3H_6})_0 &= 16.4/10.0 = 1.64\\ (n_{O_2}/n_{C_3H_6})_{\text{stoich}} &= 1.5/1 = 1.5\end{aligned}\right\} \Longrightarrow \text{O}_2 \text{ is in excess of } C_3H_6\ (1.64 > 1.5)$$

Since it is fed in less than stoichiometric proportion relative to the two other reactants, *propylene is the limiting reactant*.

To determine the percentages by which ammonia and oxygen are in excess, we must first determine the stoichiometric amounts of these reactants corresponding to the amount of propylene in the feed (10 mol) and then apply Equation 4.6-1.

$$(n_{NH_3})_{\text{stoich}} = \frac{10.0\ \text{mol } C_3H_6 \;\Big|\; 1\ \text{mol NH}_3}{1\ \text{mol } C_3H_6} = 10.0\ \text{mol NH}_3$$

$$(n_{O_2})_{\text{stoich}} = \frac{10.0\ \text{mol } C_3H_6 \;\Big|\; 1.5\ \text{mol O}_2}{1\ \text{mol } C_3H_6} = 15.0\ \text{mol O}_2$$

$$(\%\ \text{excess})_{NH_3} = \frac{(NH_3)_0 - (NH_3)_{\text{stoich}}}{(NH_3)_{\text{stoich}}} \times 100\%$$

$$= (12.0 - 10.0)/10.0 \times 100\% = \boxed{20\%\ \text{excess NH}_3}$$

$$(\%\ \text{excess})_{O_2} = (16.4 - 15.0)/15.0 \times 100\% = \boxed{9.3\%\ \text{excess O}_2}$$

If the fractional conversion of C_3H_6 is 30%, then

$$(n_{C_3H_6})_{\text{out}} = 0.700(n_{C_3H_6})_0 = \boxed{7.0\ \text{mol } C_3H_6}$$

But from Equation 4.6-4, $n_{C_3H_6} = 7.0\ \text{mol } C_3H_6 = (10.0 - \xi)\ \text{mol } C_3H_6$. The extent of reaction is therefore $\xi = 3.0$. Then also from Equation 4.6-4,

$$\begin{aligned}
n_{NH_3} &= 12.0\ \text{mol NH}_3 + \nu_{NH_3}\xi = &&\boxed{9.0\ \text{mol NH}_3}\\
n_{O_2} &= 16.0\ \text{mol O}_2 + \nu_{O_2}\xi = &&\boxed{11.9\ \text{mol O}_2}\\
n_{C_3H_3N} &= \nu_{C_3H_3N}\xi = &&\boxed{3.00\ \text{mol } C_3H_3N}\\
n_{N_2} &= (n_{N_2})_0 = &&\boxed{61.6\ \text{mol N}_2}\\
n_{H_2O} &= \nu_{H_2O}\xi = &&\boxed{9.0\ \text{mol H}_2O}
\end{aligned}$$

Reminder: The equations above are dimensionally homogeneous; for example, in the expression for n_{NH_3} the factor multiplying ξ is the stoichiometric coefficient of NH_3, which in this example is -1 mol NH_3.

4.6c Chemical Equilibrium

Two of the fundamental questions of chemical reaction engineering are: Given a set of reactive species and reaction conditions, (a) what will be the equilibrium composition of the reaction mixture, and (b) how long will the system take to reach a specified state short of equilibrium?

The field of **chemical equilibrium thermodynamics** concerns itself with the first question, and **chemical kinetics** deals with the second.

Some reactions are essentially **irreversible**: that is, the reaction proceeds only in a single direction (from reactants to products) and the concentration of the limiting reactant eventually approaches zero (although "eventually" could mean seconds for some reactions and years for others). The equilibrium composition for such a reaction is therefore the composition corresponding to complete consumption of the limiting reactant.

Other reactions (or the same reactions at different conditions) are **reversible**: reactants form products and products undergo the reverse reactions to reform the reactants. For example, consider the reversible reaction in which ethylene is hydrolyzed to ethanol:

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$

If you start with ethylene and water, the forward reaction occurs; then once ethanol is present, the reverse reaction begins to take place. As the concentrations of C_2H_4 and H_2O decrease, the rate of the forward reaction decreases, and as the C_2H_5OH concentration increases, the rate of the reverse reaction increases. Eventually a point is reached at which the rates of the forward and reverse reactions are equal. At this point no further composition change takes place, and the reaction mixture is in chemical equilibrium.

A full discussion of the relations that can be used to determine equilibrium compositions of reactive mixtures is beyond the scope of this text; however, at this point you have enough knowledge to be able to calculate equilibrium compositions if the relations are given to you. The next example illustrates such a calculation.

Example 4.6-2 Calculation of an Equilibrium Composition

Numerous chemical processes have been designed to produce hydrocarbon products from fossil fuels (coal, oil, natural gas). The first step in such processes often involves conversion of the fossil fuel to a mixture containing carbon monoxide and hydrogen, followed by the *water–gas shift reaction*, which adjusts the ratio of those species to a desired value:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Assume the reaction proceeds to equilibrium at a temperature T(K), and the mole fractions of the four reactive species satisfy the relationship

$$\frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = K(T)$$

where $K(T)$ is the reaction **equilibrium constant**. At $T = 1105$ K, $K = 1.00$.

Suppose the feed to a reactor contains 1.00 mol of CO, 2.00 mol of H_2O, and no CO_2 or H_2, and the reaction mixture comes to equilibrium at 1105 K. Calculate the equilibrium composition and the fractional conversion of the limiting reactant.

Solution The strategy is to express all mole fractions in terms of a single variable (ξ_e, the extent of reaction at equilibrium), substitute in the equilibrium relationship, solve for ξ_e, and back-substitute to calculate the mole fractions and any other desired quantity.

From Equation 4.6-4,

$$\begin{aligned} n_{CO} &= 1.00 \text{ mol CO} - \xi_e \\ n_{H_2O} &= 2.00 \text{ mol } H_2O - \xi_e \\ n_{CO_2} &= \xi_e \\ n_{H_2} &= \xi_e \\ \hline n_{total} &= 3.00 \text{ mol} \end{aligned}$$

from which

$$y_{CO} = (1.00 - \xi_e)/3.00$$
$$y_{H_2O} = (2.00 - \xi_e)/3.00$$
$$y_{CO_2} = \xi_e/3.00$$
$$y_{H_2} = \xi_e/3.00$$

Substitution of these expressions into the equilibrium relation (with $K = 1.00$) yields

$$\frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = \frac{\xi_e^2}{(1.00 - \xi_e)(2.00 - \xi_e)} = 1.00$$

This may be rewritten as a standard quadratic equation (*verify*) and solved to yield $\xi_e = 0.667$. This quantity may in turn be substituted back into the expressions for y_i to yield

$$\boxed{y_{CO} = 0.111, \quad y_{H_2O} = 0.444, \quad y_{CO_2} = 0.222, \quad y_{H_2} = 0.222}$$

The limiting reactant in this case is CO (*verify*). At equilibrium,

$$n_{CO} = (1.00 - 0.667)\ \text{mol} = 0.333\ \text{mol}$$

The fractional conversion of CO at equilibrium is therefore

$$f_{CO} = (1.00 - 0.333)\ \text{mol CO reacted}/(1.00\ \text{mol CO fed}) = \boxed{0.667}$$

4.6d Multiple Reactions, Yield, and Selectivity

In most chemical processes, reactants are brought together with the object of producing a desired product in a single reaction. Unfortunately, reactants often can combine in more than one way, and the product once formed may react to yield something less desirable. The result of these side reactions is an economic loss: (a) less of the desired product is obtained for a given quantity of raw materials, or a greater quantity of raw materials must be fed to the reactor to obtain a specified product yield, and (b) steps necessary to obtain the product in specified form and purity become more complicated.

For example, ethylene can be produced by the dehydrogenation of ethane:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Once some hydrogen is produced, it can react with ethane to produce methane:

$$C_2H_6 + H_2 \rightarrow 2CH_4$$

Moreover, ethylene can react with ethane to form propylene and methane:

$$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$$

Since the object of the process is to produce ethylene, only the first of these reactions may be regarded as desirable; the second consumes the reactant without yielding the desired product and the third consumes both the reactant and the desired product. In addition, instead of recovering ethylene from a mixture with only ethane and hydrogen, the occurrences of second and third reactions mean that the mixture also includes methane and propane, making recovery of the desired product more complex and costly. The engineer designing the reactor and specifying operating conditions for it must consider not only how to maximize the production of the desired product (C_2H_4), but also how to minimize the production of undesired by-products (CH_4, C_3H_6).

The terms **yield** and **selectivity** are used to describe the degree to which a desired reaction predominates over competing side reactions. Following are general definitions and a specific

illustration using the dehydrogenation of ethane (see previous paragraph) as an example, where ethylene (C_2H_4) is the desired product:

$$\text{Yield} = \frac{\text{moles of desired product formed}}{\text{moles that would be formed if there were no side reactions and the limiting reactant were consumed completely}} \times 100\% \quad \textbf{(4.6-5)}$$

$$\text{Selectivity} = \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}} \quad \textbf{(4.6-6)}$$

Applying these definitions to the dehydrogenation of ethane leads to the following expressions:

$$\text{Yield} = \frac{\left(n_{C_2H_4}\right)_{\text{gen}}}{\left(\nu_{C_2H_4}/\nu_{C_2H_6}\right)\left(n_{C_2H_6}\right)_{\text{input}}} \times 100\%$$

$$\text{Selectivity} = \frac{\left(n_{C_2H_4}\right)_{\text{gen}}}{\left(n_{CH_4}\right)_{\text{gen}}}$$

where $\left(n_{C_2H_4}\right)_{\text{gen}}$ is the ethylene generated, $\left(n_{C_2H_6}\right)_{\text{input}}$ is the ethane fed, $\left(n_{CH_4}\right)_{\text{gen}}$ is the methane generated, and $\nu_{C_2H_4}/\nu_{C_2H_6}$ is the ratio of stoichiometric coefficients. As defined by Equation 4.6-5, yield is a percentage, and fractional yield is determined simply by dividing by 100%. If A is the desired product and B is an undesired product, one then refers to the **selectivity of A relative to B**. In the above example, the second calculated quantity is the selectivity of ethane relative to methane. High values of yield and selectivity signify suppression of undesired side reactions relative to the desired reaction.

Besides being defined by Equation 4.6-5, yield is also sometimes defined as moles of desired product divided by either moles of reactant fed or moles of reactant consumed in the reactor. For given feed and product compositions, the yields defined in these three manners may have completely different values, so that when you see a reference to a yield it is important to be aware of the working definition. Similarly, a common alternative definition of selectivity is moles of the limiting reactant converted to the desired product divided by moles of the limiting reactant consumed × 100%.

The concept of extent of reaction can be extended to multiple reactions, only now each independent reaction has its own extent. If a set of reactions takes place in a batch or continuous steady-state reactor and ν_{ij} is the stoichiometric coefficient of substance i in reaction j (negative for reactants, positive for products), we may then write

$$n_i = n_{i0} + \sum_j \nu_{ij}\xi_j \quad \text{or} \quad \left(\dot{n}_i = \dot{n}_{i0} + \sum_j \dot{\nu}_{ij}\xi_j\right) \quad \textbf{(4.6-7)}$$

For a single reaction, this equation reduces to Equation 4.6-4.

As an example of how Equation 4.6-7 is applied, consider the pair of reactions in which ethylene is oxidized either to ethylene oxide (desired) or to carbon dioxide (undesired):

$$C_2H_4 + \tfrac{1}{2}\,O_2 \rightarrow C_2H_4O$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

The moles (or molar flow rates) of each of the five species involved in these reactions can be expressed in terms of the feed values and extents of reaction using Equation 4.6-7:

$$\begin{aligned}
\left(n_{C_2H_4}\right)_{\text{out}} &= \left(n_{C_2H_4}\right)_0 - \xi_1 - \xi_2 \\
\left(n_{O_2}\right)_{\text{out}} &= \left(n_{O_2}\right)_0 - 0.5\xi_1 - 3\xi_2 \\
\left(n_{C_2H_4O}\right)_{\text{out}} &= \left(n_{C_2H_4O}\right)_0 + \xi_1 \\
\left(n_{CO_2}\right)_{\text{out}} &= \left(n_{CO_2}\right)_0 + 2\xi_2 \\
\left(n_{H_2O}\right)_{\text{out}} &= \left(n_{H_2O}\right)_0 + 2\xi_2
\end{aligned}$$

If values of any two outlet amounts are given, the values of ξ_1 and ξ_2 may be determined from the corresponding two equations, and the remaining amounts may in turn be calculated from the remaining three equations. The next example illustrates this procedure.

Example 4.6-3 Yield and Selectivity in a Dehydrogenation Reactor

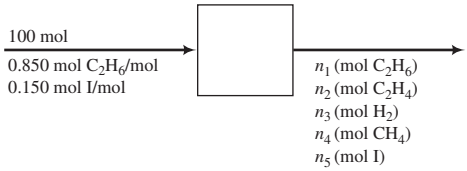
The reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
$$C_2H_6 + H_2 \rightarrow 2CH_4$$

take place in a continuous reactor at steady state. The feed contains 85.0 mole% ethane (C_2H_6) and the balance inerts (I). The fractional conversion of ethane is 0.501, and the fractional yield of ethylene is 0.471. Calculate the molar composition of the product gas and the selectivity of ethylene to methane production.

Solution

Basis: 100 mol Feed



From Equation 4.6-7, the outlet component amounts in terms of extents of reaction are as follows:

$$n_1(\text{mol } C_2H_6) = 85.0 \text{ mol } C_2H_6 - \xi_1 - \xi_2$$
$$n_2(\text{mol } C_2H_4) = \xi_1$$
$$n_3(\text{mol } H_2) = \xi_1 - \xi_2$$
$$n_4(\text{mol } CH_4) = 2\xi_2$$
$$n_5(\text{mol I}) = 15.0 \text{ mol I}$$

Ethane Conversion:

If the fractional conversion of ethane is 0.501, the fraction *un*converted (and hence leaving the reactor) must be $(1 - 0.501)$.

$$n_1 = \frac{(1 - 0.501) \text{ mol } C_2H_6 \text{ unreacted} \;\big|\; 85.0 \text{ mol } C_2H_6 \text{ fed}}{\text{mol } C_2H_6 \text{ fed}}$$
$$= 42.4 \text{ mol } C_2H_6 = 85.0 \text{ mol } C_2H_6 - \xi_1 - \xi_2 \qquad \textbf{(1)}$$

Ethylene Yield:

$$\text{maximum possible ethylene formed} = \frac{85.0 \text{ mol } C_2H_6 \text{ fed} \;\big|\; \dfrac{1 \text{ mol } C_2H_4}{1 \text{ mol } C_2H_6}}{} = 85.0 \text{ mol}$$

$$\Downarrow$$

$$n_2 = 0.471(85.0 \text{ mol } C_2H_6) = 40.0 \text{ mol } C_2H_4 \Longrightarrow \xi_1 = 40.0$$

Substituting 40.0 for ξ_1 in Equation 1 yields $\xi_2 = 2.6$. Then

$$n_3 = (\xi_1 - \xi_2) \text{ mol } H_2 = 37.4 \text{ mol } H_2$$
$$n_4 = 2\xi_2 \text{ mol } CH_4 = 5.2 \text{ mol } CH_4$$
$$n_5 = 15.0 \text{ mol I}$$

$$n_{tot} = (42.4 + 40.0 + 37.4 + 5.2 + 15.0)\,\text{mol} = 140.0\,\text{mol}$$

$$\Downarrow$$

Product: $\boxed{30.3\%\ C_2H_6, 28.6\%\ C_2H_4, 26.7\%\ H_2, 3.7\%\ CH_4, 10.7\%\ I}$

Selectivity: $= (40.0\ \text{mol}\ C_2H_4)/(5.2\ \text{mol}\ CH_4)$

$$= \boxed{7.7\ \frac{\text{mol}\ C_2H_4}{\text{mol}\ CH_4}}$$

Test Yourself

(Answers, p. 655)

Consider the following pair of reactions:

$$A \rightarrow 2B \text{ (desired)}$$
$$A \rightarrow C \text{ (undesired)}$$

Suppose 100 mol of A is fed to a batch reactor and the final product contains 10 mol of A, 160 mol of B, and 10 mol of C. Calculate

1. The fractional conversion of A.
2. The percentage yield of B.
3. The selectivity of B relative to C.
4. The extents of the first and second reactions.

4.7 BALANCES ON REACTIVE PROCESSES

4.7a Balances on Molecular and Atomic Species

Figure 4.7-1 shows a flowchart for the dehydrogenation of ethane in a steady-state continuous reactor. The reaction is

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

One hundred kmol/min of ethane is fed to the reactor. The molar flow rate of H_2 in the product stream is 40 kmol/min.

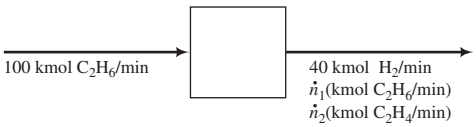


FIGURE 4.7-1 Dehydrogenation of ethane.

A number of different balances could be written on this process, including balances on total mass, C_2H_6, C_2H_4, and H_2. Of these, only the first has the simple form *input* = *output*: since the three given species all participate in the reaction, the balance equation for each of them must include a generation term (for C_2H_4 and H_2) or a consumption term (for C_2H_6).

Notice, however, that balance equations may also be written for atomic carbon and atomic hydrogen, regardless of the molecular species in which the carbon and hydrogen atoms happen to be found. Balances on atomic species *can* be written *input* = *output*, since atoms can neither be created (generation = 0) nor destroyed (consumption = 0) in a chemical reaction.

Before illustrating these balances, let us resolve an ambiguity. When we speak of a hydrogen balance, it could mean two completely different things: a balance on molecular hydrogen (H_2), existing as an independent species, or a balance on atomic hydrogen (H), bound and unbound. We

will henceforth use the terms **molecular hydrogen balance** and **atomic hydrogen balance** to represent these two types of balances, and it will be important for you to show this distinction in presenting your work.

Some of the balances that can be written for the process shown in Figure 4.7-1 are as follows. (Recall that the general balance equation for a batch process or a continuous steady-state process is input + generation = output + consumption.)

Molecular H_2 Balance: generation = output

$$\text{Gen}_{\text{H}_2}\left(\frac{\text{kmol H}_2\text{ generated}}{\text{min}}\right) = 40\ \text{kmol H}_2/\text{min}$$

C_2H_6 Balance: input = output + consumption

$$\frac{100\ \text{kmol C}_2\text{H}_6}{\text{min}} = \dot{n}_1\left(\frac{\text{kmol C}_2\text{H}_6}{\text{min}}\right) + \text{Cons}_{\text{C}_2\text{H}_6}\left(\frac{\text{kmol C}_2\text{H}_6\text{ consumed}}{\text{min}}\right)$$

C_2H_4 Balance: generation = output

$$\text{Gen}_{\text{C}_2\text{H}_4}\left(\frac{\text{kmol C}_2\text{H}_4\text{ generated}}{\text{min}}\right) = \dot{n}_2\left(\frac{\text{kmol C}_2\text{H}_4}{\text{min}}\right)$$

Atomic C Balance: input = output

$$\frac{100\ \text{kmol C}_2\text{H}_6}{\text{min}}\left|\frac{2\ \text{kmol C}}{1\ \text{kmol C}_2\text{H}_6}\right. = \dot{n}_1\frac{\text{kmol C}_2\text{H}_6}{\text{min}}\left|\frac{2\ \text{kmol C}}{1\ \text{kmol C}_2\text{H}_6}\right. + \dot{n}_2\frac{\text{kmol C}_2\text{H}_4}{\text{min}}\left|\frac{2\ \text{kmol C}}{1\ \text{kmol C}_2\text{H}_4}\right.$$

$$\Downarrow$$

$$200\ \text{kmol C/min} = 2\dot{n}_1 + 2\dot{n}_2$$

Atomic H Balance: input = output

$$\frac{100\ \text{kmol C}_2\text{H}_6}{\text{min}}\left|\frac{6\ \text{kmol H}}{1\ \text{kmol C}_2\text{H}_6}\right. = \frac{40\ \text{kmol H}_2}{\text{min}}\left|\frac{2\ \text{kmol H}}{1\ \text{kmol H}_2}\right.$$

$$+ \dot{n}_1\frac{\text{kmol C}_2\text{H}_6}{\text{min}}\left|\frac{6\ \text{kmol H}}{1\ \text{kmol C}_2\text{H}_6}\right. + \dot{n}_2\frac{\text{kmol C}_2\text{H}_4}{\text{min}}\left|\frac{4\ \text{kmol H}}{1\ \text{kmol C}_2\text{H}_4}\right.$$

$$\Downarrow$$

$$200\ \text{kmol C/min} = 2\dot{n}_1 + 2\dot{n}_2$$

You could solve for $\dot{n}_1$ and $\dot{n}_2$ either directly from the two atomic balances or by using the three molecular species balances in conjunction with the stoichiometric equation for the reaction.

In general, systems that involve chemical reactions may be analyzed using (a) molecular species balances (the approach always used for nonreactive systems), (b) atomic species balances, and (c) extents of reaction. Each approach leads to the same results, but any one of them may be more convenient for a given calculation so it's a good idea to become comfortable with all three.

To carry out degree-of-freedom analyses of reactive systems you must first understand the concepts of *independent equations*, *independent species*, and *independent chemical reactions*. We explain these concepts in the next section, following which we outline and illustrate the three approaches to reactive system balance calculations.

4.7b Independent Equations, Independent Species, and Independent Reactions

When we first described degree-of-freedom analysis in Section 4.3d, we said that the maximum number of material balances you can write for a nonreactive process equals the number of

independent species involved in the process. It is time to take a closer look at what that means and to see how to extend the analysis to reactive processes.

The key concept is that of **independent equations**. Algebraic equations are independent if you cannot obtain any one of them by adding and subtracting multiples of any of the others. For example, the equations

$$[1] \quad x + 2y = 4$$
$$[2] \quad 3x + 6y = 12$$

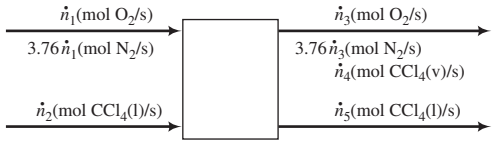
are not independent, because $[2] = 3 \times [1]$. In effect, they are really the same equation. (Convince yourself by seeing what happens if you try to solve the two equations for x and y.) Similarly but less obviously, the equations

$$[1] \quad x + 2y = 4$$
$$[2] \quad 2x - z = 2$$
$$[3] \quad 4y + z = 6$$

are not independent, because $[3] = 2 \times [1] - [2]$. (Prove it.)

If two molecular species are in the same ratio to each other wherever they appear in a process and this ratio is incorporated in the flowchart labeling, balances on those species will not be independent equations. Similarly, if two atomic species occur in the same ratio wherever they appear in a process, balances on those species will not be independent equations.

For example, consider a process in which a stream of liquid carbon tetrachloride is vaporized into a stream of air.



Since nitrogen and oxygen are shown as being in the same ratio wherever they appear on the flowchart (3.76 mol N_2/mol O_2), you cannot count them as two independent species and so you may count only two independent molecular species balances in a degree-of-freedom analysis—one for either O_2 or N_2 and one for CCl_4. (Try writing separate O_2 and N_2 balances and see what you get.)

Similarly, atomic nitrogen (N) and atomic oxygen (O) are always in the same proportion to each other in the process (again 3.76:1) as are atomic chlorine and atomic carbon (4 mol Cl/1 mol C). Consequently, even though four atomic species are involved in this process, you may count only two independent atomic species balances in the degree-of-freedom analysis—one for either O or N and one for either C or Cl. (Again, convince yourself that the O and N balances yield the same equation, as do the C and Cl balances.)

Finally, when you are using either molecular species balances or extents of reaction to analyze a reactive system, the degree-of-freedom analysis must account for the number of independent chemical reactions among the species entering and leaving the system. *Chemical reactions are independent if the stoichiometric equation of any one of them cannot be obtained by adding and subtracting multiples of the stoichiometric equations of the others.*

For example, consider the reactions

$$[1] \quad \mathrm{A} \longrightarrow 2\mathrm{B}$$
$$[2] \quad \mathrm{B} \longrightarrow \mathrm{C}$$
$$[3] \quad \mathrm{A} \longrightarrow 2\mathrm{C}$$

These three reactions are not all independent, since [3] = [1] + 2 × [2].

[1]: $A \longrightarrow 2B$

$2 \times$ [2]: $2B \longrightarrow 2C$

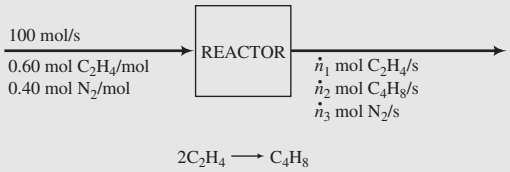
[1] + 2 × [2]: $A + 2B \longrightarrow 2B + 2C \Longrightarrow A \longrightarrow 2C$ (= [3])

However, any two of the reactions are independent. (They must be, since each one involves at least one species that does not appear in the other one.)

Test Yourself

(Answers, p. 655)

1. A mixture of ethylene and nitrogen is fed to a reactor in which some of the ethylene is dimerized to butene.



How many independent molecular species are involved in the process? How many independent atomic species are involved? Prove the latter claim by writing balances on C, H, and N.

2. Write the stoichiometric equations for the combustion of methane with oxygen to form (a) CO_2 and H_2O and (b) CO and H_2O; and for the combustion of ethane with oxygen to form (c) CO_2 and H_2O and (d) CO and H_2O. Then prove that only three of these four reactions are independent.

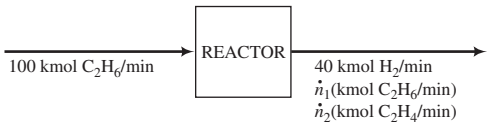
4.7c Molecular Species Balances

If molecular species balances are used to determine unknown stream variables for a reactive process, the balances on reactive species must contain generation and/or consumption terms. The degree-of-freedom analysis is as follows:

No. unknown labeled variables
+ No. independent chemical reactions (as defined in Section 4.7b)
− No. independent molecular species balances (as defined in Section 4.7b)
− No. other equations relating unknown variables
= No. degrees of freedom

Once a generation or consumption term has been calculated for a species in a given reaction, the generation and consumption terms for all other species in that reaction may be determined directly from the stoichiometric equation. (We will shortly illustrate this determination.) One generation or consumption term must therefore either be specified or calculated for each independent reaction, which is why each reaction adds a degree of freedom to the system.

We will use the dehydrogenation of ethane (Figure 4.7-1) to illustrate the required procedures. The flowchart is shown again here for ease of reference.



Degree-of-Freedom Analysis

2 unknown labeled variables ($\dot{n}_1, \dot{n}_2$)
+ 1 independent chemical reaction
− 3 independent molecular species balances (C_2H_6, C_2H_4, and H_2)
− 0 other equations relating unknown variables
= 0 degrees of freedom

The hydrogen balance will be used to determine the rate of hydrogen generation, and the outlet flow rates of ethane and ethylene will be calculated from the balances on those species. Notice how the ethane consumption and ethylene generation terms are determined directly from the hydrogen generation term.

H_2 Balance: generation = output

$$\text{Gen}_{H_2}\left(\frac{\text{kmol } H_2 \text{ generated}}{\text{min}}\right) = 40 \text{ kmol } H_2/\text{min}$$

C_2H_6 Balance: input = output + consumption

$$100\ \frac{\text{kmol } C_2H_6}{\text{min}} = \dot{n}_1\left(\frac{\text{kmol } C_2H_6}{\text{min}}\right) + \frac{40 \text{ kmol } H_2 \text{ generated}}{\text{min}} \left| \frac{1 \text{ kmol } C_2H_6 \text{ consumed}}{1 \text{ kmol } H_2 \text{ generated}} \right. \Longrightarrow \boxed{\dot{n}_1 = 60 \text{ kmol } C_2H_6/\text{min}}$$

C_2H_4 Balance: generation = output

$$\frac{40 \text{ kmol } H_2 \text{ generated}}{\text{min}} \left| \frac{1 \text{ kmol } C_2H_4 \text{ generated}}{1 \text{ kmol } H_2 \text{ generated}} \right. = \dot{n}_2\left(\frac{\text{kmol } C_2H_4}{\text{min}}\right)$$

$$\Longrightarrow \boxed{\dot{n}_2 = 40 \text{ kmol } C_2H_4/\text{min}}$$

4.7d Atomic Species Balances

All balances on atomic species (C, H, O, etc.) take the form "input = output," since atomic species can neither be generated nor consumed in chemical reactions (as opposed to nuclear reactions). The number of degrees of freedom is determined directly by subtracting equations from labeled unknowns: no additional degrees of freedom are contributed by the reactions.

No. unknown labeled variables
− No. independent atomic species balances (as defined in Section 4.7b)
− No. independent molecular species balances on nonreactive species
− No. other equations relating unknown variables
= No. degrees of freedom

In the ethane dehydrogenation process, the two unknown flow rates will be determined from balances on atomic carbon and atomic hydrogen.

Degree-of-Freedom Analysis

2 unknown labeled variables
− 2 independent atomic species balances (C and H)
− 0 independent molecular species balances on nonreactive species
− 0 other equations relating unknown variables
= 0 degrees of freedom

C Balance: input = output

$$\frac{100\ \text{kmol } C_2H_6}{\text{min}} \left| \frac{2\ \text{kmol C}}{1\ \text{kmol } C_2H_6} \right.$$

$$= \frac{\dot{n}_1(\text{kmol } C_2H_6)}{(\text{min})} \left| \frac{2\ \text{kmol C}}{1\ \text{kmol } C_2H_6} \right. + \frac{\dot{n}_2(\text{kmol } C_2H_4)}{(\text{min})} \left| \frac{2\ \text{kmol C}}{1\ \text{kmol } C_2H_4} \right.$$

$$\Downarrow$$

$$100 = \dot{n}_1 + \dot{n}_2 \tag{1}$$

H Balance: input = output

$$\frac{100\ \text{kmol } C_2H_6}{\text{min}} \left| \frac{6\ \text{kmol H}}{1\ \text{kmol } C_2H_6} \right. = \frac{40\ \text{kmol } H_2}{\text{min}} \left| \frac{2\ \text{kmol H}}{1\ \text{kmol } H_2} \right.$$

$$+ \frac{\dot{n}_1(\text{kmol } C_2H_6)}{(\text{min})} \left| \frac{6\ \text{kmol H}}{1\ \text{kmol } C_2H_6} \right. + \frac{\dot{n}_2(\text{kmol } C_2H_4)}{(\text{min})} \left| \frac{4\ \text{kmol H}}{1\ \text{kmol } C_2H_4} \right.$$

$$\Downarrow$$

$$600\ \text{mol H/min} = 80\ \text{mol H/min} + 6\dot{n}_1 + 4\dot{n}_2 \tag{2}$$

Solving Equations (1) and (2) simultaneously yields the same solutions obtained with atomic species balances:

$$\boxed{\dot{n}_1 = 60\ \text{kmol } C_2H_6/\text{min}}$$

$$\boxed{\dot{n}_2 = 40\ \text{kmol } C_2H_4/\text{min}}$$

4.7e Extent of Reaction

The third way to determine molar amounts (or unknown molar flow rates) for a reactive process is to write expressions for each product species molar amount or flow rate in terms of extents of reaction using Equation 4.6-4 (or Equation 4.6-7 for multiple reactions), substitute known feed and product flow rates, and solve for the extents of reaction and the remaining reactive species amounts or flow rates. The degree-of-freedom analysis follows:

No. unknown labeled variables
+ No. independent reactions (one unknown extent of reaction for each)
− No. independent reactive species
(one equation for each species in terms of extents of reaction)
− No. independent nonreactive species (one balance equation for each)
− No. other equations relating unknown variables
= No. degrees of freedom

In the dehydrogenation process (refer one final time to the flowchart on p. 143), DF = 2 unknown variables ($\dot{n}_1, \dot{n}_2$) + 1 independent reaction – 3 independent reactive species (C_2H_6, C_2H_4, H_2) = 0. For the same process, Equation 4.6-4 ($\dot{n}_i = \dot{n}_{i0} + \nu_i\xi$) for the three species in the process are shown below. The units for each term of the first equation are shown explicitly.

$$H_2\left(\nu = 1\ \frac{\text{kmol } H_2}{\text{min}}\right)\text{:}\ 40\ \frac{\text{kmol } H_2}{\text{min}} = 0\ \frac{\text{kmol } H_2}{\text{min}} + \left(1\ \frac{\text{kmol } H_2}{\text{min}}\right)\xi \Longrightarrow \xi = 40$$

$$C_2H_6\left(\nu = -1\ \frac{\text{kmol } C_2H_6}{\text{min}}\right)\text{:}\ \dot{n}_1\left(\frac{\text{kmol } C_2H_6}{\text{min}}\right) = 100 - \xi \Longrightarrow \dot{n}_1 = 60\ \frac{\text{kmol } C_2H_6}{\text{min}}$$

$$C_2H_4\left(\nu = 1\ \frac{\text{kmol } C_2H_6}{\text{min}}\right)\text{:}\ \dot{n}_2\left(\frac{\text{kmol } C_2H_6}{\text{min}}\right) = \xi \Longrightarrow \dot{n}_2 = 40\ \frac{\text{kmol } C_2H_4}{\text{min}}$$

Given that all three methods of carrying out material balances on reactive systems—molecular species balances, atomic species balances, and extents of reaction—necessarily yield the same results, the question is which one to use for a given reactive process. There are no hard and fast rules but we suggest the following guidelines:

- *Atomic species balances generally lead to the most straightforward solution procedure, especially when more than one reaction is involved.*
- *Extents of reaction are convenient for chemical equilibrium problems and when equation-solving software is to be used.*
- *Molecular species balances require more complex calculations than either of the other two approaches and should be used only for simple systems involving one reaction.*

The next example illustrates all three approaches for a system involving two reactions.

Example 4.7-1 Incomplete Combustion of Methane

Methane is burned with air in a continuous steady-state combustion reactor to yield a mixture of carbon monoxide, carbon dioxide, and water. The reactions taking place are

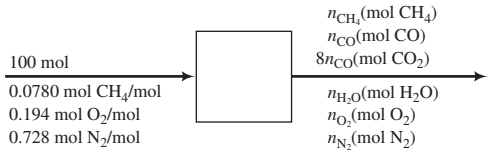
$$CH_4 + \tfrac{3}{2}O_2 \rightarrow CO + 2H_2O \quad \textbf{(1)}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \textbf{(2)}$$

The feed to the reactor contains 7.80 mole% CH_4, 19.4% O_2, and 72.8% N_2. The percentage conversion of methane is 90.0%, and the gas leaving the reactor contains 8 mol CO_2/mol CO. Carry out a degree-of-freedom analysis on the process. Then calculate the molar composition of the product stream using molecular species balances, atomic species balances, and extents of reaction.

Solution

Basis = 100 mol Feed



Degree-of-Freedom Analysis

The analysis can be based on any of the three solution methods:

- ***Molecular species balances*** (Section 4.7c). 5 unknown variables + 2 independent reactions − 6 independent molecular species balances ($CH_4, O_2, N_2, CO, CO_2, H_2O$) − 1 specified methane conversion = 0 degrees of freedom.
- ***Atomic species balances*** (Section 4.7d). 5 unknown variables − 3 independent atomic species balances (C, H, O) − 1 nonreactive molecular species balance (N_2) − 1 specified methane conversion = 0 degrees of freedom.
- ***Extents of reaction*** (Section 4.7e). 5 unknown variables + 2 independent reactions − 5 expressions for $n_i(\xi)$ ($i = CH_4, O_2, CO, CO_2, H_2O$) − 1 nonreactive molecular species balance (N_2) − 1 specified methane conversion = 0 degrees of freedom.

Before balances are written, the specified methane conversion can be used to determine n_{CH_4}.

90% CH_4 Conversion: (10% remains unconverted)

$$n_{CH_4} = 0.100(7.80 \text{ mol } CH_4 \text{ fed}) = 0.780 \text{ mol } CH_4$$

All three solution methods involve writing a balance on nitrogen (the nonreactive species in the process), so we do that next.

N_2 Balance: input = output

$$\boxed{n_{N2} = 72.8 \text{ mol } N_2}$$

It remains to determine n_{CO}, n_{H_2O}, and n_{O_2}. We will proceed by each of the indicated methods.

Molecular Species Balances

As we mentioned before, this method is the most cumbersome when multiple reactions are involved and we strongly recommend against using it. We present it here only for illustrative purposes (mainly to illustrate why we recommend against using it).

Each balance on a reactive species will contain generation and/or consumption terms. We will use the notation $C_{CH_4,1}$(mol CH_4) to denote the consumption of methane in Reaction 1, $G_{H_2O,2}$ (mol H_2O) to denote the generation of water in Reaction 2, and so on. Note that any G and C term for a specified reaction may be expressed in terms of any other G or C term for the same reaction directly from the stoichiometric equation. For example, the generation of water in Reaction 1 may be expressed in terms of the consumption of oxygen in that reaction as

$$G_{H_2O,1}(\text{mol } H_2O \text{ generated in Reaction 1}) = C_{O_2,1}(\text{mol } O_2 \text{ consumed in Reaction 1}) \times \left(\frac{2 \text{ mol } H_2O \text{ generated}}{1.5 \text{ mol } O_2 \text{ consumed}}\right) \quad (Verify!)$$

Since the balances on CO and CO_2 each involve the same unknown molar amount (n_{CO}), we will begin with those balances. Make sure you understand the form of each balance.

CO Balance: output = generation

$$n_{CO} = G_{CO,1} \tag{3}$$

CO_2 Balance: output = generation

$$8n_{CO} = G_{CO_2,2} \tag{4}$$

Since we know both the feed and output amounts of methane, a methane balance should involve only the two methane consumption terms (one for each reaction) as unknowns. Since $C_{CH_4,1}$ can be expressed in terms of $G_{CO,1}$ and $C_{CH_4,2}$ can be expressed in terms of $G_{CO_2,2}$, the CO, CO_2, and CH_4 balances will yield three equations in three unknowns—n_{CO}, $G_{CO,1}$, and $G_{CO_2,2}$

CH_4 Balance: input = output + consumption

$$7.80 \text{ mol } CH_4 = 0.780 \text{ mol } CH_4 + C_{CH_4,1} + C_{CH_4,2}$$

$$\Downarrow \quad C_{CH_4,1} = G_{CO,1} \times (1 \text{ mol } CH_4 \text{ consumed/1 mol CO generated})$$
$$\Downarrow \quad C_{CH_4,2} = G_{CO,2} \times (1 \text{ mol } CH_4 \text{ consumed/1 mol } CO_2 \text{ generated})$$

$$7.02 \text{ mol } CH_4 = G_{CO,1} + G_{CO_2,2}$$

$$\Downarrow \quad \text{Equations 3 and 4}$$

$$7.02 \text{ mol } CH_4 = n_{CO} + 8n_{CO} = 9n_{CO}$$

$$\Downarrow$$

$$\boxed{n_{CO} = 0.780 \text{ mol CO}}$$

$$\boxed{n_{CO_2} = (8 \times 0.780) \text{ mol } CO_2 = 6.24 \text{ mol } CO_2}$$

Equations 3 and 4 now yield

$$G_{CO,1} = n_{CO} = 0.780 \text{ mol CO generated} \tag{5}$$

$$G_{CO_2,2} = 8n_{CO} = 6.24 \text{ mol } CO_2 \text{ generated} \tag{6}$$

Water and oxygen balances complete the calculation of the unknown flow rates.

H_2O Balance: output = generation

$$n_{H_2O} = G_{H_2O,1} + G_{H_2O,2}$$

$$= G_{CO,1}\left(\frac{2 \text{ mol } H_2O \text{ generated}}{1 \text{ mol CO generated}}\right) + G_{CO_2,2}\left(\frac{2 \text{ mol } H_2O \text{ generated}}{1 \text{ mol } CO_2 \text{ generated}}\right)$$

$$\Downarrow G_{CO,1} = 0.780 \text{ mol CO generated}, \; G_{CO_2,2} = 6.24 \text{ mol } CO_2 \text{ generated}$$

$$\boxed{n_{H_2O} = 14.0 \text{ mol } H_2O}$$

O_2 Balance: output = generation − consumption

$$n_{O_2} = 19.4 \text{ mol } O_2 - C_{O_2,1} - C_{O_2,2}$$

$$= 19.4 \text{ mol } O_2 - G_{CO,1}\left(\frac{1.5 \text{ mol } O_2 \text{ consumed}}{1 \text{ mol CO generated}}\right) + G_{CO_2,2}\left(\frac{2 \text{ mol } O_2 \text{ consumed}}{1 \text{ mol } CO_2 \text{ generated}}\right)$$

$$\Downarrow G_{CO,1} = 0.780 \text{ mol CO generated}, \; G_{CO_2,2} = 6.24 \text{ mol } CO_2 \text{ generated}$$

$$\boxed{n_{O_2} = 5.75 \text{ mol } O_2}$$

In summary, the stack gas contains 0.780 mol CH_4, 0.780 mol CO, 6.24 mol CO_2, 14.0 mol H_2O, 5.75 mol O_2, and 72.8 mol N_2. The molar composition of the gas is therefore

$$\boxed{0.78\% \text{ } CH_4, 0.78\% \text{ CO}, 6.2\% \text{ } CO_2, 14.0\% \text{ } H_2O, 5.7\% \text{ } O_2, \text{ and } 72.5\% \text{ } N_2}$$

Atomic Species Balances

Referring to the flowchart, we see that a balance on atomic carbon involves only one unknown (n_{CO}) and a balance on atomic hydrogen also involves one unknown (n_{H_2O}), but a balance on atomic oxygen involves three unknowns. We will therefore write the C and H balances first, and then the O balance to determine the remaining unknown variable, n_{O_2}. All atomic species balances have the form *input* = *output*. We will just determine the component amounts in the product stream; calculation of the mole fractions then follows as in the previous part.

C Balance:

$$\frac{7.8 \text{ mol } CH_4}{} \left|\frac{1 \text{ mol C}}{1 \text{ mol } CH_4}\right. = \frac{0.78 \text{ mol } CH_4}{} \left|\frac{1 \text{ mol C}}{1 \text{ mol } CH_4}\right.$$

$$+ \frac{n_{CO}(\text{mol CO})}{} \left|\frac{1 \text{ mol C}}{1 \text{ mol CO}}\right. + \frac{8n_{CO}(\text{mol } CO_2)}{} \left|\frac{1 \text{ mol C}}{1 \text{ mol } CO_2}\right.$$

$$\Downarrow \text{Solve for } n_{CO}$$

$$\boxed{n_{CO} = 0.780 \text{ mol CO}}$$

$$\boxed{n_{CO_2} = 8n_{CO} = (8 \times 0.780) \text{ mol } CO_2 = 6.24 \text{ mol } CO_2}$$

H Balance:

$$\frac{7.8 \text{ mol } CH_4}{} \left|\frac{4 \text{ mol H}}{1 \text{ mol } CH_4}\right. = \frac{0.78 \text{ mol } CH_4}{} \left|\frac{4 \text{ mol H}}{1 \text{ mol } CH_4}\right.$$

$$+ \frac{n_{H_2O}(\text{mol } H_2O)}{} \left|\frac{2 \text{ mol H}}{1 \text{ mol } H_2O}\right. \Longrightarrow \boxed{n_{H_2O} = 14.0 \text{ mol } H_2O}$$

O Balance:

$$\frac{19.4\ \text{mol O}_2}{}\left|\frac{2\ \text{mol O}}{1\ \text{mol O}_2}\right. = \frac{n_{O_2}(\text{mol O}_2)}{}\left|\frac{2\ \text{mol O}}{1\ \text{mol O}_2}\right. + \frac{0.78\ \text{mol CO}}{}\left|\frac{1\ \text{mol O}}{1\ \text{mol CO}}\right.$$

$$+ \frac{6.24\ \text{mol CO}_2}{}\left|\frac{2\ \text{mol O}}{1\ \text{mol CO}_2}\right. + \frac{14.0\ \text{mol H}_2\text{O}}{}\left|\frac{1\ \text{mol O}}{1\ \text{mol H}_2\text{O}}\right.$$

$$\Longrightarrow \boxed{n_{O_2} = 5.75\ \text{mol O}_2}$$

The flow rates are the same as those calculated with molecular balances (as they must be), only this calculation involves much less effort.

Extents of Reaction

For the reactions

$$\text{CH}_4 + \tfrac{3}{2}\,\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} \tag{1}$$

$$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \tag{2}$$

Equation 4.6-7 ($n_i = n_{i0} + \Sigma \nu_{ij}\xi_j$) for the reactive species involved in the process yields the following five extent of reaction balances [(3)–(7)] in five unknowns ($\xi_1, \xi_2, n_{CO}, n_{H_2O}, n_{O_2}$):

$$\begin{aligned} n_{CH_4}(= 0.78\ \text{mol CH}_4) &= (n_{CH_4})_0 + (\nu_{CH_4})_1\xi_1 + (\nu_{CH_4})_2\xi_2 \\ &= 7.80\ \text{mol CH}_4 + (-1\ \text{mol CH}_4)\xi_1 + (-1\ \text{mol CH}_4)\xi_2 \qquad (3) \\ &= (7.80 - \xi_1 - \xi_2)\ \text{mol CH}_4 \end{aligned}$$

$$n_{CO} = (1\ \text{mol CO})\xi_1 \tag{4}$$

$$8n_{CO}(= n_{CO_2}) = (1\ \text{mol CO}_2)\xi_2 \tag{5}$$

$$n_{H_2O} = (2\ \text{mol H}_2\text{O})\xi_1 + (2\ \text{mol H}_2\text{O})\xi_2 \tag{6}$$

$$n_{O_2} = 19.4\ \text{mol O}_2 - \left(\tfrac{3}{2}\,\text{mol O}_2\right)\xi_1 - (2\ \text{mol O}_2)\xi_2 \tag{7}$$

$$\frac{n_{CO_2}}{n_{CO}} = 8\ \frac{\text{mol CO}_2}{\text{mol CO}} = \frac{(1\ \text{mol CO}_2)\xi_2}{(1\ \text{mol CO})\xi_1} \Longrightarrow \frac{\xi_2}{\xi_1} = 8 \tag{8}$$

Substituting the last of these relationships into Equation 3 and solving:

$$0.78 = 7.80 - \xi_1 - 8\xi_1$$

$$\Downarrow$$

$$\xi_1 = 0.78 \Longrightarrow \xi_2 = 6.24$$

From Equations 4 and 5

$$\boxed{\begin{aligned} n_{CO} &= 0.78\ \text{mol CO} \\ n_{CO_2} &= 6.24\ \text{mol CO}_2 \end{aligned}}$$

and from Equations 6 and 7

$$\boxed{\begin{aligned} n_{H_2O} &= 14.0\ \text{mol H}_2\text{O} \\ n_{O_2} &= 5.75\ \text{mol O}_2 \end{aligned}}$$

Once again the same flow rates have been calculated, so that the molar composition of the product gas must therefore also be the same. For this problem, atomic species balances provide the least cumbersome solution.

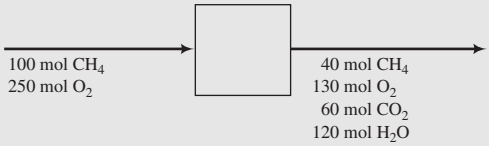
Test Yourself

(Answers, p. 656)

Methane is burned to form carbon dioxide and water in a batch reactor:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The feed to the reactor and the products obtained are shown in the following flowchart:



1. How much methane was consumed? What is the fractional conversion of methane?
2. How much oxygen was consumed? What is the fractional conversion of oxygen?
3. Write the extent of reaction equation (4.6-4) for methane, oxygen, and CO_2. Use each equation to determine the extent of reaction, ξ, substituting inlet and outlet values from the flowchart.
4. How many independent molecular species balances can be written? How many independent atomic species balances can be written?
5. Write the following balances and verify that they are all satisfied. The solution of the first one is given as an example.
   - **(a)** Methane. (I = O + C $\Longrightarrow$ 100 mol CH_4 in = 40 mol CH_4 out + 60 mol CH_4 consumed)
   - **(b)** Atomic oxygen (O).
   - **(c)** Molecular oxygen (O_2).
   - **(d)** Water.
   - **(e)** Atomic hydrogen.

4.7f Product Separation and Recycle

Two definitions of reactant conversion are used in the analysis of chemical reactors with product separation and recycle of unconsumed reactants:

$$\textit{Overall Conversion:} \quad \frac{\text{reactant input to process} - \text{reactant output from process}}{\text{reactant input to process}} \qquad \textbf{(4.7-1)}$$

$$\textit{Single-Pass Conversion:} \quad \frac{\text{reactant input to reactor} - \text{reactant output from reactor}}{\text{reactant input to reactor}} \qquad \textbf{(4.7-2)}$$

As usual, the corresponding percentage conversions are obtained by multiplying these quantities by 100%.

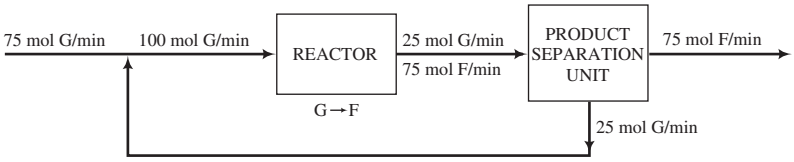
We will illustrate these two definitions with a process involving *isomerization*, a chemical reaction that rearranges the atoms in a molecule to form a second species with exactly the same atomic composition. An *enzyme*[8] (glucose isomerase) is used to catalyze[9] the isomerization of

[8] An enzyme is a protein that catalyzes a specific reaction. The name given the enzyme often is linked to the reaction catalyzed—e.g., glucose isomerase catalyzes the isomerization of glucose.

BIOENGINEERING

[9] A *catalyst* is a substance that alters the rate of a chemical reaction—possibly by many orders of magnitude—without itself being consumed in the reaction. Reactant molecules interact with the catalyst to form an intermediate species, which then further reacts to form the reaction product and regenerate the catalyst.

glucose (G) to fructose (F), an artificial sweetener used in many commercial products. A simplified labeled flowchart for the process follows:



The overall conversion of G is from Equation 4.7-1:

$$\frac{(75 \text{ mol G/min})_{\text{in}} - (0 \text{ mol G/min})_{\text{out}}}{(75 \text{ mol G/min})_{\text{in}}} \times 100\% = 100\%$$

The single-pass conversion is from Equation 4.7-2:

$$\frac{(100 \text{ mol G/min})_{\text{in}} - (25 \text{ mol G/min})_{\text{out}}}{(100 \text{ mol G/min})_{\text{in}}} \times 100\% = 75\%$$

This example provides another illustration of the object of recycle. We have achieved complete use of the reactant for which we are paying—the fresh feed—even though only 75% of the reactant entering the reactor is consumed before emerging. The reason the overall conversion is 100% is that perfect separation was assumed: any G that does not react gets sent back to the reactor. If a less-than-perfect separation were achieved and some G left with the product stream, the overall conversion would be less than 100%, although it would always be greater than the single-pass conversion.

Test Yourself What are the overall and single-pass conversions for the process shown in Figure 4.5-1?

(Answers, p. 656)

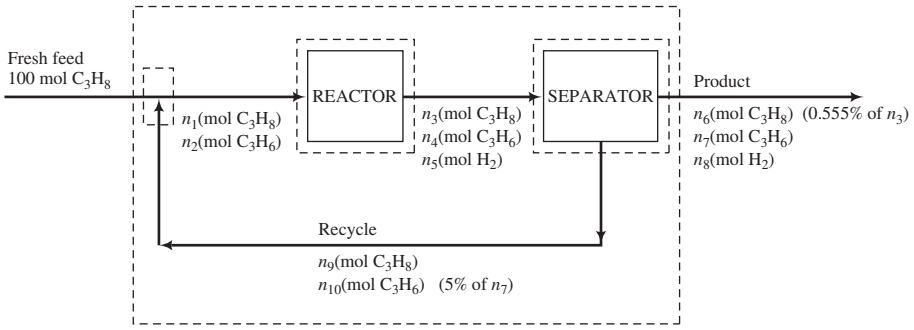
Example 4.7-2 Dehydrogenation of Propane

Propane can be dehydrogenated to form propylene in a catalytic reactor:

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

A process is to be designed for a 95% overall conversion of propane. The reaction products are separated into two streams: the first, which contains H_2, C_3H_6, and 0.555% of the propane that leaves the reactor, is taken off as product; the second stream, which contains the balance of the unreacted propane and propylene in an amount equal to 5% of that in the first stream, is recycled to the reactor. Calculate the composition of the product, the ratio (moles recycled)/(mole fresh feed), and the single-pass conversion.

Solution **Basis: 100 mol Fresh Feed**



In terms of the labeled variables, the quantities to be calculated are the mole fractions of product stream components $[n_6/(n_6 + n_7 + n_8)]$, . . . , the recycle ratio $[(n_9 + n_{10})/100 \text{ mol}]$, and the single-pass conversion $[100\% \times (n_1 - n_3)/n_1]$. We must therefore calculate n_1, n_3, and n_6 through n_{10}. As usual, we begin with the degree-of-freedom analysis to determine whether the problem is properly specified (i.e., whether we have enough information to solve it).

Degree-of-Freedom Analysis

When analyzing subsystems in which reactions occur (the overall system and the reactor), we will count atomic balances; for nonreactive subsystems (the recycle mixing point and the separation unit) we will count molecular species balances.

- ***Overall system*** (the outer dashed box on the flowchart). 3 unknown variables $(n_6, n_7, n_8) - 2$ independent atomic balances (C and H) – 1 additional relation (95% overall propane conversion) $\Longrightarrow$ 0 degrees of freedom. We will therefore be able to determine n_6, n_7, and n_8 by analyzing the overall system. Let us count these three variables as known at this point.
- ***Recycle-fresh feed mixing point.*** 4 unknown variables $(n_9, n_{10}, n_1, n_2) - 2$ balances (C_3H_8, C_3H_6) $\Longrightarrow$ 2 degrees of freedom. Since we don't have enough equations to solve for the unknowns associated with this subsystem, we proceed to the next one.
- ***Reactor.*** 5 unknown variables (n_1 through n_5) – 2 atomic balances (C and H) $\Longrightarrow$ 3 degrees of freedom. No help here. On to the remaining unit.
- ***Separator.*** 5 unknown variables $(n_3, n_4, n_5, n_9, n_{10})$ (n_6 through n_8 are known from the overall system analysis) – 3 balances (C_3H_8, C_3H_6, H_2) – 2 additional relations $(n_6 = 0.00555n_3, n_{10} = 0.05n_7)$ $\Longrightarrow$ 0 degrees of freedom.

We can therefore determine the five unknown variables associated with the separator and then return to analyze either the mixing point or the reactor. In either case we can write two atomic balances to solve for the two remaining unknowns (n_1 and n_2), thereby completing the solution. (In fact, not all of the system variables are required by the problem statement, so we will be able to stop well short of the full analysis.) The calculations follow, beginning with the analysis of the overall system.

95% Overall Propane Conversion: ($\Longrightarrow$ 5% unconverted)

$$\boxed{n_6 = 0.05(100 \text{ mol}) = 5 \text{ mol } C_3H_8}$$

We are left with two overall system atomic balances to write. An H balance involves both remaining unknowns (n_7 and n_8) but a C balance involves only n_7; we therefore begin with the latter balance.

Overall C Balance:

$$(100 \text{ mol } C_3H_8)(3 \text{ mol C/mol } C_3H_8) = [n_6(\text{mol } C_3H_8)](3 \text{ mol C/mol } C_3H_8) + [n_7(\text{mol } C_3H_6)](3 \text{ mol C/mol } C_3H_6)$$

$$\xrightarrow{n_6 = 5 \text{ mol}} \boxed{n_7 = 95 \text{ mol } C_3H_6}$$

Overall H Balance: (Fill in units.)

$$(100)(8) = n_6(8) + n_7(6) + n_8(2) \xrightarrow{n_6 = 5 \text{ mol}, n_7 = 95 \text{ mol}} \boxed{n_8 = 95 \text{ mol } H_2}$$

The product therefore contains

$$\begin{matrix} 5 \text{ mol } C_3H_8 \\ 95 \text{ mol } C_3H_6 \\ 95 \text{ mol } H_2 \end{matrix} \Longrightarrow \boxed{\begin{matrix} 2.6 \text{ mole\% } C_3H_8 \\ 48.7 \text{ mole\% } C_3H_6 \\ 48.7 \text{ mole\% } H_2 \end{matrix}}$$

Known Relations Among Separator Variables:

$$n_6 = 0.00555 n_3 \xrightarrow{n_6 = 5\ \text{mol}} \boxed{n_3 = 900\ \text{mol}\ C_3H_8}$$

$$n_{10} = 0.0500 n_7 \xrightarrow{n_7 = 95\ \text{mol}} \boxed{n_{10} = 4.75\ \text{mol}\ C_3H_6}$$

Propane Balance About Separation Unit:

$$n_3 = n_6 + n_9 \xrightarrow{n_3 = 900\ \text{mol},\ n_6 = 5\ \text{mol}} \boxed{n_9 = 895\ \text{mol}\ C_3H_8}$$

We could continue writing balances about the separation unit to determine the values of n_4 and n_5 but there is no reason to do so, since these values were not requested in the problem statement. The only value still to be determined is that of n_1, which can be calculated from a propane balance about the mixing point.

Propane Balance About Mixing Point:

$$100\ \text{mol} + n_9 = n_1 \xrightarrow{n_9 = 895\ \text{mol}} \boxed{n_1 = 995\ \text{mol}\ C_3H_8}$$

We now have all the variable values we need. The desired quantities are

$$\textit{Recycle ratio} = \frac{(n_9 + n_{10})\ \text{mol recycle}}{100\ \text{mol fresh feed}} \xrightarrow{n_9 = 895\ \text{mol},\ n_{10} = 4.75\ \text{mol}} \boxed{9.00\ \frac{\text{mol recycle}}{\text{mol fresh feed}}}$$

$$\textit{Single-pass conversion} = \frac{n_1 - n_3}{n_1} \times 100\% \xrightarrow{n_1 = 995\ \text{mol},\ n_3 = 900\ \text{mol}} \boxed{9.6\%}$$

Consider what is happening in the process just analyzed. Only about 10% of the propane entering the *reactor* is converted to propylene in a single pass; however, over 99% of the unconsumed propane in the reactor effluent is recovered in the separation unit and recycled back to the reactor, where it gets another chance to react. The net result is that 95% of the propane entering the *process* is converted and 5% leaves with the final product.

In general, high overall conversions can be achieved in two ways: (a) design the reactor to yield a high single-pass conversion, or (b) design the reactor to yield a low single-pass conversion (e.g., 10%, as in the preceding example), and follow it with a separation unit to recover and recycle unconsumed reactant. If the second scheme is used, the reactor must handle a larger throughput, but it takes a *much* larger reaction volume to achieve a 95% conversion than a 10% conversion in a single pass. The lower single-pass conversion consequently leads to a decrease in the cost of the reactor. On the other hand, the savings may be offset by the cost of the separation process unit and the pump, pipes, and fittings in the recycle line. The final design would be based on a detailed economic analysis of the alternatives.

4.7g Purging

A problem may arise in processes that involve recycling. Suppose a material that enters with the fresh feed or is produced in a reaction remains entirely in a recycle stream, rather than being carried out in a process product. If nothing were done about this situation, the substance would continuously enter the process and would have no way of leaving; it would therefore steadily accumulate, making the attainment of steady state impossible. To prevent this buildup, a portion of the recycle stream must be withdrawn as a **purge stream** to rid the process of the substance in question.

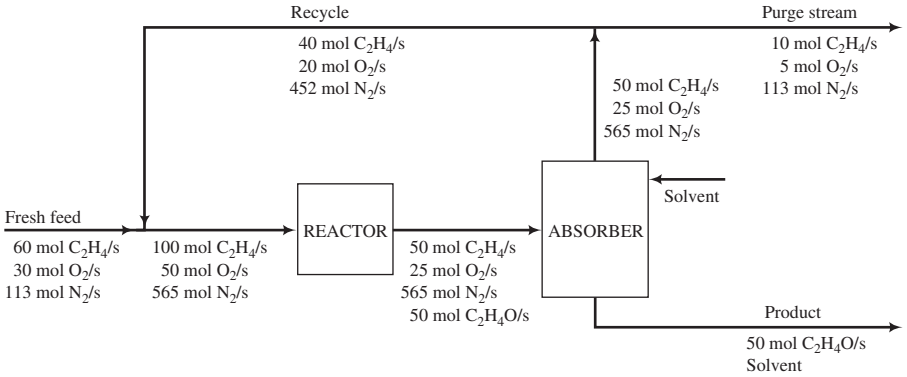


FIGURE 4.7-2
Process with recycle and purge.

ENVIRONMENTAL

Purge streams are essential in chemical processes involving recycle streams that contain species in the fresh feed that cannot be separated from unconsumed reactants. Determining how to dispose of the purge stream (for example, by incinerating it) presents a challenge, and the disposal adds cost to the process. Failure to plan for such streams can, however, create severe process and environmental problems.

The flowchart shown in Figure 4.7-2 for the production of ethylene oxide from ethylene illustrates this situation. The reaction is $2C_2H_4 + O_2 \rightarrow 2C_2H_4O$. A mixture of ethylene and air constitutes the fresh feed to the process. The effluent from the reactor passes to an absorber where it is contacted with a liquid solvent. Essentially all of the ethylene oxide is absorbed into the solvent. The gas stream leaving the absorber, which contains nitrogen and unreacted ethylene and oxygen, is recycled to the reactor.

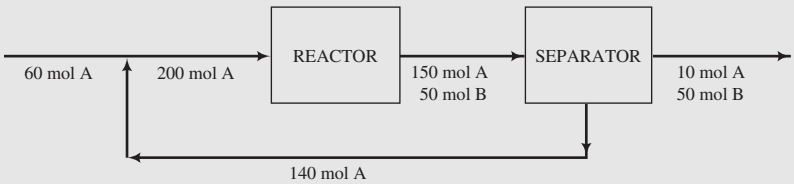
If there were no nitrogen (or any other inert and insoluble substance) in the feed, there would be no need for a purge stream. The recycle would contain only ethylene and oxygen; the fresh feed would contain just enough of these substances to make up for the amount lost in the reaction, and the system would be at steady state. However, there is nitrogen. It enters the system at a rate of 113 mol/s and must leave the system at the same rate in the purge stream. If the system were not purged, nitrogen would accumulate at this rate until something—probably unpleasant—occurred to shut down the process.

Material balance calculations on systems involving recycle and purge follow the procedures given in previous sections. When labeling the flowchart, note that the purge stream and the recycle stream before and after the purge takeoff all have the same composition.

Test Yourself

(Answers, p. 656)

A reaction with stoichiometry A → B takes place in a process with the following flowchart:



1. What is the overall conversion of A for this process? What is the single-pass conversion?
2. The separation unit and recycle pump and piping are expensive. Why not eliminate them and sell the effluent from the reactor as is? Alternatively, why not keep the separator but discard the bottom stream instead of recycling it?
3. Suppose a trace amount (say, 0.1%) of an inert material, I, is contained in the fresh feed, and all of it stays in the bottom effluent stream from the separation unit (and so is recycled). Why would the process eventually shut down? What would you have to do to get it to work?
4. Why not design the reactor to produce 10 mol A and 50 mol B from 60 mol A in a single pass, thereby eliminating the need for the separation and recycle?

Example 4.7-3 Recycle and Purge in the Synthesis of Methanol

Equipment Encyclopedia
reactor, condenser
@
www.wiley.com/college/felder

Methanol (also known as methyl alcohol and wood alcohol) is used as a raw material in the manufacture of formaldehyde, acetic acid, methyl tertiary-butyl ether (MTBE), and a number of other important chemicals. It also has many other uses, including as a solvent, a disinfectant, and a clean-burning fuel. One of the ways it can be synthesized is by reacting carbon dioxide and hydrogen:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

The fresh feed to a methanol synthesis process contains hydrogen, carbon dioxide, and 0.400 mole% inerts (I). The reactor effluent passes to a condenser that removes essentially all of the methanol and water formed and none of the reactants or inerts. The latter substances are recycled to the reactor. To avoid buildup of the inerts in the system, a purge stream is withdrawn from the recycle.

The feed to the *reactor* (not the fresh feed to the process) contains 28.0 mole% CO_2, 70.0 mole% H_2, and 2.00 mole% inerts. The single-pass conversion of hydrogen is 60.0%. Calculate the molar flow rates and molar compositions of the fresh feed, the total feed to the reactor, the recycle stream, and the purge stream for a methanol production rate of 155 kmol CH_3OH/h.

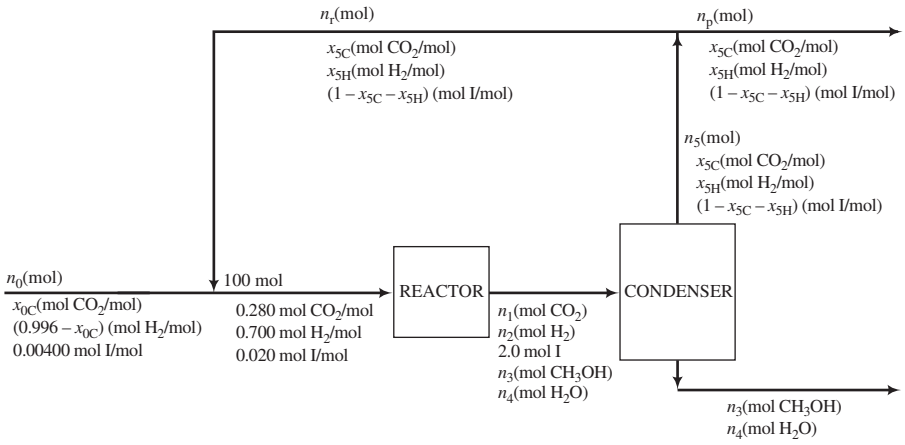
(a) Choose a basis of calculation of 100 mol of the feed to the reactor (a convenient basis since you know the composition of this stream), and draw and label a flowchart.

(b) Perform a degree-of-freedom analysis for the system. As a suggested sequence, determine the difference between the number of equations and number of variables for each of the following: overall system, recycle-fresh feed mixing point, reactor, condenser, and recycle-purge splitting point. Verify that there are zero degrees of freedom for the entire process and identify an efficient procedure for carrying out the calculations (including scaling up the calculated process variables to the desired methanol production rate).

(c) Write the system equations and use Excel's Solver to solve them for all of the variables.

Solution

(a) Basis: 100 mol Combined Feed to the Reactor



In terms of the labeled variables, the problem statement will be solved by determining $n_0, x_{0C}, n_3, x_{5C}, x_{5H}, n_p$, and n_r for the assumed basis, then scaling up n_0, 100 mol (fed to reactor), n_p, and n_r by the factor (155 kmol CH_3OH/h)/n_3.

(b) Degree-of-Freedom Analysis

In the analysis that follows, we will count molecular species balances for all systems. (We could equally well use atomic species balances or the extent of reaction.) Note that the reaction occurs within the overall system and the reactor subsystem and so must be included in the degree-of-freedom analyses for both systems.

- ***Overall system.*** 7 unknowns $(n_0, x_{0C}, n_3, n_4, n_p, x_{5C}, x_{5H}) + 1$ reaction – 5 independent balances $(CO_2, H_2, I, CH_3OH, H_2O) \Longrightarrow$ 3 degrees of freedom. Since we do not have enough equations to solve for the number of unknowns in the overall system, we check subsystems to see if one can be found with zero degrees of freedom.
- ***Recycle-fresh feed mixing point.*** 5 unknowns $(n_0, x_{0C}, n_r, x_{5C}, x_{5H}) - 3$ independent balances $(CO_2, H_2, I) \Longrightarrow$ 2 degrees of freedom.
- ***Reactor.*** 4 unknowns $(n_1, n_2, n_3, n_4) + 1$ reaction – 4 independent balances (CO_2, H_2, CH_3OH, H_2O) – 1 single-pass conversion $\Longrightarrow$ 0 degrees of freedom. We will therefore be able to determine $n_1, n_2, n_3,$ and n_4 and proceed from there.

  Notice that we only subtracted four balances and not one for each of the five species. The reason is that when we labeled the outlet flow of I as 2.0 mol, we implicitly used the balance on I (*input = output*) and so can no longer count it in the degree-of-freedom analysis. We will use the same reasoning in the analysis of the condenser.
- ***Condenser.*** 3 unknowns $(n_5, x_{5C}, x_{5H}) - 3$ independent balances $(CO_2, H_2, I) \Longrightarrow 0$ degrees of freedom. We may now presume that $n_5, x_{5C},$ and x_{5H} are known.

  In this analysis we presumed that we knew $n_1, n_2, n_3,$ and n_4 from the reactor analysis, and since we used the methanol and water balances when we labeled the bottom product stream, we only counted three available balances in the degree-of-freedom analysis.
- ***Purge–recycle splitting point.*** 2 unknowns $(n_r, n_p) - 1$ independent balance $\Longrightarrow 1$ degree of freedom. Since the labeled component mole fractions are the same in all three streams in this subsystem, balances on all three species reduce to the same equation (try it and see).
- ***Recycle–fresh feed mixing point*** (revisited). 3 unknowns $(n_0, x_{0C}, n_r) - 3$ independent balances $\Longrightarrow 0$ degrees of freedom. We can now determine $(n_0, x_{0C},$ and $n_r)$.
- ***Purge–recycle splitting point*** (revisited). 1 unknown $(n_p) - 1$ independent balance $\Longrightarrow 0$ degrees of freedom. The final unknown variable can now be calculated.

The solution procedure will therefore be to write balances on the reactor, then the condenser, then the fresh feed–recycle mixing point, and finally the purge–recycle splitting point. The flowchart may then be scaled up by the required amount to obtain a methanol production rate of 155 kmol/h. The calculations follow.

Reactor Analysis

We will use molecular balances. Recall that the stoichiometric reaction is

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

60% Single-Pass H_2 Conversion: ($\Longrightarrow 40\%$ is unconverted and emerges at the reactor outlet)

$$n_2 = 0.40(70.0 \text{ mol } H_2 \text{ fed}) = 28.0 \text{ mol } H_2$$

H_2 Balance: consumption = input − output

$$\text{Cons}_{H_2} = (70.0 - 28.0) \text{ mol } H_2 = 42.0 \text{ mol } H_2 \text{ consumed}$$

CO_2 Balance: output = input − consumption

$$n_1 = 28.0 \text{ mol } CO_2 - \frac{42.0 \text{ mol } H_2 \text{ consumed}}{} \left| \frac{1 \text{ mol } CO_2 \text{ consumed}}{3 \text{ mol } H_2 \text{ consumed}} \right. = 14.0 \text{ mol } CO_2$$

CH_3OH Balance: output = generation

$$n_3 = \frac{42.0 \text{ mol } H_2 \text{ consumed}}{} \left| \frac{1 \text{ mol } CH_3OH \text{ generated}}{3 \text{ mol } H_2 \text{ consumed}} \right. = 14.0 \text{ mol } CH_3OH$$

H_2O Balance: output = generation

$$n_4 = \frac{42.0 \text{ mol } H_2 \text{ consumed}}{3 \text{ mol } H_2 \text{ consumed}} \left| \frac{1 \text{ mol } H_2O \text{ generated}}{} \right. = 14.0 \text{ mol } H_2O$$

Condenser Analysis

Total Mole Balance: input = output

$$n_1 + n_2 + n_3 + n_4 + 2.0 \text{ mol} = n_3 + n_4 + n_5$$
$$\Downarrow n_2 = 28.0 \text{ mol}, n_1 = n_3 = n_4 = 14.0 \text{ mol}$$
$$n_5 = 44.0 \text{ mol}$$

CO_2 Balance: input = output

$$n_1 = n_5 x_{5C}$$
$$\Downarrow n_1 = 14.0 \text{ mol}, n_5 = 44.0 \text{ mol}$$
$$x_{5C} = 0.3182 \text{ mol } CO_2/\text{mol}$$

H_2 Balance: input = output

$$n_2 = n_5 x_{5H}$$
$$\Downarrow n_2 = 28.0 \text{ mol}, n_5 = 44.0 \text{ mol}$$
$$x_{5H} = 0.6364 \text{ mol } CO_2/\text{mol}$$
$$\Downarrow$$
$$x_{5I} = 1 - x_{5C} - x_{5H} = 0.04545 \text{ mol I/mol}$$

Fresh Feed–Recycle Mixing Point Analysis

Total Mole Balance: input = output

$$n_0 + n_r = 100 \text{ mol}$$

I Balance: input = output

$$n_0(0.00400) + n_r(0.04545) = 2.0 \text{ mol I}$$

Solving these two equations simultaneously yields

$$n_0 = 61.4 \text{ mol fresh feed}, n_r = 38.6 \text{ mol recycle}$$

CO_2 Balance: input = output

$$n_0 x_{0C} + n_r x_{5C} = 28.0 \text{ mol } CO_2$$
$$\Downarrow n_0 = 61.4 \text{ mol}, n_r = 38.6 \text{ mol}, x_{5C} = 0.3182 \text{ mol } CO_2/\text{mol}$$
$$x_{0C} = 0.256 \text{ mol } CO_2/\text{mol}$$
$$\Downarrow$$
$$x_{0H} = (1 - x_{0C} - x_{0I}) = 0.740 \text{ mol } H_2/\text{mol}$$

Recycle-Purge Splitting Point Analysis

Total Mole Balance: input = output

$$n_5 = n_r + n_p$$
$$\Downarrow n_5 = 44.0\ \text{mol}, n_r = 38.6\ \text{mol}$$
$$n_p = 5.4\ \text{mol purge}$$

Flowchart Scaling

For the assumed basis of 100 mol feed to the reactor, the production rate of methanol is $n_3 = 14.0$ mol CH_3OH. To scale the process to a methanol production rate of 155 kmol CH_3OH/h, we multiply each total and component molar flow rate by the factor

$$\left(\frac{155\ \text{kmol } CH_3OH/h}{14.0\ \text{mol } CH_3OH}\right) = \frac{11.1\ \text{kmol/h}}{\text{mol}}$$

The mole fractions remain unchanged by the scaling. The results follow.

Variable	Basis Value	Scaled Value
Fresh feed	61.4 mol	681 kmol/h
	25.6 mole% CO_2	25.6 mole% CO_2
	74.0 mole% H_2	74.0 mole% H_2
	0.400 mole% I	0.400 mole% I
Feed to reactor	100 mol	1110 kmol/h
	28.0 mole% CO_2	28.0 mole% CO_2
	70.0 mole% H_2	70.0 mole% H_2
	2.0 mole% I	2.0 mole% I
Recycle	38.6 mol	428 kmol/h
	31.8 mole% CO_2	31.8 mole% CO_2
	63.6 mole% H_2	63.6 mole% H_2
	4.6 mole% I	4.6 mole% I
Purge	5.4 mol	59.9 kmol/h
	31.8 mole% CO_2	31.8 mole% CO_2
	63.6 mole% H_2	63.6 mole% H_2
	4.6 mole% I	4.6 mole% I

(c) Excel solution

Just for variety, we will use atomic balances for the reactor this time. Balances that don't appear in the analysis, such as the reactor balance on I and the condenser methanol and water balances, have already been incorporated in the flow chart labeling.

Degree-of-Freedom Analysis

11 unknown variables ($n_0, x_{0C}, n_1 - n_5, x_{5C}, x_{5H}, n_r, n_p$)
– 3 equations for mixing point (balances on CO_2, H_2, I)
– 4 equations for reactor (atomic balances on C, H, O; single-pass conversion of CO_2)
– 3 equations for condenser (balances on CO_2, H_2, I)
– 1 equation for splitting point (total mole balance)
0 degrees of freedom

The complete spreadsheet calculation follows (including the scale-up calculations) for guessed values of 100 mol for each molar amount and 0.40 for each mole fraction. (Verify the equations.)

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**Solution to Example 4.7-3**												
2													
3	**Variable**	n0	x0C	x0H	n1	n2	n3	n4	n5	x5C	x5H	np	nr
4	**Value**	100	0.4	0.596	100	100	100	100	100	0.4	0.4	100	100
5													
6	**Equation**	**LHS**	**RHS**	**(LHS–RHS)^2**									
7	n0 + nr = 100	200	100	1.00E + 04									
8	n0*x0C + nr*x5C = 28	80	28	2.70E + 03									
9	n0*x0H + nr*x5H = 70	99.6	70	8.76E + 02									
10	28(1) = n1(1) + n3(1)	28	200	2.96E + 04									
11	70(2)=n2(2) + n3(4) + n4(2)	140	800	4.36E + 05									
12	28(2)=n1(2) + n3(1) + n4(1)	56	400	1.18E + 05									
13	n2 = 70(1-0.60)	100	28	5.18E + 03									
14	n1 = n5*x5C	100	40	3.60E + 03									
15	n2 = n5*x5H	100	40	3.60E + 03									
16	2 = n5*(1-x5C-x5H)	2	20	3.24E + 02									
17	n5 = np + nr	100	200	1.00E + 04									
18			Sum	5.92E + 05									
19													
20	**Scale factor**	1.55											
21	**Variable**	n0	x0C	x0H	n1	n2	n3	n4	n5	x5C	x5H	np	nr
22	**Scaled value**	155	0.4	0.596	155	155	155	155	155	0.4	0.4	155	155

[B7] = B4 + M4
[B8] = B4*C4 + M4*J4
[B9] = B4*D4 + M4*K4
[B10] 28
[B11] 140
[B12] 56
[B13] = F4
[B14] = E4
[B15] = F4
[B16] 2
[B17] = I4

[C7] 100
[C8] 28
[C9] 70
[C10] = E4 + G4
[C11] = 2*F4 + 4*G4 + 2*H4
[C12] = 2*E4 + G4 + H4
[C13] 28
[C14] = I4*J4
[C15] = I4*K4
[C16] = I4*(1–J4–K4)
[C17] = L4 + M4

[D4] = 0.996–C4
[D7] = (B7–C7)^2
[D8] = (B8–C8)^2
[D9] = (B9–C9)^2
[D10] = (B10–C10)^2
[D11] = (B11–C11)^2
[D12] = (B12–C12)^2
[D13] = (B13–C13)^2
[D14] = (B14–C14)^2
[D15] = (B15–C15)^2
[D16] = (B16–C16)^2
[D17] = (B17–C17)^2
[D18] = SUM(D7:D17)

[B20] = 155/G4
[B22] = $B$20*B4 (copy into [E22], [F22], [G22], [H22], [I22], [L22], [M22])
[C22] = C4 (copy into [D22], [J22], [K22])

Once the spreadsheet has been completely filled in, have Solver minimize the value in Cell D18 by varying the values in Cells B4 through M4. The solutions reported in Part (b) will appear immediately in Rows 4 and 22.

Example 4.7-4 Recycle of Aluminum Cans

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The use of aluminum cans in the United States increased from approximately 234 million lb_m in 1972 to 2.93 billion (2.93×10^9) lb_m in 2010.[10] In 1972, essentially all of the 6 billion aluminum beverage cans sold in the United States were discarded; that is, none were recycled.[11] By 2010, the recycling rate had increased to 58.1%, and advances in technology during that period increased the number of cans produced with 1 lb_m of aluminum from 21.75 in 1972 to 33 in 2010.[12]

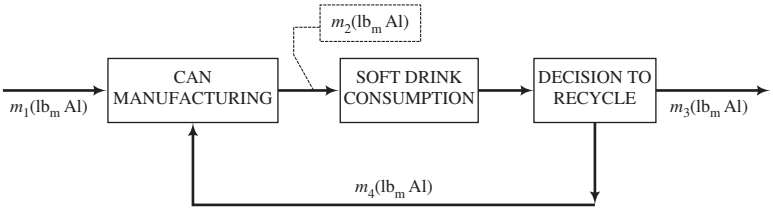
(a) Construct a flowchart showing an input of processed aluminum, utilization of cans by consumers, and a unit reflecting the cumulative decisions of consumers to either recycle or dispose of a can.

(b) Calculate the mass of aluminum that must be mined, refined, and processed for use in producing aluminum cans in the U.S. in 2010.

(c) What would that quantity be using the same 2010 consumption data but the 1972 recycling rate?

Solution Basis: 1 Year of Operation

(a) The flowchart is as follows:



where m_1 is the mass of processed aluminum, m_2 the mass of aluminum in the cans used by consumers, m_3 the mass of aluminum leaving the system, and m_4 the mass of aluminum in recycled cans.

(b) An aluminum (Al) balance around the entire system at steady state gives $m_1 = m_3$. In 2010, $m_2 = 2.9 \times 10^9$ $lb_m = m_3 + m_4$, and at the 2010 recycle rate of 58.1%,

$$\frac{m_4}{m_3 + m_4} = 0.581$$

$$\Downarrow \quad m_3 + m_4 = 2.92 \times 10^9 \text{ lb}_m$$

$$m_4 = 1.70 \times 10^9 \text{ lb}_m \Longrightarrow \boxed{m_3 = 1.22 \times 10^9 \text{ lb}_m = m_1}$$

(c) At 1972 recycle rates (0%), again using the 2010 consumption data, m_2 remains constant, but the amount of aluminum required from ore is 2.92×10^9 lb_m. In other words, the increase in recycling means that 1.22 billion lb_m of aluminum does not have to be mined, refined, and processed to satisfy the needs of this market.

CREATIVITY EXERCISE

Recycling aluminum cans has obvious benefits, as illustrated above. There are, however, other benefits to be derived: for example, recycling a can consumes only about 10% of the energy

[10] http://www.aluminum.org/Content/NavigationMenu/NewsStatistics/StatisticsReports/UsedBeverageCanRecyclingRate/UBC_Recycling_Rates_2010.pdf.

[11] http://www.container-recycling.org/index.php/number-of-aluminum-cans-recycled-and-wasted-in-the-us-from-1972-2004.

[12] http://www.aluminum.org/Content/NavigationMenu/TheIndustry/PackagingConsumerProductMarket/Can/default.htm#Aluminum%20Can%20Recycling.

required to produce a new can from bauxite ore; recycling reduces the emissions of greenhouse gases into the atmosphere; and so on. List as many other indirect benefits as you can.

4.8 COMBUSTION REACTIONS

Combustion is the rapid reaction of a substance with oxygen. Oxidation reactions of carbon to CO and CO_2, hydrogen to H_2O, sulfur to SO_2, and nitrogen to NO and NO_2 release significant quantities of energy as heat. The most important of the combustion reactions are those in which fossil fuels—such as coal, oil, and natural gas—are burned to release energy that ultimately shows up as electricity, commercial and home heating, and vehicular motion. Because common combustion products such as those listed above are released to the atmosphere in such huge quantities, considerable effort must be made to monitor and control their emission rates. Analysis of combustion reactions and reactors and the abatement and control of environmental pollution caused by combustion products are problems with which chemical engineers are heavily involved.

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In the sections that follow, we introduce terminology commonly used in the analysis of combustion reactors and discuss material balance calculations for such reactors. Chapter 9 outlines methods of determining the energy obtainable from combustion reactions.

4.8a Combustion Chemistry

Most of the fuel used in power-plant combustion furnaces is either coal (carbon, some hydrogen and sulfur, and various noncombustible materials), fuel oil (mostly high molecular weight hydrocarbons, with varying small amounts of sulfur), gaseous fuel (such as **natural gas**, which is primarily methane), or **liquefied petroleum gas**, which is usually propane and/or butane.

When a fuel is burned, carbon in the fuel reacts to form either CO_2 or CO, hydrogen forms H_2O, and sulfur forms SO_2. At temperatures greater than approximately 1800°C, some of the nitrogen in the air reacts to form nitric oxide (NO). A combustion reaction in which CO is formed is referred to as **partial combustion** or **incomplete combustion**, even though CO_2 may also be produced.

Examples:

$C + O_2 \longrightarrow CO_2$	Complete combustion of carbon
$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$	Complete combustion of propane
$C_3H_8 + \frac{7}{2}O_2 \longrightarrow 3CO + 4H_2O$	Partial combustion of propane
$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$	Complete combustion of carbon disulfide

Perry's Chemical Engineers' Handbook provides a thorough discussion of fuels and combustion.[13]

Air, which is the source of oxygen in most combustion reactors, has the following average molar composition on a dry basis:

N_2	78.03%
O_2	20.99%
Ar	0.94%
CO_2	0.03%
H_2, He, Ne, Kr, Xe	0.01%
	100.00%

Average molecular weight = 29.0

[13] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008, pp. 24-3 through 24-51.

In most combustion calculations, it is acceptable to simplify this composition to 79% N_2, 21% $O_2 \Longrightarrow$ 79 moles N_2/21 moles O_2 = 3.76 moles N_2/mole O_2.

The term **composition on a wet basis** is commonly used to denote the component mole fractions of a gas that contains water, and **composition on a dry basis** signifies the component mole fractions of the same gas without the water. For example, a gas that contains 33.3 mole% CO_2, 33.3% N_2, and 33.3% H_2O (wet basis) contains 50% CO_2 and 50% N_2 on a dry basis.

The product gas that leaves a combustion furnace is referred to as the **stack gas** or **flue gas**. When the flow rate of a gas in a stack is measured, it is the total flow rate of the gas including water; on the other hand, many common techniques for analyzing stack gases provide compositions on a dry basis. You must therefore be able to convert a composition on a dry basis to its corresponding composition on a wet basis before writing material balances on the combustion reactor. The procedure to convert a composition from one basis to another is similar to the one used to convert mass fractions to mole fractions and vice versa given in Chapter 3: assume an amount of the stack gas (e.g., 100 mol of wet gas if composition on a wet basis is known or 100 mol of dry gas if a dry-basis composition is known), calculate how much of each component is present, and use this information to calculate mole fractions on the desired basis.

Example 4.8-1 Composition on Wet and Dry Bases

1. ***Wet Basis*** $\Longrightarrow$ ***Dry Basis.***

A stack gas contains 60.0 mole% N_2, 15.0% CO_2, 10.0% O_2, and the balance H_2O. Calculate the molar composition of the gas on a dry basis.

Solution **Basis: 100 mol wet gas**

$$\begin{array}{l} 60.0 \text{ mol } N_2 \\ 15.0 \text{ mol } CO_2 \\ \underline{10.0 \text{ mol } O_2} \\ 85.0 \text{ mol dry gas} \end{array}$$

$$\Downarrow$$

$$\begin{aligned} \frac{60.0}{85.0} &= 0.706 \ \frac{\text{mol } N_2}{\text{mol dry gas}} \\ \frac{15.0}{85.0} &= 0.176 \ \frac{\text{mol } CO_2}{\text{mol dry gas}} \\ \frac{10.0}{85.0} &= 0.118 \ \frac{\text{mol } O_2}{\text{mol dry gas}} \end{aligned}$$

2. ***Dry Basis*** $\Longrightarrow$ ***Wet Basis.***

An **Orsat analysis** (a technique for stack-gas analysis) yields the following dry-basis composition:

N_2	65%
CO_2	14%
CO	11%
O_2	10%

A humidity measurement shows that the mole fraction of H_2O in the stack gas is 0.0700. Calculate the stack-gas composition on a wet basis.

Solution **Basis: 100 lb-moles dry gas**

$$0.0700 \ \frac{\text{lb-mole } H_2O}{\text{lb-mole wet gas}} \Leftrightarrow 0.930 \ \frac{\text{lb-mole dry gas}}{\text{lb-mole wet gas}}$$

$$\Downarrow$$

$$\frac{0.0700 \text{ lb-mole } H_2O/\text{lb-mole wet gas}}{0.930 \text{ lb-mole dry gas/lb-mole wet gas}} = 0.0753 \ \frac{\text{lb-mole } H_2O}{\text{lb-mole dry gas}}$$

Hence the gas in the assumed basis contains

$$\frac{100 \text{ lb-moles dry gas}}{} \left| \frac{0.0753 \text{ lb-mole } H_2O}{\text{lb-mole dry gas}} \right. = 7.53 \text{ lb-moles } H_2O$$

$$\frac{100 \text{ lb-moles dry gas}}{} \left| \frac{0.650 \text{ lb-mole } N_2}{\text{lb-mole dry gas}} \right. = 65.0 \text{ lb-moles } N_2$$

$$(100)(0.140) \text{ lb-moles } CO_2 = 14.0 \text{ lb-moles } CO_2$$

$$(100)(0.110) \text{ lb-moles CO} = 11.0 \text{ lb-moles CO}$$

$$(100)(0.100) \text{ lb-moles } O_2 = 10.0 \text{ lb-moles } O_2$$

$$107.5 \text{ lb-moles wet gas}$$

The mole fractions of each stack gas component may now easily be calculated:

$$y_{H_2O} = \frac{7.53}{107.5} \frac{\text{lb-moles } H_2O}{\text{lb-moles wet gas}} = 0.070 \frac{\text{lb-mole } H_2O}{\text{lb-mole wet gas}}, \cdots$$

Test Yourself

(Answers, p. 656)

1. What is the approximate molar composition of air? What is the approximate molar ratio of N_2 to O_2 in air? (Committing these quantities to memory will save you lots of effort.)
2. A gas contains 1 mol H_2, 1 mol O_2, and 2 mol H_2O. What is the molar composition of this gas on a wet basis? On a dry basis?
3. A flue gas contains 5 mole% H_2O. Calculate the ratios
   (a) kmol flue gas/kmol H_2O.
   (b) kmol dry flue gas/kmol flue gas.
   (c) kmol H_2O/kmol dry flue gas.

4.8b Theoretical and Excess Oxygen and Air

If two reactants participate in a reaction and one is considerably more expensive than the other, the usual practice is to feed the less expensive reactant in excess of the valuable one. Doing so has the effect of increasing the conversion of the valuable reactant at the expense of the cost of the excess reactant and additional pumping costs.

The extreme case of an inexpensive reactant is air, which is virtually free. Combustion reactions are therefore invariably run with more air than is needed to supply oxygen in stoichiometric proportion to the fuel. The following terms are commonly used to describe the quantities of fuel and air fed to a reactor.

Theoretical Oxygen: The moles (batch) or molar flow rate (continuous) of O_2 needed for complete combustion of all the fuel fed to the reactor, assuming that all carbon in the fuel is oxidized to CO_2, all the hydrogen is oxidized to H_2O, and all the sulfur is converted to SO_2.

Theoretical Air: The quantity of air that contains the theoretical oxygen.

Excess Air: The amount by which the air fed to the reactor exceeds the theoretical air.

Percent Excess Air:

$$\frac{(\text{moles air})_{\text{fed}} - (\text{moles air})_{\text{theoretical}}}{(\text{moles air})_{\text{theoretical}}} \times 100\% \qquad \textbf{(4.8-1)}$$

If you know the fuel feed rate and the stoichiometric equation(s) for complete combustion of the fuel, you can calculate the theoretical O_2 and air feed rates. If in addition you know the actual feed rate of air, you can calculate the percent excess air from Equation 4.8-1. It is also easy to calculate the air feed rate from the theoretical air and a given value of the percentage excess: if 50% excess air is supplied, for example, then

$$(\text{moles air})_{\text{fed}} = 1.5\,(\text{moles air})_{\text{theoretical}}$$

Example 4.8-2 Theoretical and Excess Air

One hundred mol/h of butane (C_4H_{10}) and 5000 mol/h of air are fed to a combustion reactor. Calculate the percent excess air.

Solution First, calculate the theoretical air from the feed rate of fuel and the stoichiometric equation for complete combustion of butane:

$$C_4H_{10} + \tfrac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O$$

$$(\dot{n}_{O_2})_{\text{theoretical}} = \frac{100 \text{ mol } C_4H_{10}}{\text{h}} \left| \frac{6.5 \text{ mol } O_2 \text{ required}}{\text{mol } C_4H_{10}} \right.$$

$$= 650 \frac{\text{mol } O_2}{\text{h}}$$

$$(\dot{n}_{\text{air}})_{\text{theoretical}} = \frac{650 \text{ mol } O_2}{\text{h}} \left| \frac{4.76 \text{ mol air}}{\text{mol } O_2} \right. = 3094 \frac{\text{mol air}}{\text{h}}$$

Hence

$$\%\text{ excess air} = \frac{(\dot{n}_{\text{air}})_{\text{fed}} - (\dot{n}_{\text{air}})_{\text{theoretical}}}{(\dot{n}_{\text{air}})_{\text{theoretical}}} \times 100\% = \frac{5000 - 3094}{3094} \times 100\% = \boxed{61.6\%}$$

If instead you had been *given* 61.6% excess air, you could have calculated the feed rate of air as $(\dot{n}_{\text{air}})_{\text{fed}} = 1.616(\dot{n}_{\text{air}})_{\text{theoretical}} = 1.616(3094 \text{ mol/h}) = 5000 \text{ mol/h}$.

Two points of confusion often arise in the calculation of theoretical and excess air, both of which are caused by ignoring the definitions of these terms.

1. *The theoretical air required to burn a given quantity of fuel does not depend on how much is actually burned.* The fuel may not react completely, and it may react to form both CO and CO_2, but the theoretical air is still that which would be required to react with *all* of the fuel to form CO_2 only.
2. *The value of the percent excess air depends only on the theoretical air and the air feed rate, and not on how much O_2 is consumed in the reactor or whether combustion is complete or partial.*

Test Yourself

(Answers, p. 656)

Methane burns in the reactions

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
$$CH_4 + \tfrac{3}{2}O_2 \longrightarrow CO + 2H_2O$$

One hundred mol/h of methane is fed to a reactor.

1. What is the theoretical O_2 flow rate if complete combustion occurs in the reactor?
2. What is the theoretical O_2 flow rate assuming that only 70% of the methane reacts? (Careful!)
3. What is the theoretical air flow rate?
4. If 100% excess air is supplied, what is the flow rate of air entering the reactor?
5. If the actual flow rate of air is such that 300 mol O_2/h enters the reactor, what is the percent excess air?

CREATIVITY EXERCISES

Equipment Encyclopedia
heat transfer—boilers
www.wiley.com/college/felder

1. Years ago it was common to operate boiler furnaces with air fed in 20% excess or more, while today improved boiler designs enable the use of 5–10% excess air. Cite as many possible negative consequences as you can think of for the air-to-fuel feed ratio being (a) too low and (b) too high.
2. The costs of petroleum and natural gas have increased dramatically since the early 1970s, and there is some question about their continued long-term availability. List as many alternative energy sources as you can think of, being as creative as you can, and then go back and suggest possible drawbacks to each one.

4.8c Material Balances on Combustion Reactors

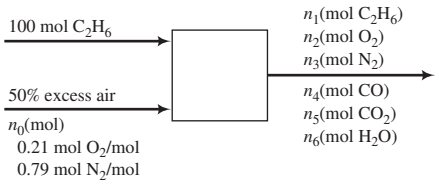
The procedure for writing and solving material balances for a combustion reactor is the same as that for any other reactive system. Bear these points in mind, however:

1. When you draw and label the flowchart, be sure the outlet stream (the stack gas) includes (a) unreacted fuel unless you are told that all the fuel is consumed, (b) unreacted oxygen, (c) water and carbon dioxide, as well as carbon monoxide if the problem statement says any is present, and (d) nitrogen if the fuel is burned with air and not pure oxygen.
2. To calculate the oxygen feed rate from a specified percent excess oxygen or percent excess air (both percentages have the same value, so it doesn't matter which one is stated), first calculate the theoretical O_2 from the fuel feed rate and the reaction stoichiometry for complete combustion, then calculate the oxygen feed rate by multiplying the theoretical oxygen by (1 + fractional excess oxygen).
3. If only one reaction is involved, all three balance methods (molecular species balances, atomic species balances, extent of reaction) are equally convenient. If several reactions occur simultaneously, however—such as combustion of a fuel to form both CO and CO_2—molecular species balances should generally be avoided.

Example 4.8-3 Combustion of Ethane

Ethane is burned with 50% excess air. The percentage conversion of the ethane is 90%; of the ethane burned, 25% reacts to form CO and the balance reacts to form CO_2. Calculate the molar composition of the stack gas on a dry basis and the mole ratio of water to dry stack gas.

Solution **Basis: 100 mol C_2H_6 Fed**



$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$C_2H_6 + \frac{5}{2}O_2 \longrightarrow 2CO + 3H_2O$$

Notes

1. Since no product stream mole fractions are known, subsequent calculations are easier if individual component amounts rather than a total amount and mole fractions are labeled.
2. The composition of air is taken to be approximately 21 mole% O_2, 79 mole% N_2.

3. If the ethane reacted completely, n_1 would be omitted. Since excess air is supplied, O_2 *must* appear in the product stream.

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4. In material balance calculations on combustion processes it is reasonable to assume that nitrogen is inert—that is, to neglect the trace amounts of NO, NO_2, and N_2O_4 (collectively referred to as NO_x) that might form in the burner. On the other hand, in environmental impact studies NO_x may not automatically be neglected; trace amounts of nitrogen oxides may have little impact on the nitrogen balance but may have a significant polluting effect if they are released into the atmosphere.

Degree-of-Freedom Analysis:

$$\begin{aligned} &7 \text{ unknowns } (n_0, n_1, \ldots, n_6) \\ &-3 \text{ atomic balances (C, H, O)} \\ &-1 \ N_2 \text{ balance} \\ &-1 \text{ excess air specification (relates } n_0 \text{ to the quantity of fuel fed)} \\ &-1 \text{ ethane conversion specification} \\ &-1 \ CO/CO_2 \text{ ratio specification} \\ &= 0 \text{ degrees of freedom} \end{aligned}$$

50% Excess Air:

$$(n_{O_2})_{\text{theoretical}} = \frac{100 \text{ mol } C_2H_6}{1} \left| \frac{3.50 \text{ mol } O_2}{1 \text{ mol } C_2H_6} \right. = 350 \text{ mol } O_2$$

$$\Downarrow \ 50\% \text{ excess air}$$

$$0.21 n_0 = 1.50(350 \text{ mol } O_2) \Longrightarrow n_0 = 2500 \text{ mol air fed}$$

90% Ethane Conversion: ($\Longrightarrow$ 10% unreacted)

$$n_1 = 0.100(100 \text{ mol } C_2H_6 \text{ fed}) = \boxed{10.0 \text{ mol } C_2H_6}$$

$$0.900(100 \text{ mol } C_2H_6 \text{ fed}) = 90.0 \text{ mol } C_2H_6 \text{ react}$$

25% Conversion to CO:

$$n_4 = \frac{(0.25 \times 90.0) \text{ mol } C_2H_6 \text{ react to form CO}}{1} \left| \frac{2 \text{ mol CO generated}}{1 \text{ mol } C_2H_6 \text{ react}} \right. = \boxed{45.0 \text{ mol CO}}$$

Nitrogen Balance: output = input

$$n_3 = 0.79(2500) \text{ mol} = \boxed{1975 \text{ mol } N_2}$$

Atomic Carbon Balance: input = output

$$\frac{100 \text{ mol } C_2H_6}{1} \left| \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right. = \frac{n_1(\text{mol } C_2H_6)}{1} \left| \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right. + \frac{n_4(\text{mol CO})}{1} \left| \frac{1 \text{ mol C}}{1 \text{ mol CO}} \right.$$

$$+ \frac{n_5(\text{mol } CO_2)}{1} \left| \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \right.$$

$$\Downarrow \begin{matrix} n_1 = 10 \text{ mol} \\ n_4 = 45 \text{ mol} \end{matrix}$$

$$\boxed{n_5 = 135 \text{ mol } CO_2}$$

Atomic Hydrogen Balance: input = output

$$\frac{100\ \text{mol } C_2H_6}{}\left|\frac{6\ \text{mol H}}{1\ \text{mol } C_2H_6}\right. = \frac{10\ \text{mol } C_2H_6}{}\left|\frac{6\ \text{mol H}}{1\ \text{mol } C_2H_6}\right. + \frac{n_6(\text{mol } H_2O)}{}\left|\frac{2\ \text{mol H}}{1\ \text{mol } H_2O}\right.$$

$$\Downarrow$$

$$\boxed{n_6 = 270\ \text{mol } H_2O}$$

Atomic Oxygen Balance: input = output

$$\frac{525\ \text{mol } O_2}{}\left|\frac{2\ \text{mol O}}{1\ \text{mol } O_2}\right. = \frac{n_2(\text{mol } O_2)}{}\left|\frac{2\ \text{mol O}}{1\ \text{mol } O_2}\right. + \frac{45\ \text{mol CO}}{}\left|\frac{1\ \text{mol O}}{1\ \text{mol CO}}\right.$$

$$+ \frac{135\ \text{mol } CO_2}{}\left|\frac{2\ \text{mol O}}{1\ \text{mol } CO_2}\right. + \frac{270\ \text{mol } H_2O}{}\left|\frac{1\ \text{mol O}}{1\ \text{mol } H_2O}\right.$$

$$\Downarrow$$

$$\boxed{n_2 = 232\ \text{mol } O_2}$$

The analysis of the stack gas is now complete. Summarizing:

$$\begin{aligned} n_1 &= 10\ \text{mol } C_2H_6 \\ n_2 &= 232\ \text{mol } O_2 \\ n_3 &= 1974\ \text{mol } N_2 \\ n_4 &= 45\ \text{mol CO} \\ n_5 &= 135\ \text{mol } CO_2 \\ \hline \text{Total dry stack gas} &= 2396\ \text{mol dry gas} \\ +n_6 &= 270\ \text{mol } H_2O \\ \hline \text{Total stack gas} &= 2666\ \text{mol} \end{aligned}$$

Hence the stack gas composition on a dry basis is

$$\boxed{\begin{aligned} y_1 &= \frac{10\ \text{mol } C_2H_6}{2396\ \text{mol dry gas}} = 0.00417\ \frac{\text{mol } C_2H_6}{\text{mol}} \\ y_2 &= \frac{232\ \text{mol } O_2}{2396\ \text{mol dry gas}} = 0.0970\ \frac{\text{mol } O_2}{\text{mol}} \\ y_3 &= \frac{1974\ \text{mol } N_2}{2396\ \text{mol dry gas}} = 0.824\ \frac{\text{mol } N_2}{\text{mol}} \\ y_4 &= \frac{45\ \text{mol CO}}{2396\ \text{mol dry gas}} = 0.019\ \frac{\text{mol CO}}{\text{mol}} \\ y_5 &= \frac{135\ \text{mol } CO_2}{2396\ \text{mol dry gas}} = 0.0563\ \frac{\text{mol } CO_2}{\text{mol}} \end{aligned}}$$

and the mole ratio of water to dry stack gas is

$$\frac{270\ \text{mol } H_2O}{2396\ \text{mol dry stack gas}} = \boxed{0.113\ \frac{\text{mol } H_2O}{\text{mol dry stack gas}}}$$

If a fuel of unknown composition is burned, you may be able to deduce something about its composition by analyzing the combustion products and writing and solving atomic species balances. The procedure is illustrated in the next example.

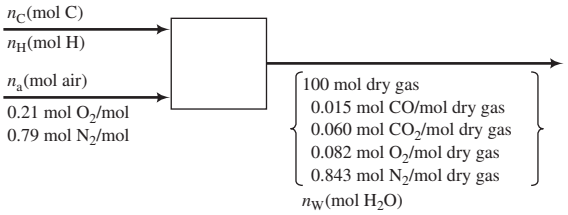
Example 4.8-4 Combustion of a Hydrocarbon Fuel of Unknown Composition

A hydrocarbon gas is burned with air. The dry-basis product gas composition is 1.5 mole% CO, 6.0% CO_2, 8.2% O_2, and 84.3% N_2. There is no atomic oxygen in the fuel. Calculate the ratio of hydrogen to carbon in the fuel gas and speculate on what the fuel might be. Then calculate the percent excess air fed to the reactor.

Solution

Basis: 100 mol Product Gas

Since the molecular composition of the fuel is unknown, we label its atomic species composition. We also recognize that since the fuel is a hydrocarbon, water must be one of the combustion products.



$$C + O_2 \rightarrow CO_2$$
$$2C + O_2 \rightarrow 2CO$$
$$4H + O_2 \rightarrow 2H_2O$$

Degree-of-Freedom Analysis:

4 unknowns (n_H, n_C, n_a, n_w)
− 3 independent atomic balances (C, H, O)
− 1 N_2 balance
= 0 degrees of freedom

A solution procedure that does not require solving simultaneous equations is as follows:

N_2 Balance: $0.79n_a = (100)(0.843)\text{ mol } N_2 \Longrightarrow n_a = 106.7\text{ mol air}$

Atomic C Balance: $$n_C = \frac{100\text{ mol}}{\text{mol}} \left| \frac{0.015\text{ mol CO}}{1\text{ mol CO}} \right| \frac{1\text{ mol C}}{1\text{ mol CO}} + (100)(0.060)(1)\text{ mol C}$$
$$\Longrightarrow n_C = 7.5\text{ mol C}$$

Atomic O Balance: $$0.21n_a(2) = n_w(1) + 100[\overbrace{(0.015)(1)}^{\text{CO}} + \overbrace{(0.060)(2)}^{CO_2} + \overbrace{(0.082)(2)}^{O_2}]\text{ mol O}$$
$$\xrightarrow{n_a = 106.7\text{ mol}} n_w = 14.9\text{ mol } H_2O$$

Atomic H Balance: $$n_H = \overbrace{n_w(2)}^{H_2O} \xrightarrow{n_w = 14.9\text{ mol}} n_H = 29.8\text{ mol H}$$

C/H Ratio in the Fuel: $$\frac{n_H}{n_C} = \frac{29.8\text{ mol H}}{7.5\text{ mol C}} = \boxed{3.97\text{ mol H/mol C}}$$

The fuel composition may therefore be described by the formula $(CH_{3.97})_N$.

Since there is only one hydrocarbon for which the ratio of H to C is close to 3.97—that is, CH_4—we may conclude in this case that the fuel is essentially pure methane, perhaps with trace amounts of other hydrocarbons. [If we had obtained, say, $n_H/n_C \approx 2$, we could have gone no further than to label the fuel as $(CH_2)_n$; from the information given, there would have been no way to distinguish between C_2H_4, C_3H_6, a mixture of CH_4 and C_2H_2, and so on.]

Percent Excess Air

We must first determine the theoretical oxygen required to consume the carbon and hydrogen in the fuel. The reactions may be written as

$$\begin{aligned} C + O_2 &\longrightarrow CO_2 \\ 4H + O_2 &\longrightarrow 2H_2O \end{aligned}$$

$$\Downarrow$$

$$(n_{O_2})_{\text{theoretical}} = \frac{7.5 \text{ mol C}}{} \left| \frac{1 \text{ mol } O_2}{1 \text{ mol C}} + \frac{29.8 \text{ mol H}}{} \right| \frac{1 \text{ mol } O_2}{4 \text{ mol H}} = 14.95 \text{ mol } O_2$$

$$(n_{O_2})_{\text{fed}} = 0.21(106.7 \text{ mol air}) = 22.4 \text{ mol } O_2$$

$$\%\text{ excess air} = \frac{(n_{O_2})_{\text{fed}} - (n_{O_2})_{\text{theoretical}}}{(n_{O_2})_{\text{theoretical}}} \times 100\% = \frac{(22.4 - 14.95) \text{ mol } O_2}{14.95 \text{ mol } O_2} \times 100\%$$

$$= \boxed{49.8\% \text{ excess air}}$$

4.9 SOME ADDITIONAL CONSIDERATIONS ABOUT CHEMICAL PROCESSES

The methods we present in this chapter and the rest of the text are applied universally in the chemical process industry. There are several features of industrial processes that tend not to show up in textbooks, however. You will find out about them as soon as you go to work as a chemical engineer, but it could be helpful to know about them in advance.

- Textbook processes always work the way they are designed to work. In practice, unexpected occurrences are common, especially when processes are first run.
- Textbook process variables are measured with relatively high precision. In practice, measurements with varying degrees of accuracy and precision can introduce errors.
- The invisible people who run textbook processes never do anything wrong. Real process operators and managers, being human, sometimes make mistakes.
- In textbooks you always have exactly the data you need to determine what you want to know, no matter how complex the problem may be. In practice, you may not have all the data you need, and you may have to either get the missing data yourself or use approximations and make assumptions based on experience.
- In textbooks, the **closure** of every steady-state material balance [defined as (output/input) × 100%] is 100%. In practice, measurement imprecision and inaccurate assumptions may lead to closures that differ—possibly significantly—from 100%. Also, in practice there is no such thing as true steady state: variable values *always* fluctuate or drift to some extent.
- Textbook problems usually have one and only one correct answer, and your job is to follow prescribed procedures to determine it. In practice you may have trouble even defining what the real problem is, and once you have defined it you can usually find a variety of solutions, each of which has advantages and disadvantages. Making the choice involves considerations of technological capability, short-range profit, long-range profit, safety, environmental protection, and ethics. Textbooks provide little help with this type of problem.

Since our purpose in this text is to help you to develop skills in certain basic methods of chemical process analysis, we have intentionally omitted most of the complicating factors that can

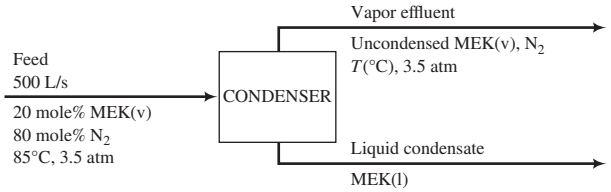
make industrial processes so difficult to manage. Once you have mastered the basics, you can start learning how to adjust for the complications.

Example 4.9-1 Material Balances in Process Design and Process Operation

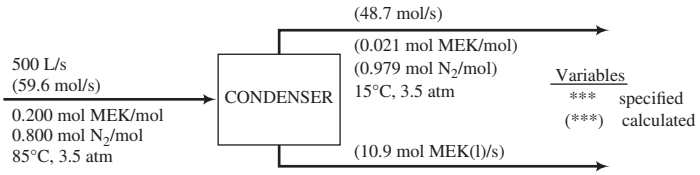
Equipment Encyclopedia
condenser

www.wiley.com/college/felder

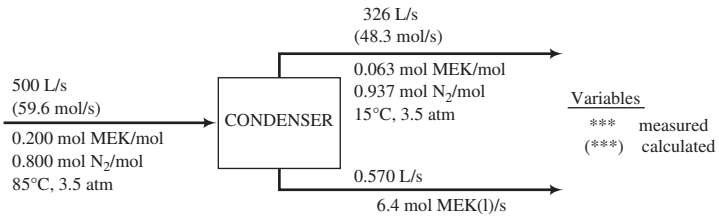
Methyl ethyl ketone (MEK) is used extensively as a solvent in a wide range of applications. For example, it is a key ingredient in the dry-erase markers used in many classrooms. When used as a solvent in industrial processes, there are both economic and environmental incentives for its recovery and reuse. In one such process, MEK is to be recovered from a gas mixture containing 20.0 mole% MEK and 80.0 mole% N_2 at 85°C and 3.5 atm. A stream of this mixture is fed to a condenser at a rate of 500 L/s and cooled at constant pressure, causing most of the MEK to condense.



The design engineer (a) converts the volumetric flow rate of the feed stream to a molar flow rate using the *ideal-gas equation of state*—an approximate relationship among the pressure, temperature, volumetric flow rate, and molar flow rate of a gas (Chapter 5); (b) specifies a condenser temperature of 15°C; (c) calculates the mole fraction of MEK in the vapor product using *Raoult's law*—an approximate relationship between the compositions of liquid and vapor phases in equilibrium with each other at a specified temperature and pressure (Chapter 6); and (d) calculates the molar flow rates of the vapor and liquid products from nitrogen and MEK balances (input = output). The results follow.



A condenser is then installed and run at the design temperature and pressure. The volumetric flow rates of the feed stream and the vapor and liquid product streams are measured with rotameters, and the MEK mole fractions in the feed and vapor effluent streams are measured with a gas chromatograph. The feed stream flow rate is set to 500 L/s and enough time is allowed to pass for the product stream rotameter readings to reach steady levels. The feed and product gas flow rates are then converted to molar flow rates using the ideal-gas equation of state, and the product liquid flow rate is converted to a molar flow rate using a tabulated MEK density and the molecular weight of MEK. Here are the results.



1. Calculate the MEK balance closures for the condenser design and the experimental condenser.
2. List possible reasons for the differences between the design predictions and the experimental values of the output stream variables and for the failure of the experimental system balance to close.

Solution **1. Material balance closures.**

Design

$$\text{MEK in} = (59.6\ \text{mol/s})(0.200\ \text{mol MEK/mol}) = 11.9\ \text{mol MEK/s}$$
$$\text{MEK out} = (48.7\ \text{mol/s})(0.021\ \text{mol MEK/mol}) + 10.9\ \text{mol MEK/s} = 11.9\ \text{mol MEK/s}$$
$$\Downarrow$$
$$\text{Closure} = \frac{\text{MEK out}}{\text{MEK in}} \times 100\% = \frac{11.9\ \text{mol/s}}{11.9\ \text{mol/s}} \times 100\% = \boxed{100\%\ \text{closure}}$$

The nitrogen balance closure is 100% (*verify*).

Experiment

$$\text{MEK in} = (59.6\ \text{mol/s})(0.200\ \text{mol MEK/mol}) = 11.9\ \text{mol MEK/s}$$
$$\text{MEK out} = (48.3\ \text{mol/s})(0.063\ \text{mol MEK/mol}) + 6.4\ \text{mol MEK/s} = 9.44\ \text{mol MEK/s}$$
$$\Downarrow$$
$$\text{Closure} = \frac{\text{MEK out}}{\text{MEK in}} \times 100\% = \frac{9.44\ \text{mol/s}}{11.9\ \text{mol/s}} \times 100\% = \boxed{79\%\ \text{closure}}$$

The nitrogen balance closure is 95% (*verify*).

2. Possible reasons for differences between design values and experimental values.

- ***Human errors, instrument errors, and random data scatter.*** Plant or laboratory personnel are responsible for setting and maintaining the process operating conditions, reading the feed and product stream flowmeters, and drawing samples of the product gas and analyzing them. Any error that any of these individuals makes could lead to errors in measured variable values and values calculated from them. Moreover, any measured value (e.g., an input or output stream volumetric flow rate, the mole fraction of MEK in the feed or vapor product stream, any stream temperature or pressure) is subject to errors due to a faulty instrument (e.g., a malfunctioning or poorly calibrated flowmeter or gas chromatograph) or random data scatter.
- ***Impurities in the feed.*** The design calculations were based on an assumption that the feed contains only MEK vapor and nitrogen. Impurities present in the feed could react with the MEK, or they could condense and affect the vapor–liquid equilibrium distribution of MEK in the products.
- ***Incorrect assumption of steady state.*** Closure should be expected only after the system reaches steady state, so that input = output. In the experimental run, steady state was declared when the operator could no longer see changes in the outlet stream rotameter readings. It is possible that the flow rates were still changing but the rotameter was not sensitive enough to show the changes. It is also possible that MEK was still accumulating in the system—for example, by adsorbing on the container walls—and much more time would be required for the buildup to be complete.
- ***Incorrect assumption that MEK is not reactive.*** If MEK undergoes a reaction in the system—decomposition, for example, or reaction with something on the reactor wall—then input = output + consumption. The output would then necessarily be less than the input and the balance would not close.
- ***Errors due to approximations in the experimental data analysis.*** Several potential errors were introduced when the measured volumetric flow rates were converted to molar flow rates. Volumetric gas flow rates were converted using the ideal-gas equation of state, which is approximate, and the volumetric liquid flow rate was converted using a tabulated density that may not have been measured at the system temperature. Also, the fact that a physical property value has been published is no guarantee that it is correct.
- ***Approximations in the design analysis.*** Like the ideal-gas equation of state, Raoult's law is an approximation that may be excellent or seriously in error, depending on the experimental process conditions.

There are other possibilities, but you get the idea. The point is that no matter how carefully you design a process, you cannot predict exactly what the real process will do. Approximations and assumptions must be made for every process design; closures on real process material balances are never exactly 100%; nothing can be measured with complete accuracy; and everyone sometimes makes mistakes.

Experienced design engineers know these things and account for them with *overdesign factors*. If they calculate that they need a 2500-liter reactor, they might order a 3000-liter or 3500-liter reactor to make sure they have enough reactor capacity to meet both current and anticipated product demands. The more uncertainties in the design or the projected product demand, the greater the overdesign. A large part of what engineers do involves reducing the uncertainties and thus lowering the required overdesign, resulting in major reductions in equipment purchase and maintenance costs.

4.10 SUMMARY

Every chemical process analysis involves writing and solving material balances to account for all process species in feed and product streams. This chapter outlines and illustrates a systematic approach to material balance calculations. The procedure is to draw and label a flowchart, perform a degree-of-freedom analysis to verify that enough equations can be written to solve for all unknown process variables, and write and solve the equations.

- **The general balance equation** is

  $$input + generation - output - consumption = accumulation$$

  A **differential balance** applies to an instant of time and each term is a rate (mass/time or moles/time). An **integral balance** applies to a time interval and each term is an amount (mass or moles). Balances may be applied to total mass, individual species, or energy. (They may also be applied to momentum, but we will not consider momentum balances in this text.)
- For a differential balance on a continuous process (material flows in and out throughout the process) at steady-state (no process variables change with time), the accumulation term in the balance (the rate of buildup or depletion of the balanced species) equals zero. For an integral balance on a batch process (no material flows in or out during the process), the input and output terms equal zero and accumulation = initial input − final output. In both cases, the balance simplifies to

  $$input + generation = output + consumption$$

  If the balance is on total mass or on a nonreactive species, the equation simplifies further to

  $$input = output$$

- A process stream on a flowchart is *completely labeled* if values or variable names are assigned to one of the following sets of stream variables: (a) total mass flow rate or total mass and component mass fractions; (b) mass flow rates or masses of each stream component; (c) total molar flow rate or total moles and component mole fractions; and (d) molar flow rates or moles of each stream component. *If a total amount or flow rate or one or more component fractions are known for a stream, use* (*a*) *or* (*c*) *to incorporate the known values into the labeling. If neither the total nor any fractions are known, using* (*b*) *or* (*d*) (*component amounts or flow rates*) *often leads to easier algebra.* Volumetric quantities should be labeled only if they are either given or requested in the problem statement. A flowchart is completely labeled if every stream is completely labeled.
- A **basis of calculation** for a process is an amount or flow rate of one of the process streams. If two or more stream flow rates or amounts are given in the problem statement, they constitute the basis of calculation. If one is given, it may be assumed as a basis but it may also be convenient to assume another basis and then scale the flowchart to the specified value. If no flow rates or amounts are given, assume one as a basis, preferably an amount of a stream with known composition.
- To perform a **degree-of-freedom analysis on a single-unit nonreactive process**, count unknown variables on the flowchart, then subtract independent relations among them. The difference, which equals the number of degrees of freedom for the process, must equal zero for a unique solution of the problem to be determinable. Relations include material balances (as many as there are independent species in the feed and product streams), process specifications, density relations between labeled masses and volumes, and physical constraints (e.g., the sum of the component mass or mole fractions of a stream must add up to 1).
- To perform a **degree-of-freedom analysis on a multiple-unit process**, perform separate analyses on the overall process, each process unit, each stream mixing or stream splitting point, and, if necessary, on combinations of process units. When you find a system with zero degrees of freedom, assume that you can solve for the unknown variables in the feed and output streams for that system; then, considering those variables as known, try to find another system with zero degrees of freedom. This procedure helps you to find an efficient solution procedure before you undertake time-consuming calculations.
- Once you have written the system equations for a process, you may solve them either manually or using an equation-solving computer program. *If you solve system equations manually, write them in an order that minimizes the number that must be solved simultaneously, starting with equations that only involve one unknown variable.*
- **Recycle** is a common feature of chemical processes. Its most common use is to send unused raw materials emerging from a

process unit back to the unit. Overall system balances are usually (but not always) convenient starting points for analyzing a process with recycle. A **purge** stream is withdrawn from a process when a species enters in the process feed and is completely recycled. If this species were not removed in the purge, it would keep accumulating in the process system and eventually lead to shutdown.

- The **limiting reactant** in a reactive process is the one that would be completely consumed if the reaction proceeded to completion. All other reactants must either be fed in **stoichiometric proportion** to the limiting reactant (the feed rates are in the ratio of the stoichiometric coefficients) or in **excess** of the limiting reactant (in greater than stoichiometric proportion to it).
- The **theoretical requirement** for an excess reactant is the amount required to react completely with the limiting reactant. The **percentage excess** of the reactant is

$$\%\ \text{excess} = \frac{\text{amount fed} - \text{amount theoretically required}}{\text{amount theoretically required}}$$

  The percentage excess depends only on the feed rates of the excess and limiting reactants and on their stoichiometric coefficients; it does *not* depend on how much actually reacts or on anything else that happens in the reactor.
- The **fractional conversion** of a reactant is the ratio of amount reacted to amount fed. The fractional conversions of different reactants are generally different unless the reactants are fed in stoichiometric proportion.
- The **extent of reaction**, ξ is a species-independent dimensionless quantity that satisfies the equation

$$n_i = n_{i0} + \nu_i \xi \quad \text{or} \quad \dot{n}_i = \dot{n}_{i0} + \dot{\nu}_i \xi$$

  where n_{i0} ($\dot{n}_{i0}$) is the number of moles (molar flow rate) of species i in the feed to the reactor, n_i ($\dot{n}_i$) is the number of moles (molar flow rate) of species i in the stream leaving the reactor, and ν_i (mol i) [or $\dot{\nu}_i$ (mol i/s)] is the **stoichiometric coefficient** of species i (negative for reactants, positive for products, and zero for nonreactive species). If you know the inlet and outlet amounts or flow rates of any reactive species, you can determine ξ by applying this equation to that species. You may then substitute the calculated value into the equations for the other species in the stream leaving the reactor to determine the amounts or flow rates of those species.
- You may analyze reactive processes using (a) **molecular species balances** (the only method used for nonreactive processes), (b) **atomic species balances**, or (c) **extents of reaction**. Molecular species balances on reactive processes are often cumbersome: they must include generation and consumption terms for each species, and one degree of freedom must be added for each independent reaction. Atomic species balances have the simple form *input* = *output* and are usually more straightforward than either of the other two methods. Extents of reaction are particularly convenient for reaction equilibrium calculations.
- **Combustion** is a rapid reaction between a fuel and oxygen. The carbon in the fuel is oxidized to CO_2 (**complete combustion**) or CO (**partial combustion**) and the hydrogen in the fuel is oxidized to water. Other species in the fuel like sulfur and nitrogen may be partially or completely converted to their oxides. Combustion reactions are carried out commercially either to generate heat or to consume waste products.

PROBLEMS

4.1. Water enters a 2.00-m^3 tank at a rate of 6.00 kg/s and is withdrawn at a rate of 3.00 kg/s. The tank is initially half full.

(a) Is this process continuous, batch, or semibatch? Is it transient or steady state?

(b) Write a mass balance for the process (see Example 4.2-1). Identify the terms of the general balance equation (Equation 4.2-1) present in your equation and state the reason for omitting any terms.

(c) How long will the tank take to overflow?

4.2. Rain is falling on a poorly designed 150-m^2 flat roof of a contemporary home. The design flaw requires the water level on the roof to reach approximately 5 cm above the plane of the roof before the water flows into drains.

(a) Taking the accumulated rain on the roof as the system, can the process before the water level reaches 5 cm be considered batch, semi-batch, or continuous? Is it transient or steady-state? Once the water starts to flow into the drains, how do your answers change?

(b) Before the water starts draining, which of the terms in the general balance equation (Equation 4.2-1) can be omitted? Why? How do your responses change after water starts draining?

(c) Water begins flowing from the roof after 30 minutes of rainfall. What will the rate of draining (L/s) be if rain continues to fall at the same rate?

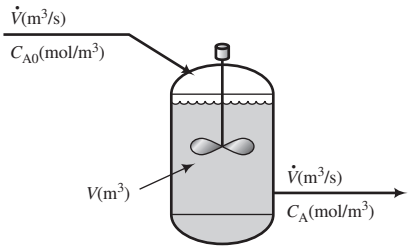
ENVIRONMENTAL

(d) The home owner is considering installation of a "green" roof that is partially or completely covered with vegetation. If this is done, how would your answers to Parts (a) and (b) change? List at least two concerns and two environmental benefits of the new roof.

4.3. A liquid-phase chemical reaction A → B takes place in a well-stirred tank. The concentration of A in the feed is C_{A0} (mol/m^3), and that in the tank and outlet stream is C_A (mol/m^3). Neither concentration varies with time. The volume of the tank contents is V(m^3) and the volumetric flow rate of the inlet and outlet streams is $\dot{V}$ (m^3/s). The **reaction rate** (the rate at which A is consumed by reaction in the tank) is given by the expression

$$r(\text{mol A consumed/s}) = kVC_A$$

where k is a constant.



(a) Is this process continuous, batch, or semibatch? Is it transient or steady-state?

(b) What would you expect the reactant concentration C_A to equal if $k = 0$ (no reaction)? What should it approach if $k \to \infty$ (infinitely rapid reaction)?

(c) Write a differential balance on A, stating which terms in the general balance equation (*accumulation* = *input* + *generation* − *output* − *consumption*) you discarded and why you discarded them. Use the balance to derive the following relation between the inlet and outlet reactant concentrations:

$$C_A = \frac{C_{A0}}{1 + kV/\dot{V}}$$

Verify that this relation predicts the results in Part (b).

4.4. A stream consisting of 44.6 mole% benzene and 55.4% toluene is fed at a constant rate to a process unit that produces two product streams, one a vapor and the other a liquid. The vapor flow rate is initially zero and asymptotically approaches half of the molar flow rate of the feed stream. Throughout this entire period, no material accumulates in the unit. When the vapor flow rate has become constant, the liquid is analyzed and found to be 28.0 mole% benzene.

(a) Sketch a plot of liquid and vapor flow rates versus time from startup to when the flow rates become constant.

(b) Is this process batch or continuous? Is it transient or steady-state before the vapor flow rate reaches its asymptotic limit? What about after it becomes constant?

(c) For a feed rate of 100 mol/min, draw and fully label a flowchart for the process after the vapor flow rate has reached its limiting value, and then use balances to calculate the molar flow rate of the liquid and the composition of the vapor in mole fractions.

4.5. Draw and label the given streams and derive expressions for the indicated quantities in terms of labeled variables. The solution of Part (a) is given as an illustration.

(a) A continuous stream contains 40.0 mole% benzene and the balance toluene. Write expressions for the molar and mass flow rates of benzene, $\dot{n}_B$(mol C_6H_6/s) and $\dot{m}_B$(kg C_6H_6/s), in terms of the total molar flow rate of the stream, $\dot{n}$(mol/s).

Solution

$$\dot{n}(\text{mol/s}) \longrightarrow \begin{matrix} 0.400 \text{ mol } C_6H_6/\text{mol} \\ 0.600 \text{ mol } C_7H_8/\text{mol} \end{matrix}$$

$$\dot{n}_B = \boxed{0.400\dot{n} \text{ (mol } C_6H_6/\text{s)}}$$

$$\dot{m}_B = \frac{0.400\dot{n} \text{ (mol } C_6H_6) \quad \left| \quad 78.1 \text{ g } C_6H_6 \right.}{\text{mol}} = \boxed{31.2\dot{n}(\text{g } C_6H_6/\text{s})}$$

(b) The feed to a batch process contains equimolar quantities of nitrogen and methane. Write an expression for the kilograms of nitrogen in terms of the total moles n(mol) of this mixture.

(c) A stream containing ethane, propane, and butane has a mass flow rate of 100.0 g/s. Write an expression for the molar flow rate of ethane, $\dot{n}_E$(lb-mole C_2H_6/h), in terms of the mass fraction of this species, x_E.

(d) A continuous stream of humid air contains water vapor and dry air, the latter containing approximately 21 mole% O_2 and 79% N_2. Write expressions for the molar flow rate of O_2 and for the mole fractions of H_2O and O_2 in the gas in terms of $\dot{n}_1$(lb-mole H_2O/s) and $\dot{n}_2$(lb-mole dry air/s).

(e) The product from a batch reactor contains NO, NO_2, and N_2O_4. The mole fraction of NO is 0.400. Write an expression for the gram-moles of N_2O_4 in terms of n(mol mixture) and y_{NO_2}(mol NO_2/mol).

4.6. A liquid mixture of acetone and water contains 35 mole% acetone. The mixture is to be partially evaporated to produce a vapor that is 75 mole% acetone and leave a residual liquid that is 18.7 mole% acetone.

(a) Suppose the process is to be carried out continuously and at steady state with a feed rate of 10.0 kmol/h. Let $\dot{n}_v$ and $\dot{n}_l$ be the flow rates of the vapor and liquid product streams, respectively. Draw and label a process flowchart, then write and solve balances on total moles and on acetone to determine the values of $\dot{n}_v$ and $\dot{n}_l$. For each balance, state which terms in the general balance equation (*accumulation* = *input* + *generation* − *output* − *consumption*) can be discarded and why. (See Example 4.2-2.)

(b) Now suppose the process is to be carried out in a closed container that initially contains 10.0 kmol of the liquid mixture. Let n_v and n_l be the moles of final vapor and liquid phases, respectively. Draw and label a process flowchart, then write and solve integral balances on total moles and on acetone. For each balance, state which terms of the general balance equation can be discarded and why.

(c) Returning to the continuous process, suppose the vaporization unit is built and started and the product stream flow rates and compositions are measured. The measured acetone content of the vapor stream is 75 mole% acetone, and the product stream flow rates have the values calculated in Part (a). However, the liquid product stream is found to contain 22.3 mole% acetone. It is possible that there is an error in the measured composition of the liquid stream, but give at least five other reasons for the discrepancy. [Think about assumptions made in obtaining the solution of Part (a).]

4.7. **(a)** Draw a flowchart for the catalytic dehydrogenation of propane from the description of this process that begins Section 4.3a. Label all feed, product, and connecting streams between units.

(b) Write clear statements of the overall objective of the process and the functions of each of the process units (the preheater, the reactor, the absorption and stripping towers, and the distillation column).

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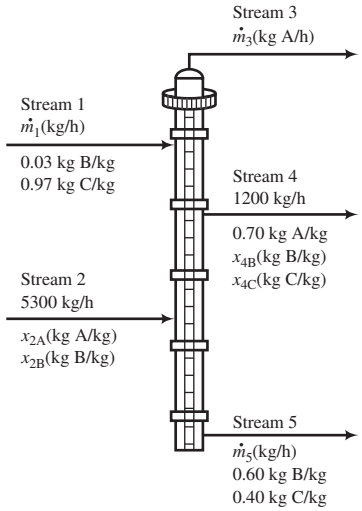
4.8. A **distillation column** is a process unit in which a feed mixture is separated by multiple partial vaporizations and condensations to form two or more product streams. The overhead product stream is rich in the most volatile components of the feed mixture (the ones that vaporize most readily), and the bottom product stream is rich in the least volatile components.

The following flowchart shows a distillation column with two feed streams and three product streams:

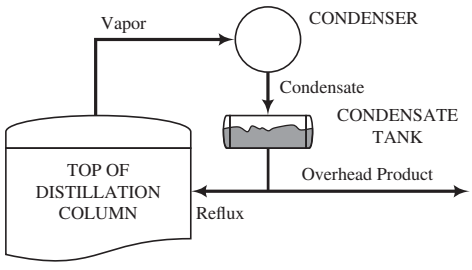


(a) How many independent material balances may be written for this system?

(b) How many of the unknown flow rates and/or mole fractions must be specified before the others may be calculated? (See Example 4.3-4. Also, remember what you know about the component mole fractions of a mixture—for example, the relationship between x_{2A} and x_{2B}.) Briefly explain your answer.

(c) Suppose values are given for $\dot{m}_1$ and x_{2A}. Give a series of equations, each involving only a single unknown, for the remaining variables. Circle the variable for which you would solve. (Once a variable has been calculated in one of these equations, it may appear in subsequent equations without being counted as an unknown.)

4.9. Inside a distillation column (see Problem 4.8), a downward-flowing liquid and an upward-flowing vapor maintain contact with each other. For reasons we will discuss in greater detail in Chapter 6, the vapor stream becomes increasingly rich in the more volatile components of the mixture as it moves up the column, and the liquid stream is enriched in the less volatile components as it moves down. The vapor leaving the top of the column goes to a condenser. A portion of the condensate is taken off as a product (the **overhead product**), and the remainder (the **reflux**) is returned to the top of the column to begin its downward journey as the liquid stream. The condensation process can be represented as shown below:



A distillation column is being used to separate a liquid mixture of ethanol (more volatile) and water (less volatile). A vapor mixture containing 89.0 mole% ethanol and the balance water enters the overhead condenser at a rate of 100 lb-mole/h. The liquid condensate has a density of 49.0 lb_m/ft^3, and

the reflux ratio is 3 lb_m reflux/lb_m overhead product. When the system is operating at steady state, the tank collecting the condensate is half full of liquid and the mean residence time in the tank (volume of liquid/volumetric flow rate of liquid) is 10.0 minutes. Determine the overhead product volumetric flow rate (ft^3/min) and the condenser tank volume (gal).

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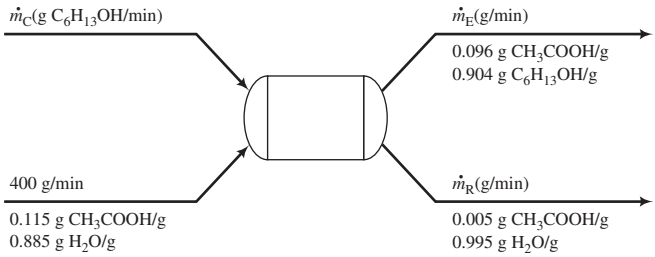
4.10. **Liquid extraction** is an operation used to separate the components of a liquid mixture of two or more species. In the simplest case, the mixture contains two components: a solute (A) and a liquid solvent (B). The mixture is contacted in an agitated vessel with a second liquid solvent (C) that has two key properties: A dissolves in it, and B is immiscible or nearly immiscible with it. (For example, B may be water, C a hydrocarbon oil, and A a species soluble in both water and oil.) Some of the A transfers from B to C, and then the B-rich phase (the raffinate) and the C-rich phase (the extract) separate from each other in a settling tank. If the raffinate is then contacted with fresh C in another stage, more A will be transferred from it. This process can be repeated until essentially all of the A has been extracted from the B.

Shown below is a flowchart of a process in which acetic acid (A) is extracted from a mixture of acetic acid and water (B) into 1-hexanol (C), a liquid immiscible with water.



(a) What is the maximum number of independent material balances that can be written for this process?

(b) Calculate $\dot{m}_C$, $\dot{m}_E$, and $\dot{m}_R$, using the given mixture feed rate as a basis and writing balances in an order such that you never have an equation that involves more than one unknown variable.

(c) Calculate the difference between the amount of acetic acid in the feed mixture and that in the 0.5% mixture, and show that it equals the amount that leaves in the 9.6% mixture.

(d) Acetic acid is relatively difficult to separate completely from water by distillation (see Problem 4.8) and relatively easy to separate from hexanol by distillation. Sketch a flowchart of a two-unit process that might be used to recover nearly pure acetic acid from an acetic acid–water mixture.

BIOENGINEERING

4.11. In the production of soybean oil, dried and flaked soybeans are brought into contact with a solvent (often hexane) that extracts the oil and leaves behind the residual solids and a small amount of oil.

(a) Draw a flowchart of the process, labeling the two feed streams (beans and solvent) and the leaving streams (solids and extract).

(b) The soybeans contain 18.5 wt% oil and the remainder insoluble solids, and the hexane is fed at a rate corresponding to 2.0 kg hexane per kg beans. The residual solids leaving the extraction unit contain 35.0 wt% hexane, all of the non-oil solids that entered with the beans, and 1.0% of the oil that entered with the beans. For a feed rate of 1000 kg/h of dried flaked soybeans, calculate the mass flow rates of the extract and residual solids, and the composition of the extract.

(c) The product soybean oil must now be separated from the extract. Sketch a flowchart with two units, the extraction unit from Parts (a) and (b) and the unit separating soybean oil from hexane. Propose a use for the recovered hexane.

4.12. Eggs are sorted into two sizes (large and extra large) at the Cheerful Chicken Coop. Recently, the economic downturn has not allowed Cheerful Chicken to repair the egg-sorting machine bought in 2000. Instead, the company has Chick Poulet, one of the firm's sharper-eyed employees, stamp the big eggs with a "Large" rubber stamp in her right hand and the really big eggs with an "X-large" stamp in her left as the eggs go by on a conveyor belt. Down the line, another employee puts the eggs into one of two hoppers, each egg according to its stamp. On average Chick breaks 8% of the 120 eggs that pass by

her each minute. At the same time, a check of the "X-large" stream reveals a flow rate of 70 eggs/min, of which 8 eggs/min are broken.

(a) Draw and label a flowchart for this process.

(b) Write and solve balances about the egg sorter on total eggs and broken eggs.

(c) How many "large" eggs leave the plant each minute, and what fraction of them are broken?

(d) Is Chick right- or left-handed?

4.13. A process is carried out in which a mixture containing 25.0 wt% methanol, 42.5% ethanol, and the balance water is separated into two fractions. A technician draws and analyzes samples of both product streams and reports that one stream contains 39.8% methanol and 31.5% ethanol and the other contains 19.7% methanol and 41.2% ethanol. You examine the reported figures and tell the technician that they must be wrong and that stream analyses should be carried out again.

(a) Prove your statement.

(b) How many streams do you ask the technician to analyze? Explain.

4.14. Strawberries contain about 15 wt% solids and 85 wt% water. To make strawberry jam, crushed strawberries and sugar are mixed in a 45:55 mass ratio, and the mixture is heated to evaporate water until the residue contains one-third water by mass.

(a) Draw and label a flowchart of this process.

(b) Do the degree-of-freedom analysis and show that the system has zero degrees of freedom (i.e., the number of unknown process variables equals the number of equations relating them). If you have too many unknowns, think about what you might have forgotten to do.

(c) Calculate how many pounds of strawberries are needed to make a pound of jam.

(d) Making a pound of jam is something you could accomplish in your own kitchen (or maybe even a dorm room). However, a typical manufacturing line for jam might produce 1500 lb_m/h. List technical and economic factors you would have to take into account as you scaled up this process from your kitchen to a commercial operation.

4.15. Two streams flow into a 500-gallon tank. The first stream is 10.0 wt% ethanol and 90.0% hexane (the mixture density, ρ_1, is 0.68 g/cm^3) and the second is 90.0 wt% ethanol, 10.0% hexane ($\rho_2 = 0.78$ g/cm^3). After the tank has been filled, which takes 22 min, an analysis of its contents determines that the mixture is 60.0 wt% ethanol, 40.0% hexane. You wish to estimate the density of the final mixture and the mass and volumetric flow rates of the two feed streams.

(a) Draw and label a flowchart of the mixing process and do the degree-of-freedom analysis.

(b) Perform the calculations and state what you assumed.

4.16. A fuel distributor supplies four liquid fuels, each of which has a different ratio of ethanol to gasoline. Five percent of the demand is for E100 (pure ethanol), 15% for E85 (85.0 volume% ethanol), 40% for E10 (10.0% ethanol), and the remainder for pure gasoline. The distributor blends gasoline and ethanol to produce E85 and E10, and the four products are produced continuously.

(a) Draw and label a flowchart for the blending operation, letting $\dot{V}$ represent the combined volumetric flow rate of all four fuels and $\dot{V}_G$ and $\dot{V}_E$ represent the volumetric flow rates of gasoline and ethanol sold as fuels and sent to the blending operation.

(b) Assuming volume additivity when blending ethanol and gasoline, determine the volumetric flow rates of all streams when delivery of 100,000 L/d of E10 is specified.

(c) Tank trucks are to transport the fuel from the blending operation to service stations in the area. The gross weight of a loaded truck, which has a tare (empty) weight of 12,700 kg, cannot exceed 36,000 kg. Assuming the specific gravity of pure gasoline is 0.73, estimate the maximum volume (L) of each fuel that can be loaded onto a truck.

SAFETY

4.17. If the percentage of fuel in a fuel-air mixture falls below a certain value called the **lower flammability limit (LFL)**, which sometimes is referred to as the **lower explosion limit (LEL)**, the mixture cannot be ignited. In addition there is an **upper flammability limit (UFL)**, which also is known as the **upper explosion limit (UEL)**. For example, the LFL of propane in air is 2.3 mole% C_3H_8 and the UFL is 9.5%.[14]

[14] R. J. Lewis Sr. (ed), *Hazardous Chemicals Desk Reference*, 6th ed., John Wiley & Sons, Inc., New York, 2002, p. 1176.

If the percentage of propane in a propane-air mixture is greater than 2.3% and less than 9.5%, the gas mixture can ignite if it is exposed to a flame or spark.

A mixture of propane in air containing 4.03 mole% C_3H_8 (*fuel gas*) is the feed to a combustion furnace. If there is a problem in the furnace, a stream of pure air (*dilution air*) is added to the fuel mixture prior to the furnace inlet to make sure that ignition is not possible.

(a) Draw and label a flowchart of the fuel gas-dilution air mixing unit, presuming that the gas entering the furnace contains propane at the LFL, and do the degree-of-freedom analysis.

(b) If propane flows at a rate of 150 mol C_3H_8/s in the original fuel–air mixture, what is the minimum molar flow rate of the dilution air?

(c) How would the actual dilution air feed rate probably compare with the value calculated in Part (b)? (>, <, =) Explain.

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4.18. One thousand kilograms per hour of a mixture containing equal parts by mass of methanol and water is distilled. Product streams leave the top and the bottom of the distillation column. The flow rate of the bottom stream is measured and found to be 673 kg/h, and the overhead stream is analyzed and found to contain 96.0 wt% methanol.

(a) Draw and label a flowchart of the process and do the degree-of-freedom analysis.

(b) Calculate the mass and mole fractions of methanol and the molar flow rates of methanol and water in the bottom product stream.

(c) Suppose the bottom product stream is analyzed and the mole fraction of methanol is found to be significantly higher than the value calculated in Part (b). List as many possible reasons for the discrepancy as you can think of. Include in your list possible violations of assumptions made in Part (b).

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4.19. L-Serine is an amino acid that often is provided when intravenous feeding solutions are used to maintain the health of a patient. It has a molecular weight of 105, is produced by fermentation and recovered and purified by crystallization at 10°C. Yield is enhanced by adding methanol to the system, thereby reducing serine solubility in aqueous solutions.

An aqueous serine solution containing 30 wt% serine and 70% water is added along with methanol to a batch crystallizer that is allowed to equilibrate at 10°C. The resulting crystals are recovered by filtration; liquid passing through the filter is known as **filtrate**, and the recovered crystals may be assumed in this problem to be free of adhering filtrate. The crystals contain a mole of water for every mole of serine and are known as a *monohydrate*. The crystal mass recovered in a particular laboratory run is 500 g, and the filtrate is determined to be 2.4 wt% serine, 48.8% water, and 48.8% methanol.

(a) Draw and label a flowchart for the operation and carry out a degree-of-freedom analysis. Determine the ratio of mass of methanol added per unit mass of feed.

(b) The laboratory process is to be scaled to produce 750 kg/h of product crystals. Determine the required aqueous serine solution rates of aqueous serine solution and methanol.

4.20. A 100 kmol/h stream that is 97 mole% carbon tetrachloride (CCl_4) and 3% carbon disulfide (CS_2) is to be recovered from the bottom of a distillation column. The feed to the column is 16 mole% CS_2 and 84% CCl_4, and 2% of the CCl_4 entering the column is contained in the overhead stream leaving the top of the column.

(a) Draw and label a flowchart of the process and do the degree-of-freedom analysis.

(b) Calculate the mass and mole fractions of CCl_4 in the overhead stream, and determine the molar flow rates of CCl_4 and CS_2 in the overhead and feed streams.

(c) Suppose the overhead stream is analyzed and the mole fraction of CS_2 is found to be significantly lower than the value calculated in Part (b). List as many reasons as you can for the discrepancy, including possible violations of assumptions made in Part (b).

4.21. A pharmaceutical product, P, is made in a batch reactor. The reactor effluent goes through a purifiation process to yield a final product stream and a waste stream. The initial charge (feed) to the reactor and the final product are each weighed, and the reactor effluent, final product, and waste stream are each analyzed for P. The analyzer calibration is a series of meter readings, R, corresponding to known mass fractions of P, x_P.

x_P	0.08	0.16	0.25	0.45
R	105	160	245	360

(a) Plot the analyzer calibration data on logarithmic axes and determine an expression for $x_P(R)$.

(b) The data sheet for one run is shown below:

Batch #: 23601 Date: 10/4
Mass charged to reactor: 2253 kg
Mass of purified product: 1239 kg
Reactor effluent analysis: $R = 388$
Final product analysis: $R = 583$
Waste stream analysis: $R = 140$

Calculate the mass fractions of P in all three streams. Then calculate the percentage yield of the purification process,

$$Y_P = \frac{\text{kg P in final product}}{\text{kg P in reactor effluent}} \times 100\%$$

(c) You are the engineer in charge of the process. You review the given run sheet and the calculations of Part (b), perform additional balance calculations, and realize that all of the recorded run data cannot possibly be correct. State how you know, itemize possible causes of the problem, state which cause is most likely, and suggest a step to correct it.

4.22. A liquid mixture containing ethanol (55.0 wt%) and the balance water enters a separation process unit at a rate of 90.5 kg/s. A technician draws samples of the two product streams leaving the separator and analyzes them with a gas chromatograph, obtaining values of 86.2 wt% ethanol (Product Stream 1) and 10.9% ethanol (Product Stream 2). The technician then reads a manometer attached to an orifice meter mounted in the pipe carrying Product Stream 1, converts the reading to a volumetric flow rate using a calibration curve, and converts that result to a mass flow rate using the average density of ethanol and water. The result is 54.0 kg/s. Finally, the technician calculates the mass flow rate of the second product stream using a material balance and reports the calculated product stream flow rates and compositions to you. You examine them, do some calculations, and reject them.

(a) Draw and label a flow chart of the separation process.

(b) Carry out the calculations that led you to reject the submitted results and explain how you knew the values were wrong.

(c) List up to five possible reasons for the incorrect results. For each one, briefly state how you might determine whether it was in fact a cause of error and what you might do to correct it if it was.

4.23. A stream of humid air containing 1.50 mole% $H_2O(v)$ and the balance dry air is to be humidified to a water content of 10.0 mole% H_2O. For this purpose, liquid water is fed through a flowmeter and evaporated into the air stream. The flowmeter reading, R, is 95. The only available calibration data for the flowmeter are two points scribbled on a sheet of paper, indicating that readings $R = 15$ and $R = 50$ correspond to flow rates $\dot{V} = 40.0\ \text{ft}^3/\text{h}$ and $\dot{V} = 96.9\ \text{ft}^3/\text{h}$, respectively.

(a) Assuming that the process is working as intended, draw and label the flowchart, do the degree-of-freedom analysis, and estimate the molar flow rate (lb-mole/h) of the humidified (outlet) air if (i) the volumetric flow rate is a linear function of R and (ii) the reading R is a linear function of $\dot{V}^{0.5}$.

(b) Suppose the outlet air is analyzed and found to contain only 7% water instead of the desired 10%. List as many possible reasons as you can think of for the discrepancy, concentrating on assumptions made in the calculation of Part (a) that might be violated in the real process.

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4.24. A liquid mixture contains 60.0 wt% ethanol (E), 5.0 wt% of a dissolved solute (S), and the balance water. A stream of this mixture is fed to a continuous distillation column operating at steady state. Product streams emerge at the top and bottom of the column. The column design calls for the product streams to have equal mass flow rates and for the top stream to contain 90.0 wt% ethanol and no S.

(a) Assume a basis of calculation, draw and fully label a process flowchart, do the degree-of-freedom analysis, and verify that all unknown stream flows and compositions can be calculated. (Don't do any calculations yet.)

(b) Calculate (i) the mass fraction of S in the bottom stream and (ii) the fraction of the ethanol in the feed that leaves in the bottom product stream (i.e., kg E in bottom stream/kg E in feed) if the process operates as designed.

(c) An analyzer is available to determine the composition of ethanol–water mixtures. The calibration curve for the analyzer is a straight line on a plot *on logarithmic axes* of mass fraction of ethanol, x (kg E/kg mixture), versus analyzer reading, R. The line passes through the points ($R = 15, x = 0.100$) and ($R = 38, x = 0.400$). Derive an expression for x as a function of $R(x = \cdots)$ based on the calibration, and use it to determine the value of R that should be obtained if the *top* product stream from the distillation column is analyzed.

(d) Suppose a sample of the top stream is taken and analyzed and the reading obtained is not the one calculated in Part (c). Assume that the calculation in Part (c) is correct and that the plant operator followed the correct procedure in doing the analysis. Give five significantly different possible causes for the deviation between R_{measured} and $R_{\text{predicted}}$, including several assumptions made when writing the balances of Part (c). For each one, suggest something that the operator could do to check whether it is in fact the problem.

BIOENGINEERING

*4.25. Certain vegetables and fruits contain plant pigments called *carotenoids* that are metabolized in the body to produce Vitamin A. Lack of Vitamin A causes an estimated 250,000 to 500,000 children worldwide to become blind every year. An approach to reducing blindness and other childhood health problems resulting from this deficiency is to use **genetic engineering** of rice—a food staple in developing countries and economically disadvantaged regions of the world—so that rice becomes a dietary source of Vitamin A. For example, a strain known as **Golden Rice** has been genetically engineered so that it can produce and store carotenoids such as β-carotene (which helps give carrots and squash their yellow-orange color). One type of Golden Rice contains approximately 30 micrograms of carotenoids (81% β-carotene, 16% α-carotene, and 3% β-cryptoxanthin) per gram of uncooked rice. A study has reported that when a person eats Golden Rice, their body metabolizes 1 microgram of Vitamin A for every 3.8 micrograms of β-carotene they consume.

(a) It is recommended that children between 1 and 3 years of age should get 300 micrograms of Vitamin A per day. Considering only the metabolism of β-carotene given above, how many grams of Golden Rice would a child have to eat in order to obtain this much Vitamin A? Does this seem like a reasonable amount of rice to eat in one day, if one cup of cooked rice is approximately 175 g?

(b) α-carotene and β-cryptoxanthin can also be converted into Vitamin A, but when compared to β-carotene, it takes twice as much of each of these compounds to produce one unit of Vitamin A. Considering all of the carotenoids in Golden Rice as potential sources of Vitamin A, how many grams of Golden Rice would a three-year-old child have to eat in order to obtain the recommended daily amount of Vitamin A?

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(c) Some individuals are not convinced that genetically modified foods are safe to grow or to eat. What kinds of risks or uncertainties are cited by these individuals? What kinds of measures are taken by farmers and suppliers of genetically modified seeds to minimize these risks?

(d) Some people do not believe that Golden Rice is a practical, viable solution to Vitamin A deficiency around the world. Summarize the major arguments for and against production and distribution of Golden Rice.

4.26. Two aqueous sulfuric acid solutions containing 20.0 wt% H_2SO_4 (SG = 1.139) and 60.0 wt% H_2SO_4 (SG = 1.498) are mixed to form a 4.00 molar solution (SG = 1.213).

(a) Calculate the mass fraction of sulfuric acid in the product solution.

(b) Taking 100 kg of the 20% feed solution as a basis, draw and label a flowchart of this process, labeling both masses and volumes, and do the degree-of-freedom analysis. Calculate the feed ratio (liters 20% solution/liter 60% solution).

(c) What feed rate of the 60% solution (L/h) would be required to produce 1250 kg/h of the product?

4.27. A paint mixture containing 25.0% of a pigment and the balance binders (which help the pigment stick to the surface) and solvents (which ensure that the paint stays in liquid form) sells for $18.00/kg, and a mixture containing 12.0% sells for $10.00/kg.

* Adapted from a problem contributed by Kay C. Dee and Glen Livesay of Rose-Hulman Institute of Technology.

(a) If a paint retailer produces a blend containing 17.0% pigment, for how much ($/kg) should it be sold to yield a 10% profit?

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(b) Paint manufacturers have begun to market "low VOC" paint as a more environmentally friendly product. What are VOCs? List some ways in which paint products can be altered to lower the VOC content.

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4.28. In the commercial production of sugar (sucrose), the product crystals are washed and centrifuged to partial dryness. The crystals are then sent through a rotary dryer where they are contacted with a hot stream of air that reduces the moisture content from 1.0 wt% to 0.1 wt%. The ratio of wet sugar to inlet air fed to the dryer is 3.3 kg wet sugar/kg inlet air. The inlet air contains 1.5 mole% water.

(a) Draw and label the flowchart and do the degree-of-freedom analysis.

(b) Taking a basis of 100 kg of wet sugar fed to the dryer, calculate the mass of water and its mole fraction in the air leaving the dryer.

(c) If 1000 tons/day of dried sugar is to be produced, at what rate (lb_m/h) is water evaporated from the sugar?

(d) Determine the current price of sugar and estimate in $/year the current income (not the same as profit) from operation in Part (c).

(e) Samples of the product crystals are analyzed routinely for water content. The mass fractions of water in the samples on successive days of operation are shown in the following table.

Day	1	2	3	4	5	6	7	8	9	10
x_W	0.00102	0.00097	0.00099	0.00101	0.00107	0.00099	0.00102	0.00094	0.000101	0.00098

The quality of the product during these days of operation has been graded acceptable, and it is decided that the process will be shut down for maintenance when the value of measured value of x_W is more than three standard deviations from the mean of this series of runs. What are the maximum and minimum values of x_W?

4.29. A sedimentation process is to be used to separate pulverized coal from slate. A suspension of finely divided particles of galena (lead sulfide, SG = 7.44) in water is prepared. The overall specific gravity of the suspension is 1.48.

(a) Four hundred kilograms of galena and a quantity of water are loaded into a tank and stirred to obtain a uniform suspension with the required specific gravity. Draw and label the flowchart (label both the masses and volumes of the galena and water), do the degree-of-freedom analysis, and calculate how much water (m^3) must be fed to the tank.

(b) A mixture of coal and slate is placed in the suspension. The coal rises to the top and is skimmed off, and the slate sinks. What can you conclude about the specific gravities of coal and slate?

(c) The separation process works well for several hours, but then a region of clear liquid begins to form at the top of the cloudy suspension and the coal sinks to the bottom of this region, making skimming more difficult. What might be happening to cause this behavior and what corrective action might be taken? Now what can you say about the specific gravity of coal?

SAFETY

4.30. A garment to protect the wearer from toxic agents may be made of a fabric that contains an adsorbent, such as activated carbon. In a test of such a fabric, a gas stream containing 7.76 mg/L of carbon tetrachloride (CCl_4) was passed through a 7.71-g sample of the fabric at a rate of 1.0 L/min, and the concentration of CCl_4 in the gas leaving the fabric was monitored. The run was continued for 15.5 min with no CCl_4 being detected, after which the CCl_4 concentration began to rise.

(a) How much CCl_4 was fed to the system during the first 15.5 min of the run? How much was adsorbed? Using this information as a guide, sketch the expected concentration of CCl_4 in the exit gas as a function of time, showing the curve from $t = 0$ to $t \gg 15.5$ min.

(b) Assuming a linear relationship between amount of CCl_4 adsorbed and mass of fabric, what fabric mass would be required if the feed concentration is 5 mg/L, the feed rate 1.4 L/min, and it is desired that no CCl_4 leave the fabric earlier than 30 min?

4.31. A dilute aqueous solution of H_2SO_4 (Solution A) is to be mixed with a solution containing 90.0 wt% H_2SO_4 (Solution B) to produce a 75.0 wt% solution (Solution C).

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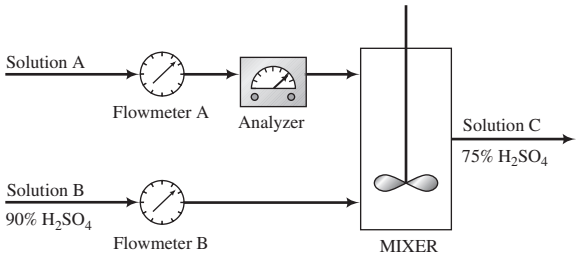

The flow rate and concentration of Solution A change periodically, so that it is necessary to adjust the flow rate of Solution B to keep the product H_2SO_4 concentration constant.

Flowmeters A and B have linear calibration plots of mass flow rate ($\dot{m}$) versus meter reading (R), which pass through the following points:

$$\begin{aligned} &\text{Flowmeter A:} && \dot{m}_A = 150\ \text{lb}_m/\text{h}, && R_A = 25 \\ &&& \dot{m}_A = 500\ \text{lb}_m/\text{h}, && R_A = 70 \\ &\text{Flowmeter B:} && \dot{m}_B = 200\ \text{lb}_m/\text{h}, && R_B = 20 \\ &&& \dot{m}_B = 800\ \text{lb}_m/\text{h}, && R_B = 60 \end{aligned}$$

The analyzer calibration is a straight line on a semilog plot of $\%H_2SO_4(x)$ on a logarithmic scale versus meter reading (R_x) on a linear scale. The line passes through the points ($x = 20\%, R_x = 4.0$) and ($x = 100\%, R_x = 10.0$).

(a) Calculate the flow rate of Solution B needed to process 300 lb_m/h of 55% H_2SO_4 (Solution A), and the resulting flow rate of Solution C. (The calibration data are not needed for this part.)

(b) Derive the calibration equations for $\dot{m}_A(R_A)$, $\dot{m}_B(R_B)$, and $x(R_x)$. Calculate the values of R_A, R_B, and R_x corresponding to the flow rates and concentrations of Part (a).

(c) The process technician's job is to read Flowmeter A and the analyzer periodically, and then to adjust the flow rate of Solution B to its required value. Derive a formula that the technician can use for R_B in terms of R_A and R_x, and then check it by substituting the values of Part (a).

4.32. Gas streams containing hydrogen and nitrogen in different proportions are produced on request by blending gases from two feed tanks: Tank A (hydrogen mole fraction = x_A) and Tank B (hydrogen mole fraction = x_B). The requests specify the desired hydrogen mole fraction, x_P, and *mass* flow rate of the product stream, $\dot{m}_P$(kg/h).

(a) Suppose the feed tank compositions are $x_A = 0.10$ mol H_2/mol and $x_B = 0.50$ mol H_2/mol, and the desired blend–stream mole fraction and mass flow rate are $x_P = 0.20$ mol H_2/mol and $\dot{m}_P = 100$ kg/h. Draw and label a flowchart and calculate the required *molar* flow rates of the feed mixtures, $\dot{n}_A$(kmol/h) and $\dot{n}_B$(kmol/h).

(b) Derive a series of formulas for $\dot{n}_A$ and $\dot{n}_B$ in terms of x_A, x_B, x_P, and $\dot{m}_P$. Test them using the values in Part (a).

(c) Write a spreadsheet that has column headings $x_A, x_B, x_P, \dot{m}_P, \dot{n}_A$, and $\dot{n}_B$. The spreadsheet should calculate entries in the last two columns corresponding to data in the first four. In the first six data rows of the spreadsheet, do the calculations for $x_A = 0.10$, $x_B = 0.50$, and $x_P =$ 0.10, 0.20, 0.30, 0.40, 0.50, and 0.60, all for $\dot{m}_P = 100$ kg/h. Then in the next six rows repeat the calculations for the same values of x_A, x_B, and x_P for $\dot{m}_P = 250$ kg/h. *Explain any of your results that appear strange or impossible.*

(d) Enter the formulas of Part (b) into an equation-solving program. Run the program to determine $\dot{n}_A$ and $\dot{n}_B$ for the 12 sets of input variable values given in Part (c) and explain any physically impossible results.

BIOENGINEERING

4.33. An **artificial kidney** is a device that removes water and waste metabolites from blood. In one such device, the **hollow fiber hemodialyzer**, blood flows from an artery through the insides of a bundle

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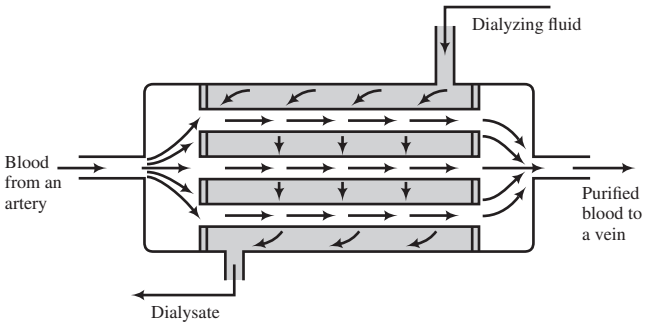
of hollow cellulose acetate fibers, and **dialyzing fluid**, which consists of water and various dissolved salts, flows on the outside of the fibers. Water and waste metabolites—principally urea, creatinine, uric acid, and phosphate ions—pass through the fiber walls into the dialyzing fluid, and the purified blood is returned to a vein.



At some time during a dialysis the arterial and venous blood conditions are as follows:

	Arterial (entering) Blood	Venous (exiting) Blood
Flow Rate	200.0 mL/min	195.0 mL/min
Urea (H_2NCONH_2) Concentration	1.90 mg/mL	1.75 mg/mL

(a) Calculate the rates at which urea and water are being removed from the blood.
(b) If the dialyzing fluid enters at a rate of 1500 mL/min and the exiting solution (*dialysate*) leaves at approximately the same rate, calculate the concentration of urea in the dialysate.
(c) Suppose we want to reduce the patient's urea level from an initial value of 2.7 mg/mL to a final value of 1.1 mg/mL. If the total blood volume is 5.0 liters and the average rate of urea removal is that calculated in Part (a), how long must the patient be dialyzed? (Neglect the loss in total blood volume due to the removal of water in the dialyzer.)

Exploratory Exercises—Research and Discover

(d) The device described in this problem is external to the body and requires that the patient travel to a dialysis center several times a week. What types of challenges would be encountered if an artificial kidney were implanted in the patient's body?
(e) Briefly describe current state-of-the-art designs for artificial kidneys.

4.34. The **indicator-dilution method** is a technique used to determine flow rates of fluids in channels for which devices like rotameters and orifice meters cannot be used (e.g., rivers, blood vessels, and large-diameter pipelines). A stream of an easily measured substance (the **tracer**) is injected into the channel at a known rate, and the tracer concentration is measured at a point far enough downstream of the injection point for the tracer to be completely mixed with the flowing fluid. The larger the flow rate of the fluid, the lower the tracer concentration at the measurement point.

A gas stream that contains 1.50 mole% CO_2 flows through a pipeline. Twenty (20.0) kilograms of CO_2 per minute is injected into the line. A sample of the gas is drawn from a point in the line 150 meters downstream of the injection point and found to contain 2.3 mole% CO_2.

(a) Estimate the gas flow rate (kmol/min) upstream of the injection point.
(b) Eighteen seconds elapse from the instant the additional CO_2 is first injected to the time the CO_2 concentration at the measurement point begins to rise. Assuming that the tracer travels at the average velocity of the gas in the pipeline (i.e., neglecting diffusion of CO_2), estimate the average velocity (m/s). If the molar gas density is 0.123 kmol/m^3, what is the pipe diameter?

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4.35. A variation of the indicator-dilution method (see preceding problem) is used to measure total blood volume. A known amount of a tracer is injected into the bloodstream and disperses uniformly throughout the circulatory system. A blood sample is then withdrawn, the tracer concentration in the sample is measured, and the measured concentration [which equals (tracer injected)/(total blood volume) if no tracer is lost through blood vessel walls] is used to determine the total blood volume.

In one such experiment, 0.60 cm^3 of a solution containing 5.00 mg/L of a dye is injected into an artery of a grown man. About 10 minutes later, after the tracer has had time to distribute itself uniformly throughout the bloodstream, a blood sample is withdrawn and placed in the sample chamber of a spectrophotometer. A beam of light passes through the chamber, and the spectrophotometer measures the intensity of the transmitted beam and displays the value of the solution absorbance (a quantity that increases with the amount of light absorbed by the sample). The value displayed is 0.18. A calibration curve of absorbance A versus tracer concentration C (micrograms dye/liter blood) is a straight line through the origin and the point ($A = 0.9$, $C = 3$ μg/L). Estimate the patient's total blood volume from these data.

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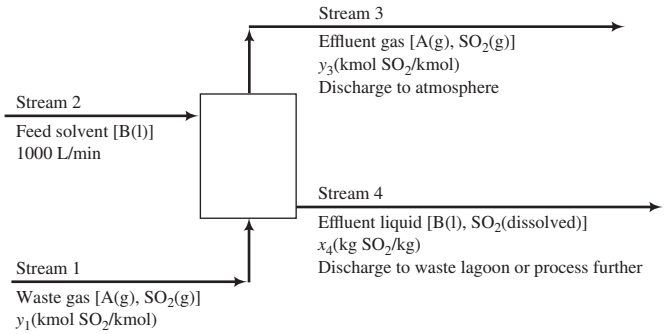
ENVIRONMENTAL

4.36. **Gas absorption** or **gas scrubbing** is a commonly used method for removing environmentally undesirable species from waste gases in chemical manufacturing and combustion processes. The waste gas is contacted with a liquid solvent in which the potential pollutants are soluble and the other species in the waste gas are relatively insoluble. Most of the pollutants go into solution and emerge with the liquid effluent from the scrubber, and the cleaned gas is discharged to the atmosphere. The liquid effluent may be sent to a waste lagoon or subjected to further treatment to recover the solvent and/or to convert the pollutant to a species that can be released safely to the environment.

A waste gas containing SO_2 (a precursor of acid rain) and several other species (collectively designated as A) is fed to a scrubbing tower where it contacts a solvent (B) that absorbs SO_2. The solvent feed rate to the tower is 1000 L/min. The specific gravity of the solvent is 1.30. Absorption of A and evaporation of B in the scrubber may be neglected.



The gas in the scrubber rises through a series of *trays* (metal plates perforated with many small holes), and the solvent flows over the trays and through *downcomers* to the trays below. Gas bubbles emerge from the holes in each tray and rise through the covering liquid, and SO_2 transfers from the bubbles and into solution.

The volumetric flow rate of the feed gas is determined with an orifice meter, with a differential mercury manometer being used to measure the pressure drop across the orifice. Calibration data for the meter are tabulated here:

h(mm)	$\dot{V}$(m^3/min)
100	142
200	204
300	247
400	290

The molar density of the feed gas may be determined from the formula

$$\rho\left(\frac{\text{mol}}{\text{liter}}\right) = \frac{12.2P(\text{atm})}{T(\text{K})}$$

where P and T are the absolute pressure and temperature of the gas. An electrochemical detector is used to measure the SO_2 concentration in the inlet and outlet gas streams: SO_2 in the sampled gas is absorbed in a solution across which a fixed voltage is applied, and the mole fraction of SO_2 in the gas is determined from

the resulting current. The calibration curve for the analyzer is a straight line on a semilog plot of y (mol SO_2/mol total) versus R (analyzer reading) that passes through the following points:

y (log scale)	R (rectangular scale)
0.00166	20
0.1107	90

The following data are taken:

$$\left.\begin{array}{l} T = 75°\text{F} \\ P = 150\ \text{psig} \\ h(\text{orifice meter}) = 210\ \text{mm} \\ R(SO_2\ \text{analyzer}) = 82.4 \end{array}\right\} \text{(feed gas)}$$

$$R(SO_2\ \text{analyzer}) = 116 \quad \text{(outlet gas)}$$

(a) Draw and completely label a process flowchart. Include in the labeling the molar flow rates and SO_2 mole fractions of the gas streams and the mass flow rates and SO_2 mass fractions of the liquid streams. Show that the scrubber has zero degrees of freedom.

(b) Determine (i) the orifice meter calibration formula by plotting $\dot{V}$ versus h on logarithmic axes and (ii) the SO_2 analyzer calibration formula.

(c) Calculate (i) the mass fraction of SO_2 in the liquid effluent stream and (ii) the rate at which SO_2 is removed from the feed gas (kg SO_2/min).

(d) The scrubber column trays commonly have diameters on the order of 1–5 meters and perforation holes on the order of 4–12 mm in diameter, leading to the formation of many tiny bubbles in the liquid on each tray. Speculate on the advantages of making the bubbles as small as possible.

ENVIRONMENTAL

*__4.37.__ The SO_2 scrubbing tower described in Problem 4.36 is to be used to reduce the SO_2 mole fraction in the waste gas to a level that meets air-quality standards. The solvent feed rate must be large enough to keep the SO_2 mass fraction in the exit liquid below a specified maximum value.

(a) Draw and label a flowchart of the tower. Along with the molar flow rates and SO_2 mole fractions of the four process streams, label the feed gas temperature and pressure [T_1(°F), P_1(psig)], the feed gas orifice meter reading [h_1(mm)], the SO_2 analyzer reading for the feed gas (R_1), the volumetric feed rate of solvent to the column [$\dot{V}_2$(m^3/min)], and the SO_2 analyzer reading for the exit gas (R_3). (The temperature and pressure units are taken from the calibration curves for the gauges used to measure these variables.)

(b) Derive a series of equations relating all of the labeled variables on the flowchart. The equations should include the calibration formulas calculated in Part (b) of Problem 4.36. Determine the number of degrees of freedom for the process system.

In the remainder of the problem, you will be given values of measured feed gas stream variables [T_1(°F), P_1(psig), h_1(mm), and R_1], the maximum allowed SO_2 mole fraction in the exit solution [x_4], and the specified SO_2 mole fraction in the exit gas (y_3), and asked to calculate the expected SO_2 analyzer reading for the exit gas (R_3) and the minimum volumetric flow rate of solvent ($\dot{V}_2$). Part (c) involves using a spreadsheet for the calculation, and Part (d) calls for an independent calculation using an equation-solving program.

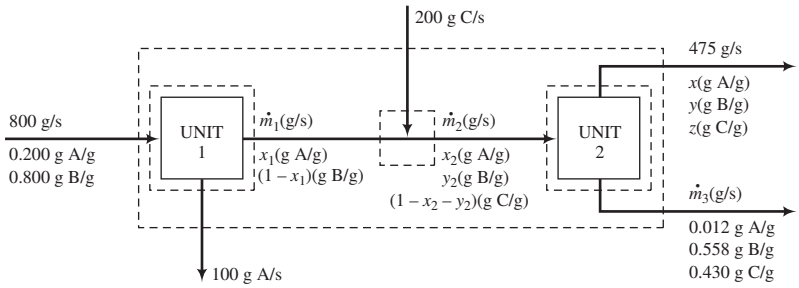
(c) Create a spreadsheet to store input values of T_1, P_1, h_1, R_1, x_4, and y_3 and to calculate R_3 and $\dot{V}_2$. In the first five rows, insert the values $T_1 = 75, P_1 = 150, h_1 = 210, R_1 = 82.4, x_4 = 010,$ and $y_3 = 0.05, 0.025, 0.01, 0.005,$ and 0.001. In the next five rows, insert the same input values except make $x_4 = 0.02$. On a single graph, draw plots of $\dot{V}_2$ versus y_3 for each of the two given values of x_4 (preferably using the spreadsheet program to generate the graph). Briefly explain the shape of the curves and their position relative to each other.

(d) Enter the equations of Part (b) into an equation-solving program. Use the program to calculate R_3 and $\dot{V}_2$ corresponding to $T_1 = 75, P_1 = 150, h_1 = 210, R_1 = 82.4, x_4 = 0.10,$ and $y_3 = 0.05, 0.025,$

* It is advisable to solve Problem 4.36 before attempting this problem.

0.01, 0.005, and 0.001, and then $T_1 = 75, P_1 = 150, h_1 = 210, R_1 = 82.4, x_4 = 0.02$, and $y_3 = 0.05, 0.025, 0.01, 0.005$, and 0.001. If you did not already do so in Part (c), draw on a single graph plots of $\dot{V}_2$ versus y_3 for each of the two given values of x_4 and briefly explain the shape of the curves and their position relative to each other.

4.38. Following is a labeled flowchart for a steady-state two-unit process, with boundaries shown to denote subsystems about which balances can be taken. State the maximum number of balances that can be written for each subsystem and the order in which you would write balances to determine the unknown process variables. (See Example 4.4-1.)



BIOENGINEERING

*4.39. The hormone *estrogen* is produced in the ovaries of females and elsewhere in the body in men and postmenopausal women, and it is also administered in estrogen replacement therapy, a common treatment for women who have undergone a hysterectomy. Unfortunately, it also binds to estrogen receptors in breast tissue and can activate cells to become cancerous. *Tamoxifen* is a drug that also binds to estrogen receptors but does not activate cells, in effect blocking the receptors from access to estrogen and inhibiting the growth of breast-cancer cells.

Tamoxifen is administered in tablet form. In the manufacturing process, a finely ground powder contains tamoxifen (tam) and two inactive fillers—lactose monohydrate (lac) and corn starch (cs). The powder is mixed with a second stream containing water and suspended solid particles of polyvinylpyrrolidone (pvp) binder, which keeps the tablets from easily crumbling. The slurry leaving the mixer goes to a dryer, in which 94.2% of the water fed to the process is vaporized. The wet powder leaving the dryer contains 8.80 wt% tam, 66.8% lac, 21.4% cs, 2.00% pvp, and 1.00% water. After some additional processing, the powder is molded into tablets. To produce a hundred thousand tablets, 17.13 kg of wet powder is required.

(a) Taking a basis of 100,000 tablets produced, draw and label a process flowchart, labeling masses of individual components rather than total masses and component mass fractions. It is unnecessary to label the stream between the mixer and the dryer. Carry out a degree-of-freedom analysis of the overall two-unit process.

(b) Calculate the masses and compositions of the streams that must enter the mixer to make 100,000 tablets.

(c) Why was it unnecessary to label the stream between the mixer and the dryer? Under what circumstances would it have been necessary?

(d) Go back to the flowchart of Part (a). Without using the mass of the wet powder (17.13 kg) or any of the results from Part (b) in your calculations, determine the mass fractions of the stream components in the powder fed to the mixer and verify that they match your solution to Part (b). (Hint: Take a basis of 100 kg of wet powder.)

(e) Suppose a student does Part (d) before Part (b), and re-labels the powder feed to the mixer on the flowchart of Part (a) with an unknown total mass (m_1) and the three now known mole fractions. (Sketch the resulting flowchart.) The student then does a degree-of-freedom analysis, counts four unknowns (the masses of the powder, pvp, and water fed to the mixer, and the mass of water evaporated in the dryer), and six equations (five material balances for five species and the percentage evaporation), for a net of −2 degrees of freedom. Since there are more equations than unknowns, it should not be possible to get a unique solution for the four unknowns. Nevertheless, the student writes four equations, solves for the four unknowns, and verifies that all of

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater. (2010). "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses – Part I." http://pharmahub.org/resources/360.

the balance equations are satisfied. There must have been a mistake in the degree-of-freedom calculation. What was it?

Equipment Encyclopedia
distillation column

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4.40. A liquid mixture containing 30.0 mole% benzene (B), 25.0% toluene (T), and the balance xylene (X) is fed to a distillation column. The bottoms product contains 98.0 mole% X and no B, and 96.0% of the X in the feed is recovered in this stream. The overhead product is fed to a second column. The overhead product from the second column contains 97.0% of the B in the feed to this column. The composition of this stream is 94.0 mole% B and the balance T.

(a) Draw and label a flowchart of this process and do the degree-of-freedom analysis to prove that for an assumed basis of calculation, molar flow rates and compositions of all process streams can be calculated from the given information. Write in order the equations you would solve to calculate unknown process variables. In each equation (or pair of simultaneous equations), circle the variable(s) for which you would solve. Do not do the calculations.

(b) Calculate (i) the percentage of the benzene in the process feed (i.e., the feed to the first column) that emerges in the overhead product from the second column and (ii) the percentage of toluene in the process feed that emerges in the bottom product from the second column.

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evaporator

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4.41. Seawater containing 3.50 wt% salt passes through a series of 10 evaporators. Roughly equal quantities of water are vaporized in each of the 10 units and then condensed and combined to obtain a product stream of fresh water. The brine leaving each evaporator but the tenth is fed to the next evaporator. The brine leaving the tenth evaporator contains 5.00 wt% salt.

(a) Draw a flowchart of the process showing the first, fourth, and tenth evaporators. Label all the streams entering and leaving these three evaporators.

(b) Write in order the set of equations you would solve to determine the fractional yield of fresh water from the process (kg H_2O recovered/kg H_2O in process feed) and the weight percent of salt in the solution leaving the fourth evaporator. Each equation you write should contain no more than one previously undetermined variable. In each equation, circle the variable for which you would solve. Do not do the calculations.

(c) Solve the equations derived in Part (b) for the two specified quantities.

Exploratory Exercise—Research and Discover

(d) The problem statement made no mention of the disposition of the 5 wt% effluent from the tenth evaporator. Suggest two possibilities for its disposition and describe any environmental concerns that might need to be considered.

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distillation column

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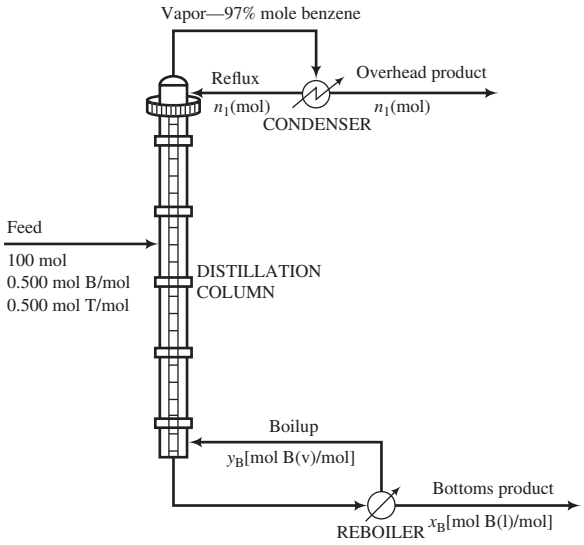
4.42. An equimolar liquid mixture of benzene and toluene is separated into two product streams by distillation. A process flowchart and a somewhat oversimplified description of what happens in the process follow:



Inside the column a liquid stream flows downward and a vapor stream rises. At each point in the column some of the liquid vaporizes and some of the vapor condenses. The vapor leaving the top of the column, which contains 97 mole% benzene, is completely condensed and split into two equal fractions: one is taken off as the overhead product stream, and the other (the **reflux**) is recycled to the top of the column. The overhead product stream contains 89.2% of the benzene fed to the column. The liquid leaving the bottom of the column is fed to a partial reboiler in which 45% of it is vaporized. The vapor generated in the reboiler (the **boilup**) is recycled to become the rising vapor stream in the column, and the residual reboiler liquid is taken off as the bottom product stream. The compositions of the streams leaving the reboiler are governed by the relation

$$\frac{y_B/(1-y_B)}{x_B/(1-x_B)} = 2.25$$

where y_B and x_B are the mole fractions of benzene in the vapor and liquid streams, respectively.

(a) Take a basis of 100 mol fed to the column. Draw and completely label a flowchart, and for each of four systems (overall process, column, condenser, and reboiler), do the degree-of-freedom analysis and identify a system with which the process analysis might appropriately begin (one with zero degrees of freedom).

(b) Write in order the equations you would solve to determine all unknown variables on the flowchart, circling the variable for which you would solve in each equation. Do not do the calculations in this part.

(c) Calculate the molar amounts of the overhead and bottoms products, the mole fraction of benzene in the bottoms product, and the percentage recovery of toluene in the bottoms product (100 × moles toluene in bottoms/mole toluene in feed).

4.43. The popularity of orange juice, especially as a breakfast drink, makes this beverage an important factor in the economy of orange-growing regions. Most marketed juice is concentrated and frozen and then reconstituted before consumption, and some is "not-from-concentrate." Although concentrated juices are less popular in the United States than they were at one time, they still have a major segment of the market for orange juice.

The approaches to concentrating orange juice include evaporation, **freeze concentration**, and **reverse osmosis**. Here we examine the evaporation process by focusing only on two constituents in the juice: solids and water. Fresh orange juice contains approximately 10 wt% solids (sugar, citric acid, and other ingredients) and frozen concentrate contains approximately 42 wt% solids. The frozen concentrate is obtained by evaporating water from the fresh juice to produce a mixture that is approximately 65 wt% solids. However, so that the flavor of the concentrate will closely approximate that of fresh juice, the concentrate from the evaporator is blended with fresh orange juice (and other additives) to produce a final concentrate that is approximately 42 wt% solids.

(a) Draw and label a flowchart of this process, neglecting the vaporization of everything in the juice but water. First prove that the subsystem containing the point where the bypass stream splits off from the evaporator feed has one degree of freedom. (If you think it has zero degrees, try determining the unknown variables associated with this system.) Then perform the degree-of-freedom analysis for the overall system, the evaporator, and the bypass–evaporator product mixing point, and write in order the equations you would solve to determine all unknown stream variables. In each equation, circle the variable for which you would solve, but don't do any calculations.

(b) Calculate the amount of product (42% concentrate) produced per 100 kg fresh juice fed to the process and the fraction of the feed that bypasses the evaporator.

(c) Most of the volatile ingredients that provide the taste of the concentrate are contained in the fresh juice that bypasses the evaporator. You could get more of these ingredients in the final product by evaporating to (say) 90% solids instead of 65%; you could then bypass a greater fraction of the fresh juice and thereby obtain an even better tasting product. Suggest possible drawbacks to this proposal.

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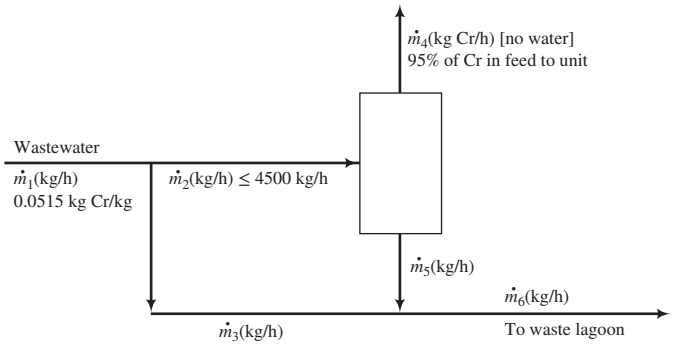
4.44. Effluents from metal-finishing plants have the potential of discharging undesirable quantities of metals, such as cadmium, nickel, lead, manganese, and chromium, in forms that are detrimental to water and air quality. A local metal-finishing plant has identified a wastewater stream that contains 5.15 wt% chromium (Cr) and devised the following approach to lowering risk and recovering the valuable metal. The wastewater stream is fed to a treatment unit that removes 95% of the chromium in the feed and recycles it to

the plant. The residual liquid stream leaving the treatment unit is sent to a waste lagoon. The treatment unit has a maximum capacity of 4500 kg wastewater/h. If wastewater leaves the finishing plant at a rate higher than the capacity of the treatment unit, the excess (anything above 4500 kg/h) bypasses the unit and combines with the residual liquid leaving the unit, and the combined stream goes to the waste lagoon.



(a) Without assuming a basis of calculation, draw and label a flowchart of the process.
(b) Wastewater leaves the finishing plant at a rate $\dot{m}_1 = 6000$ kg/h. Calculate the flow rate of liquid to the waste lagoon, $\dot{m}_6$(kg/h), and the mass fraction of Cr in this liquid, x_6(kg Cr/kg).
(c) Calculate the flow rate of liquid to the waste lagoon and the mass fraction of Cr in this liquid for $\dot{m}_1$ varying from 1000 kg/h to 10,000 kg/h in 1000 kg/h increments. Generate a plot of x_6 versus $\dot{m}_1$. (*Suggestion:* Use a spreadsheet for these calculations.)
(d) The company has hired you as a consultant to help them determine whether or not to add capacity to the treatment unit to increase the recovery of chromium. What would you need to know to make this determination?
(e) What concerns might need to be addressed regarding the waste lagoon?

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4.45. An evaporation–crystallization process of the type described in Example 4.5-2 is used to obtain solid potassium sulfate from an aqueous solution of this salt. The fresh feed to the process contains 19.6 wt% K_2SO_4. The wet filter cake consists of solid K_2SO_4 crystals and a 40.0 wt% K_2SO_4 solution, in a ratio 10 kg crystals/kg solution. The filtrate, also a 40.0% solution, is recycled to join the fresh feed. Of the water fed to the evaporator, 45.0% is evaporated. The evaporator has a maximum capacity of 175 kg water evaporated/s.

(a) Assume the process is operating at maximum capacity. Draw and label a flowchart and do the degree-of-freedom analysis for the overall system, the recycle–fresh feed mixing point, the evaporator, and the crystallizer. Then write in an efficient order (minimizing simultaneous equations) the equations you would solve to determine all unknown stream variables. In each equation, circle the variable for which you would solve, but don't do the calculations.
(b) Calculate the maximum production rate of solid K_2SO_4, the rate at which fresh feed must be supplied to achieve this production rate, and the ratio kg recycle/kg fresh feed.
(c) Calculate the composition and feed rate of the stream entering the crystallizer if the process is scaled to 75% of its maximum capacity.
(d) The wet filter cake is subjected to another operation after leaving the filter. Suggest what it might be. Also, list what you think the principal operating costs for this process might be.
(e) Use an equation-solving computer program to solve the equations derived in Part (a). Verify that you get the same solutions determined in Part (b).

BIOENGINEERING

**4.46.* Mammalian cells can be cultured for a variety of purposes, including synthesis of vaccines. They must be maintained in growth media containing all of the components required for proper cellular function to ensure their survival and propagation. Traditionally, growth media were prepared by blending a powder, such as Dulbecco's Modified Eagle Medium (DMEM) with sterile deionized water. DMEM contains glucose, buffering agents, proteins, and amino acids. Using a sterile (i.e., bacterial-, fungal-,

* Adapted from a problem contributed by Adam Melvin of Louisiana State University.

and yeast-free) growth medium ensures proper cell growth, but sometimes the water (or powder) can become contaminated, requiring the addition of antibiotics to eliminate undesired contaminants. The culture medium is supplemented with fetal bovine serum (FBS) that contains additional growth factors required by the cells.

Suppose an aqueous stream (SG = 0.90) contaminated with bacteria is split, with 75% being fed to a mixing unit to dissolve a powdered mixture of DMEM contaminated with the same bacteria found in the water. The ratio of impure feed water to powder entering the mixer is 4.4:1. The stream leaving the mixer (containing DMEM, water, and bacteria) is combined with the remaining 25% of the aqueous stream and fed to a filtration unit to remove all of the bacteria that have contaminated the system, a total of 20.0 kg. Once the bacteria have been removed, the sterile medium is combined with FBS and the antibiotic cocktail PSG (Penicillin-Streptomycin-L-Glutamine) in a shaking unit to generate 5000 L of growth medium (SG = 1.2). The final composition of the growth medium is 66.0 wt% H_2O, 11.0% FBS, 8.0% PSG, and the balance DMEM.

(a) Draw and label the process flowchart.

(b) Do a degree-of-freedom analysis around each piece of equipment (mixer, filter, and shaker), the splitter, the mixing point, and the overall system. Based on the analysis, identify which system or piece of equipment should be the starting point for further calculations.

(c) Calculate all of the unknown process variables.

(d) Determine a value for (i) the mass ratio of sterile growth medium product to feed water and (ii) the mass ratio of bacteria in the water to bacteria in the powder.

(e) Suggest two reasons why the bacteria should be removed from the system.

Equipment Encyclopedia
adsorber stripper

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4.47. In an **absorption tower** (or **absorber**), a gas is contacted with a liquid under conditions such that one or more species in the gas dissolve in the liquid. A **stripping tower** (or **stripper**) also involves a gas contacting a liquid, but under conditions such that one or more components of the feed liquid come out of solution and exit in the gas leaving the tower.

A process consisting of an absorption tower and a stripping tower is used to separate the components of a gas containing 30.0 mole% carbon dioxide and the balance methane. A stream of this gas is fed to the bottom of the absorber. A liquid containing 0.500 mole% dissolved CO_2 and the balance methanol is recycled from the bottom of the stripper and fed to the top of the absorber. The product gas leaving the top of the absorber contains 1.00 mole% CO_2 and essentially all of the methane fed to the unit. The CO_2-rich liquid solvent leaving the bottom of the absorber is fed to the top of the stripper and a stream of nitrogen gas is fed to the bottom. Ninety percent of the CO_2 in the liquid feed to the stripper comes out of solution in the column, and the nitrogen/CO_2 stream leaving the column passes out to the atmosphere through a stack. The liquid stream leaving the stripping tower is the 0.500% CO_2 solution recycled to the absorber.

The absorber operates at temperature T_a and pressure P_a and the stripper operates at T_s and P_s. Methanol may be assumed to be nonvolatile—that is, none enters the vapor phase in either column—and N_2 may be assumed insoluble in methanol.

(a) In your own words, explain the overall objective of this two-unit process and the functions of the absorber and stripper in the process.

(b) The streams fed to the tops of each tower have something in common, as do the streams fed to the bottoms of each tower. What are these commonalities and what is the probable reason for them?

(c) Taking a basis of 100 mol/h of gas fed to the absorber, draw and label a flowchart of the process. For the stripper outlet gas, label the component molar flow rates rather than the total flow rate and mole fractions. Do the degree-of-freedom analysis and write in order the equations you would solve to determine all unknown stream variables *except the nitrogen flow rate entering and leaving the stripper*. Circle the variable(s) for which you would solve each equation (or set of simultaneous equations), but don't do any of the calculations yet.

(d) Calculate the fractional CO_2 removal in the absorber (moles absorbed/mole in gas feed) and the molar flow rate and composition of the liquid feed to the stripping tower.

(e) Calculate the molar feed rate of gas to the absorber required to produce an absorber product gas flow rate of 1000 kg/h.

(f) Would you guess that T_s would be higher or lower than T_a? Explain. (*Hint:* Think about what happens when you heat a carbonated soft drink and what you want to happen in the stripper.) What about the relationship of P_s to P_a?

(g) What properties of methanol would you guess make it the solvent of choice for this process? (In more general terms, what would you look for when choosing a solvent for an absorption–stripping process to separate one gas from another?)

Equipment Encyclopedia
extractor, filter, evaporator, heat exchanger

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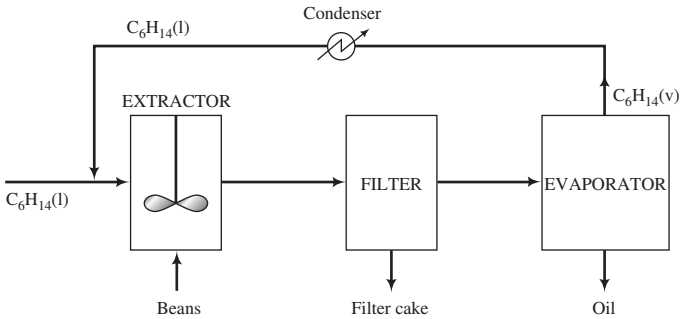
4.48. In the production of a bean oil, beans containing 13.0 wt% oil and 87.0% solids are ground and fed to a stirred tank (the **extractor**) along with a recycled stream of liquid *n*-hexane. The feed ratio is 3 kg hexane/kg beans. The ground beans are suspended in the liquid, and essentially all of the oil in the beans is extracted into the hexane. The extractor effluent passes to a filter where the solids are collected and form a **filter cake**. The filter cake contains 75.0 wt% bean solids and the balance bean oil and hexane, the latter two in the same ratio in which they emerge from the extractor. The filter cake is discarded and the liquid filtrate is fed to a heated evaporator in which the hexane is vaporized and the oil remains as a liquid. The oil is stored in drums and shipped. The hexane vapor is subsequently cooled and condensed, and the liquid hexane condensate is recycled to the extractor.



(a) Draw and label a flowchart of the process, do the degree-of-freedom analysis, and write in an efficient order the equations you would solve to determine all unknown stream variables, circling the variables for which you would solve.

(b) Calculate the yield of bean oil product (kg oil/kg beans fed), the required fresh hexane feed (kg C_6H_{14}/kg beans fed), and the recycle to fresh feed ratio (kg hexane recycled/kg fresh feed).

(c) It has been suggested that a **heat exchanger** might be added to the process. This process unit would consist of a bundle of parallel metal tubes contained in an outer shell. The liquid filtrate would pass from the filter through the inside of the tubes and then go on to the evaporator. The hot hexane vapor on its way from the evaporator to the extractor would flow through the shell, passing over the outside of the tubes and heating the filtrate. How might the inclusion of this unit lead to a reduction in the operating cost of the process?

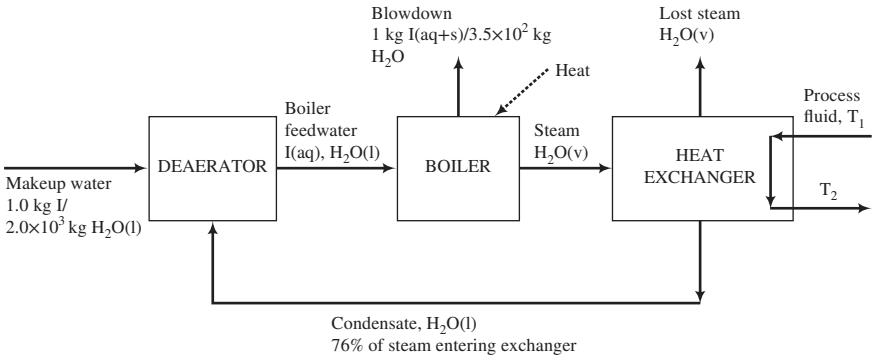
(d) Suggest additional steps that might improve the process economics.

SAFETY

*__4.49.__ Boilers are used in most chemical plants to generate steam for various purposes, such as to preheat process streams fed to reactors and separation units. In one such process, steam and a cold process fluid are fed to a heat exchanger where enough energy is transferred from the steam to cause a large fraction of it to condense. The uncondensed steam is vented to the atmosphere, and the liquid condensate is recycled to a deaerator into which another liquid stream (*makeup water*) is fed. The makeup water contains some dissolved impurities and other chemicals that help prevent deposition of solids on boiler walls and heating elements, which would lead to a reduction in operating efficiency and eventually to safety hazards, possibly including explosions. The liquid leaving the deaerator is the feed to the boiler. In the boiler, most of the water in the feed evaporates to form steam, and some of the impurities in the feedwater precipitate to form solid particles suspended in the liquid (kept in suspension by the chemical additives in the makeup water). The liquid and suspended solids are drawn off as *boiler blowdown*, either in manual bursts or with a continuous blowdown system.

A diagram of the system is shown below. The symbol I is used for combined impurities and chemical additives. The makeup water contains $1.0\,\text{kg I}/2.0\times10^3\,\text{kg H}_2\text{O}$, and the ratio in the blowdown is $1.0\,\text{kg I}/3.5\times10^2\,\text{kg H}_2\text{O}$. Of the steam fed to the heat exchanger, 76% is condensed.

* Adapted from a problem contributed by Carol Clinton of the National Institute of Occupational Safety and Health.



(a) In your own words, describe why makeup water, chemical additives to the makeup water, and blowdown are necessary in this process. Speculate on the probable disadvantage of making the I/H_2O ratio in the blowdown (i) too small, and (ii) too large.

(b) Assume a basis of calculation and draw and fully label a flowchart of the process. (When you draw the heat exchanger you can omit the process fluid, which plays no role in the problem.)

(c) Carry out a degree-of-freedom analysis and outline a solution procedure (which equations would you write in which order to calculate all of the unknowns on the chart?).

(d) Calculate the ratio (mass of makeup water/100 kg steam produced in boiler) and the percentage of the boiler feedwater taken off as blowdown.

(e) A proposal has been made to use highly purified water as makeup. List the benefits that would result from doing so and the most likely reason for not doing it.

Equipment Encyclopedia
filter
@
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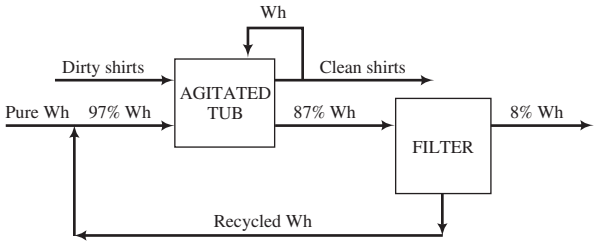
4.50. Following is a diagram of the shirt-cleaning process used by the Floods of Suds One-Day Laundry Services, Inc. The shirts are soaked in an agitated tub containing Whizzo, the Wonder Detergent, and are then wrung out and sent to a rinse stage. The dirty Whizzo is sent to a filter in which most of the dirt is removed, and the cleaned detergent is recycled back to join a stream of pure Whizzo, with the combined stream serving as the feed to the washtub.



Data:

1. Each 100 lb_m of dirty shirts contains 2.0 lb_m of dirt.
2. The washing removes 95% of the dirt in the dirty shirts.
3. For each 100 lb_m of dirty shirts, 25 lb_m of Whizzo leaves with the clean shirts, of which 22 lb_m is wrung back into the tub.
4. The detergent that enters the tub contains 97% Whizzo, and that which enters the filter contains 87%. The wet dirt that leaves the filter contains 8.0% Whizzo.

(a) How much pure Whizzo must be supplied per 100 lb_m of dirty shirts?

(b) What is the composition of the recycled stream?

Equipment Encyclopedia
filter, stripping column, extractor
@
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BIOENGINEERING

4.51. A drug (D) is produced in a three-stage extraction from the leaves of a tropical plant. About 1000 kg of leaf is required to produce 1 kg of the drug. The extraction solvent (S) is a mixture containing 16.5 wt% ethanol (E) and the balance water (W). The following process is carried out to extract the drug and recover the solvent.

1. A mixing tank is charged with 3300 kg of S and 620 kg of leaf. The mixer contents are stirred for several hours, during which a portion of the drug contained in the leaf goes into solution. The contents of the mixer are then discharged through a filter. The liquid filtrate, which carries over roughly 1% of the leaf fed to the mixer, is pumped to a holding tank, and the solid cake (spent leaf and entrained liquid) is sent to a second mixer. The entrained liquid has the same composition as the

filtrate and a mass equal to 15% of the mass of liquid charged to the mixer. The extracted drug has a negligible effect on the total mass and volume of the spent leaf and the filtrate.

2. The second mixer is charged with the spent leaf from the first mixer and with the filtrate from the previous batch in the third mixer. The leaf is extracted for several more hours, and the contents of the mixer are then discharged to a second filter. The filtrate, which contains 1% of the leaf fed to the second mixer, is pumped to the same holding tank that received the filtrate from the first mixer, and the solid cake—spent leaf and entrained liquid—is sent to the third mixer. The entrained liquid mass is 15% of the mass of liquid charged to the second mixer.
3. The third mixer is charged with the spent leaf from the second mixer and with 2720 kg of solvent S. The mixer contents are filtered; the filtrate, which contains 1% of the leaf fed to the third mixer, is recycled to the second mixer; and the solid cake is discarded. As before, the mass of the entrained liquid in the solid cake is 15% of the mass of liquid charged to the mixer.
4. The contents of the filtrate holding tank are filtered to remove the carried-over spent leaf, and the wet cake is pressed to recover entrained liquid, which is combined with the filtrate. A negligible amount of liquid remains in the wet cake. The filtrate, which contains D, E, and W, is pumped to an extraction unit (another mixer).
5. In the extraction unit, the alcohol–water–drug solution is contacted with another solvent (F), which is almost but not completely immiscible with ethanol and water. Essentially all of the drug (D) is extracted into the second solvent, from which it is eventually separated by a process of no concern in this problem. Some ethanol but no water is also contained in the extract. The solution from which the drug has been extracted (the **raffinate**) contains 13.0 wt% E, 1.5% F, and 85.5% W. It is fed to a stripping column for recovery of the ethanol.
6. The feeds to the stripping column are the solution just described and steam. The two streams are fed in a ratio such that the overhead product stream from the column contains 20.0 wt% E and 2.6% F, and the bottom product stream contains 1.3 wt% E and the balance W.

Draw and label a flowchart of the process, taking as a basis one batch of leaf processed. Then calculate

(a) the masses of the components of the filtrate holding tank.
(b) the masses of the components D and E in the extract stream leaving the extraction unit.
(c) the mass of steam fed to the stripping column, and the masses of the column overhead and bottoms products.

4.52. Acetylene is hydrogenated to form ethane. The feed to the reactor contains 1.50 mol H_2/mol C_2H_2.

(a) Calculate the stoichiometric reactant ratio (mol H_2 react/mol C_2H_2 react) and the yield ratio (kmol C_2H_6 formed/kmol H_2 react).
(b) Determine the limiting reactant and calculate the percentage by which the other reactant is in excess.
(c) Calculate the mass feed rate of hydrogen (kg/s) required to produce 4×10^6 metric tons of ethane per year, assuming that the reaction goes to completion and that the process operates for 24 hours a day, 300 days a year.
(d) There is a definite drawback to running with one reactant in excess rather than feeding the reactants in stoichiometric proportion. What is it? [*Hint:* In the process of Part (c), what does the reactor effluent consist of and what will probably have to be done before the product ethane can be sold or used?]

4.53. Ammonia is oxidized to nitric oxide in the following reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

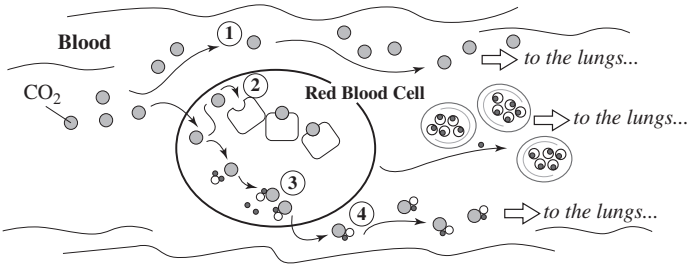
(a) Calculate the ratio (lb-mole O_2 react/lb-mole NO formed).
(b) If ammonia is fed to a continuous reactor at a rate of 100.0 kmol NH_3/h, what oxygen feed rate (kmol/h) would correspond to 40.0% excess O_2?
(c) If 50.0 kg of ammonia and 100.0 kg of oxygen are fed to a batch reactor, determine the limiting reactant, the percentage by which the other reactant is in excess, and the extent of reaction and mass of NO produced (kg) if the reaction proceeds to completion.

BIOENGINEERING

*4.54. The respiratory process involves **hemoglobin** (Hgb), an iron-containing compound found in red blood cells. In the process, carbon dioxide diffuses from tissue cells as molecular CO_2, while O_2 simultaneously

* Adapted from a problem contributed by Kay C. Dee and Glen Livesay of Rose-Hulman Institute of Technology.

enters the tissue cells. A significant fraction of the CO_2 leaving the tissue cells enters red blood cells and reacts with hemoglobin; the CO_2 that does not enter the red blood cells (① in the figure below) remains dissolved in the blood and is transported to the lungs. Some of the CO_2 entering the red blood cells reacts with hemoglobin to form a compound ($Hgb{\cdot}CO_2$; ② in the figure). When the red blood cells reach the lungs, the $Hgb{\cdot}CO_2$ dissociates, releasing free CO_2. Meanwhile, the CO_2 that enters the red blood cells but does not react with hemoglobin combines with water to form carbonic acid, H_2CO_3, which then dissociates into hydrogen ions and bicarbonate ions (③ in the figure). The bicarbonate ions diffuse out of the cells (④ in the figure), and the ions are transported to the lungs via the bloodstream.



For adult humans, every deciliter of blood transports a total of 1.6×10^{-4} mol of carbon dioxide in its various forms (dissolved CO_2, $Hgb{\cdot}CO_2$, and bicarbonate ions) from tissues to the lungs under normal, resting conditions. Of the total CO_2, 1.1×10^{-4} mol are transported as bicarbonate ions. In a typical resting adult human, the heart pumps approximately 5 liters of blood per minute. You have been asked to determine how many moles of CO_2 are dissolved in blood and how many moles of $Hgb{\cdot}CO_2$ are transported to the lungs during an hour's worth of breathing.

(a) Draw and fully label a flowchart and do a degree-of-freedom analysis. Write the chemical reactions that occur, and generate, but do not solve, a set of independent equations relating the unknown variables on the flowchart.

(b) If you have enough information to obtain a unique numerical solution, do so. If you do not have enough information, identify a specific piece/pieces of information that (if known) would allow you to solve the problem, and show that you could solve the problem if that information were known.

Exploratory Exercise—Research and Discover

(c) When someone loses a great deal of blood due to an injury, they "go into shock": their total blood volume is low, and carbon dioxide is not efficiently transported away from tissues. The carbon dioxide reacts with water in the tissue cells to produce very high concentrations of carbonic acid, some of which can dissociate (as shown in this problem) to produce high levels of hydrogen ions. What is the likely effect of this occurrence on the blood pH near the tissue and the tissue cells? How is this likely to affect the injured person?

4.55. A stream containing H_2S and inert gases and a second stream of pure SO_2 are fed to a sulfur recovery reactor, where the reaction

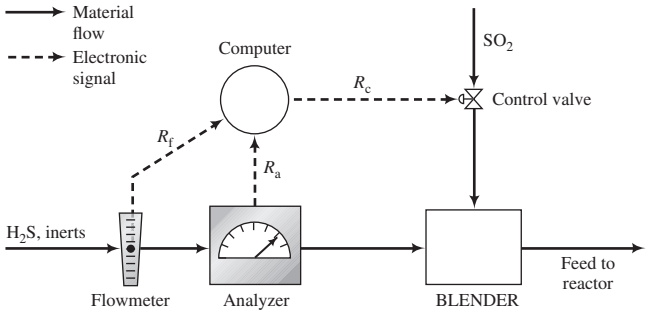
$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

takes place. The feed rates are adjusted so that the ratio of H_2S to SO_2 in the combined feed is always stoichiometric.

In the normal operation of the reactor the flow rate and composition of the H_2S feed stream both fluctuate. In the past, each time either variable changed the required SO_2 feed rate had to be reset by adjusting a valve in the feed line. A control system has been installed to automate this process. The H_2S feed stream passes through an electronic flowmeter that transmits a signal R_f directly proportional to the molar flow rate of the stream, $\dot{n}_f$. When $\dot{n}_f = 100$ kmol/h, the transmitted signal $R_f = 15$ mV. The mole fraction of H_2S in this stream is measured with a thermal conductivity detector, which transmits a signal R_a. Analyzer calibration data are as follows:

R_a(mV)	0	25.4	42.8	58.0	71.9	85.1
x(mol H_2S/mol)	0.00	0.20	0.40	0.60	0.80	1.00

The controller takes as input the transmitted values of R_f and R_a and calculates and transmits a voltage signal R_c to a flow control valve in the SO_2 line, which opens and closes to an extent dependent on the value of R_c. A plot of the SO_2 flow rate, $\dot{n}_c$, versus R_c on rectangular coordinates is a straight line through the points ($R_c = 10.0$ mV, $\dot{n}_c = 25.0$ kmol/h) and ($R_c = 25.0$ mV, $\dot{n}_c = 60.0$ kmol/h).



ENVIRONMENTAL

(a) Why would it be important to feed the reactants in stoichiometric proportion? (*Hint:* SO_2 and especially H_2S are serious pollutants.) What are several likely reasons for wanting to automate the SO_2 feed rate adjustment?

(b) If the first stream contains 85.0 mole% H_2S and enters the unit at a rate of $\dot{n}_f = 3.00 \times 10^2$ kmol/h, what must the value of $\dot{n}_c$(kmol SO_2/h) be?

(c) Fit a function to the H_2S analyzer calibration data to derive an expression for x as a function of R_a. Check the fit by plotting both the function and the calibration data on the same graph.

(d) Derive a formula for R_c from specified values of R_f and R_a, using the result of Part (c) in the derivation. (This formula would be built into the controller.) Test the formula using the flow rate and composition data of Part (a).

(e) The system has been installed and made operational, and at some point the concentration of H_2S in the feed stream suddenly changes. A sample of the blended gas is collected and analyzed a short time later and the mole ratio of H_2S to SO_2 is not the required 2:1. List as many possible reasons as you can think of for this apparent failure of the control system.

4.56. The reaction between ethylene and hydrogen bromide to form ethyl bromide is carried out in a continuous reactor. The product stream is analyzed and found to contain 51.7 mole% C_2H_5Br and 17.3% HBr. The feed to the reactor contains only ethylene and hydrogen bromide. Calculate the fractional conversion of the limiting reactant and the percentage by which the other reactant is in excess. If the molar flow rate of the feed stream is 165 mol/s, what is the extent of reaction?

4.57. In the Deacon process for the manufacture of chlorine, HCl and O_2 react to form Cl_2 and H_2O. Sufficient air (21 mole% O_2, 79% N_2) is fed to provide 35% excess oxygen, and the fractional conversion of HCl is 85%.

(a) Calculate the mole fractions of the product stream components, using atomic species balances in your calculation.

(b) Again calculate the mole fractions of the product stream components, only this time use the extent of reaction in the calculation.

(c) An alternative to using air as the oxygen source would be to feed pure oxygen to the reactor. Running with oxygen imposes a significant extra process cost relative to running with air, but also offers the potential for considerable savings. Speculate on what the cost and savings might be. What would determine which way the process should be run?

MATERIALS

*__4.58.__ **Carbon nanotubes** (CNT) are among the most versatile building blocks in nanotechnology. These unique pure carbon materials resemble rolled-up sheets of graphite with diameters of several nanometers and lengths up to several micrometers. They are stronger than steel, have higher thermal conductivities

* Adapted from a problem contributed by Vinay K. Gupta of the University of South Florida. See also A. E. Agboola, R. W. Pike, T. A. Hertwig, and H. H. Lou, "Conceptual Design of Carbon Nanotube Processes," *Clean Technologies and Environmental Policy*, **9**, 289–311 (2007).

than most known materials, and have electrical conductivities like that of copper but with higher current-carrying capacity. Molecular transistors and biosensors are among their many applications.

While most carbon nanotube research has been based on laboratory-scale synthesis, commercial applications involve large industrial-scale processes. In one such process, carbon monoxide saturated with an organo-metallic compound (iron penta-carbonyl) is decomposed at high temperature and pressure to form CNT, amorphous carbon, and CO_2. Each "molecule" of CNT contains roughly 3000 carbon atoms. The reactions by which such molecules are formed are:

Decomposition of $Fe(CO)_5$ to form iron, which catalyzes Reaction (2)

$$Fe(CO)_5(g) \longrightarrow Fe(s) + 5CO(g) \quad \textbf{(1)}$$

Decomposition of CO to form CNT

$$6000CO(g) \longrightarrow C_{3000}(s) + 3000CO_2(g) \quad \textbf{(2)}$$

Decomposition of CO to form amorphous carbon

$$2CO(g) \longrightarrow C(s) + CO_2(g) \quad \textbf{(3)}$$

In the process to be analyzed, a fresh feed of CO saturated with $Fe(CO)_5$(v) contains 19.2 wt% of the latter component. The feed is joined by a recycle stream of pure CO and fed to the reactor, where all of the iron penta-carbonyl decomposes. Based on laboratory data, 20.0% of the CO fed to the reactor is converted, and the selectivity of CNT to amorphous carbon production is (9.00 kmol CNT/kmol C). The reactor effluent passes through a complex separation process that yields three product streams: one consists of solid CNT, C, and Fe; a second is CO_2; and the third is the recycled CO. You wish to determine the flow rate of the fresh feed (SCM/h), the total CO_2 generated in the process (kg/h), and the ratio (kmol CO recycled/kmol CO in fresh feed).

(a) Take a basis of 100 kmol fresh feed. Draw and fully label a process flow chart and do degree-of-freedom analyses for the overall process, the fresh-feed/recycle mixing point, the reactor, and the separation process. Base the analyses for reactive systems on atomic balances.

(b) Write and solve overall balances, and then scale the process to calculate the flow rate (SCM/h) of fresh feed required to produce 1000 kg CNT/h and the mass flow rate of CO_2 that would be produced.

(c) In your degree-of-freedom analysis of the reactor, you might have counted separate balances for C (atomic carbon) and O (atomic oxygen). In fact, those two balances are not independent, so one but not both of them should be counted. Revise your analysis if necessary, and then calculate the ratio (kmol CO recycled/kmol CO in fresh feed).

(d) Prove that the atomic carbon and oxygen balances on the reactor are not independent equations.

MATERIALS →

4.59. Titanium dioxide (TiO_2) is used extensively as a white pigment. It is produced from an ore that contains ilmenite ($FeTiO_3$) and ferric oxide (Fe_2O_3). The ore is digested with an aqueous sulfuric acid solution to produce an aqueous solution of titanyl sulfate [$(TiO)SO_4$] and ferrous sulfate ($FeSO_4$). Water is added to hydrolyze the titanyl sulfate to H_2TiO_3, which precipitates, and H_2SO_4. The precipitate is then roasted, driving off water and leaving a residue of pure titanium dioxide. (Several steps to remove iron from the intermediate solutions as iron sulfate have been omitted from this description.)

Suppose an ore containing 24.3% Ti by mass is digested with an 80% H_2SO_4 solution, supplied in 50% excess of the amount needed to convert all the ilmenite to titanyl sulfate and all the ferric oxide to ferric sulfate [$Fe_2(SO_4)_3$]. Further suppose that 89% of the ilmenite actually decomposes. Calculate the masses (kg) of ore and 80% sulfuric acid solution that must be fed to produce 1000 kg of pure TiO_2.

ENVIRONMENTAL →

*__4.60.__ Under the FutureGen 2.0 project (http://www.futuregenalliance.org/) sponsored by the U.S. Department of Energy, a novel process is used to convert coal into electricity with minimal greenhouse gas (CO_2) emissions to the atmosphere. In the process, coal is combusted in a boiler with pure O_2; the heat released produces steam, which is then used for heating and to drive turbines that generate electricity. An excess of O_2 is supplied to the boiler to convert all the coal into a flue gas consisting of carbon dioxide, steam, and any unreacted oxygen. The mass flow rate of coal to the boiler is 50 kg/s, and O_2 is

* Adapted from a problem contributed by Paul Blowers of the University of Arizona.

fed in 8.33% excess. For the purposes of this analysis, the chemical formula of coal can be approximated as $C_5H_8O_2$.

(a) Draw and label the flowchart and carry out the degree-of-freedom analysis using balances on atomic species.

(b) Determine the molar flow of oxygen supplied to the boiler.

(c) Solve for the remaining unknown flow rates and mole fractions. Determine the molar composition of the flue gas on a dry basis.

(d) A feature that makes the FutureGen power plant unique is the intent to capture the CO_2 generated, compress it, and pump it into deep geological formations in which it will be permanently stored. List at least two safety or environmental issues that should be considered in the construction and operation of this plant.

(e) List at least two pros and two cons of using pure O_2 versus air.

ENVIRONMENTAL

4.61. Coal containing 5.0 wt% S is burned at a rate of 1250 lb_m/min in a boiler furnace. All of the sulfur in the coal is oxidized to SO_2. The product gas is sent to a scrubber in which most of the SO_2 is removed, and the scrubbed gas then passes out of a stack to the atmosphere. An Environmental Protection Agency regulation requires that the gas in the stack must contain no more than 0.018 lb_m SO_2/lb_m coal burned. To test compliance with this regulation a flowmeter and an SO_2 analyzer are mounted in the stack. The volumetric flow rate of the scrubbed gas is found to be 2867 ft^3/s, and the SO_2 analyzer reading is 37. Calibration data for the analyzer are given in the table below.

SO_2 Analyzer Calibration Data

C(g SO_2/m^3 gas)	Reading (0–100 scale)
0.30	10
0.85	28
2.67	48
7.31	65
18.2	81
30.0	90

(a) Determine the equation that relates SO_2 concentration in lb_m/ft^3 to the analyzer reading.

(b) Is the process in compliance with the EPA regulation?

(c) What percentage of the SO_2 produced in the furnace is removed in the scrubber?

(d) An earlier EPA regulation set a limit on the mole fraction of SO_2 in the gas emerging from the stack (as opposed to the quantity of SO_2 emitted per mass of coal burned), but a way was found to release large quantities of SO_2 from stacks without violating this regulation. Speculate on what the method of getting around the old regulation was. (*Hint:* It involved feeding a second stream to the base of the stack.) Explain why this method no longer worked when the new regulation was imposed.

BIOENGINEERING

*__4.62.__ Oxygen consumed by a living organism in aerobic reactions is used in adding mass to the organism and/or the production of chemicals and carbon dioxide. Since we may not know the molecular compositions of all species in such a reaction, it is common to define the ratio of moles of CO_2 produced per mole of O_2 consumed as the **respiratory quotient**, RQ, where

$$RQ = \frac{n_{CO_2}}{n_{O_2}} \left(\text{or } \frac{\dot{n}_{CO_2}}{\dot{n}_{O_2}} \right)$$

Since it generally is impossible to predict values of RQ, they must be determined from operating data.

Mammalian cells are used in a bioreactor to convert glucose to glutamic acid by the reaction

$$C_6H_{12}O_6 + aNH_3 + bO_2 \rightarrow pC_5H_9NO_4 + qCO_2 + rH_2O$$

The feed to the bioreactor comprises 1.00×10^2 mol $C_6H_{12}O_6$/day, 1.20×10^2 mol NH_3/day, and 1.10×10^2 mol O_2/day. Data on the system show that $RQ = 0.45$ mol CO_2 produced/mol O_2 consumed.

* Adapted with permission from a problem in A. Saterbak, L. V. McIntire, and K.-Y. San, *Bioengineering Fundamentals*, Pearson/Prentice Hall, New Jersey, 2007.

(a) Determine the five stoichiometric coefficients and the limiting reactant.
(b) Assuming that the limiting reactant is consumed completely, calculate the molar and mass flow rates of all species leaving the reactor and the fractional conversions of the non-limiting reactants.

BIOENGINEERING

*__4.63.__ A genetically engineered strain of ***Escherichia coli*** (*E. coli*) is used to synthesize human insulin for people suffering from type I diabetes mellitus. In the following simplified reaction scheme, bacteria consume all of the limiting reactant under aerobic conditions and produce insulin and biomass.

$$C_6H_{12}O_6 + aNH_3 + bO_2 \longrightarrow$$
$$pC_{2.3}H_{2.8}O_{1.8}N(\text{insulin}) + qCH_{1.9}O_{0.3}N_{0.3}(\text{biomass}) + rCO_2 + sH_2O$$

Feed containing 150 mM glucose (that is, 150×10^{-3} mol $C_6H_{12}O_6$/L) and 50 mM ammonia enters a bioreactor at a rate of 100 L/h. Pure oxygen enters the reactor as a gas at the same molar flow rate as the ammonia. The product stream leaves at a rate of 100 L/h. The respiratory quotient (see Problem 4.62) $RQ = 0.50$ mol CO_2 produced/mol O_2 consumed, and the molar ratio of biomass to insulin produced in the reaction is 1.5. The system operates at steady state.
(a) Determine the six stoichiometric coefficients and the limiting reactant.
(b) What are the fractional conversion of glucose and the production rates (g/h) of insulin and biomass?

4.64. The gas-phase reaction between methanol and acetic acid to form methyl acetate and water

$$\underset{(A)}{CH_3OH} + \underset{(B)}{CH_3COOH} \rightleftharpoons \underset{(C)}{CH_3COOCH_3} + \underset{(D)}{H_2O}$$

takes place in a batch reactor. When the reaction mixture comes to equilibrium, the mole fractions of the four reactive species are related by the reaction equilibrium constant

$$K_y = \frac{y_C y_D}{y_A y_B} = 4.87$$

(a) Suppose the feed to the reactor consists of $n_{A0}, n_{B0}, n_{C0}, n_{D0}$, and n_{I0} gram-moles of A, B, C, D, and an inert gas, I, respectively. Let ξ be the extent of reaction. Write expressions for the gram-moles of each reactive species in the final product, $n_A(\xi), n_B(\xi), n_C(\xi)$, and $n_D(\xi)$. Then use these expressions and the given equilibrium constant to derive an equation for ξ_e, the equilibrium extent of reaction, in terms of $n_{A0}, \ldots, n_{I0}$. (see Example 4.6-2.)
(b) If the feed to the reactor contains equimolar quantities of methanol and acetic acid and no other species, calculate the equilibrium fractional conversion.
(c) It is desired to produce 70 mol of methyl acetate starting with 75 mol of methanol. If the reaction proceeds to equilibrium, how much acetic acid must be fed? What is the composition of the final product?
(d) Suppose it is important to reduce the concentration of methanol by making its conversion at equilibrium as high as possible, say 99%. Again assuming the feed to the reactor contains only methanol and acetic acid and that it is desired to produce 70 mol of methyl acetate, determine the extent of reaction and quantities of methanol and acetic acid that must be fed to the reactor.
(e) If you wanted to carry out the process of Part (b) or (c) commercially, what would you need to know besides the equilibrium composition to determine whether the process would be profitable? (List several things.)

4.65. At low to moderate pressures, the equilibrium state of the water–gas shift reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is approximately described by the relation

$$\frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = K_e(T) = 0.0247 \exp[4020/T(K)]$$

where T is the reactor temperature, K_e is the reaction equilibrium constant, and y_i is the mole fraction of species i in the reactor contents at equilibrium.

* Adapted from a problem in A. Saterbak, L. V. McIntire, and K.-Y. San, *Bioengineering Fundamentals*, Pearson/Prentice Hall, New Jersey, 2007.

The feed to a batch shift reactor contains 20.0 mole% CO, 10.0% CO_2, 40.0% water, and the balance an inert gas. The reactor is maintained at $T = 1123$ K.

(a) Assume a basis of 1 mol feed and draw and label a flowchart. Carry out a degree-of-freedom analysis of the reactor based on extents of reaction and use it to prove that you have enough information to calculate the composition of the reaction mixture at equilibrium. Do no calculations.

(b) Calculate the total moles of gas in the reactor at equilibrium (if it takes you more than 5 seconds you're missing the point) and then the equilibrium mole fraction of hydrogen in the product. (*Suggestion:* Begin by writing expressions for the moles of each species in the product gas in terms of the extent of reaction, and then write expressions for the species mole fractions.)

(c) Suppose a gas sample is drawn from the reactor and analyzed shortly after startup and the mole fraction of hydrogen is significantly different from the calculated value. Assuming that no calculation mistakes or measurement errors have been made, what is a likely explanation for the discrepancy between the calculated and measured hydrogen yields?

(d) Write a spreadsheet to take as input the reactor temperature and the feed component mole fractions x_{CO}, x_{H_2O}, and x_{CO_2} (assume no hydrogen is fed) and to calculate the mole fraction y_{H_2} in the product gas when equilibrium is reached. The spreadsheet column headings should be

T x(CO) x(H2O) x(CO2) Ke ⋯ y(H2)

Columns between Ke and y(H2) may contain intermediate quantities in the calculation of y_{H_2}. First test your program for the conditions of Part (a) and verify that it is correct. Then try a variety of values of the input variables and draw conclusions about the conditions (reactor temperature and feed composition) that maximize the equilibrium yield of hydrogen.

4.66. Methanol is formed from carbon monoxide and hydrogen in the gas-phase reaction

$$\underset{(A)}{CO} + \underset{(B)}{2H_2} \rightleftharpoons \underset{(C)}{CH_3OH}$$

The mole fractions of the reactive species at equilibrium satisfy the relation

$$\frac{y_C}{y_A y_B^2}\frac{1}{P^2} = K_e(T)$$

where P is the total pressure (atm), K_e the reaction equilibrium constant (atm^{-2}), and T the temperature (K). The equilibrium constant K_e equals 10.5 at 373 K, and 2.316×10^{-4} at 573 K. A semilog plot of K_e (logarithmic scale) versus $1/T$ (rectangular scale) is approximately linear between $T = 300$ K and $T = 600$ K.

(a) Derive a formula for $K_e(T)$, and use it to show that $K_e(450\text{ K}) = 0.0548\ atm^{-2}$.

(b) Write expressions for n_A, n_B, and n_C (gram-moles of each species), and then y_A, y_B, and y_C, in terms of n_{A0}, n_{B0}, n_{C0}, and ξ, the extent of reaction. Then derive an equation involving only n_{A0}, n_{B0}, n_{C0}, P, T, and ξ_e, where ξ_e is the extent of reaction at equilibrium.

(c) Suppose you begin with equimolar quantities of CO and H_2 and no CH_3OH, and the reaction proceeds to equilibrium at 423 K and 2.00 atm. Calculate the molar composition of the product (y_A, y_B, and y_C) and the fractional conversion of CO.

(d) The conversion of CO and H_2 can be enhanced by removing methanol from the reactor while leaving unreacted CO and H_2 in the vessel. Review the equations you derived in solving Part (c) and determine any physical constraints on ξ_e associated with $n_{A0} = n_{B0} = 1$ mol. Now suppose that 90% of the methanol is removed from the reactor as it is produced; in other words, only 10% of the methanol formed remains in the reactor. Estimate the fractional conversion of CO and the total gram moles of methanol produced in the modified operation.

(e) Repeat Part (d), but now assume that $n_{B0} = 2$ mol. Explain the significant increase in fractional conversion of CO.

(f) Write a set of equations for y_A, y_B, y_C, and f_A (the fractional conversion of CO) in terms of y_{A0}, y_{B0}, T, and P (the reactor temperature and pressure at equilibrium). Enter the equations in an equation-solving program. Check the program by running it for the conditions of Part (c), then use it to determine the effects on f_A (increase, decrease, or no effect) of separately increasing, (i) the fraction of CH_3OH in the feed, (ii) temperature, and (iii) pressure.

4.67. Methane and oxygen react in the presence of a catalyst to form formaldehyde. In a parallel reaction, methane is oxidized to carbon dioxide and water:

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The feed to the reactor contains equimolar amounts of methane and oxygen. Assume a basis of 100 mol feed/s.

(a) Draw and label a flowchart. Use a degree-of-freedom analysis based on extents of reaction to determine how many process variable values must be specified for the remaining variable values to be calculated.

(b) Use Equation 4.6-7 to derive expressions for the product stream component flow rates in terms of the two extents of reaction, ξ_1 and ξ_2.

(c) The fractional conversion of methane is 0.900 and the fractional yield of formaldehyde is 0.855. Calculate the molar composition of the reactor output stream and the selectivity of formaldehyde production relative to carbon dioxide production.

(d) A classmate of yours makes the following observation: "*If you add the stoichiometric equations for the two reactions, you get the balanced equation*

$$2CH_4 + 3O_2 \rightarrow HCHO + CO_2 + 3H_2O$$

The reactor output must therefore contain one mole of CO_2 for every mole of HCHO, so the selectivity of formaldehyde to carbon dioxide must be 1.0. Doing it the way the book said to do it, I got a different selectivity. Which way is right, and why is the other way wrong?" What is your response?

4.68. Ethane is chlorinated in a continuous reactor:

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

Some of the product monochloroethane is further chlorinated in an undesired side reaction:

$$C_2H_5Cl + Cl_2 \rightarrow C_2H_4Cl_2 + HCl$$

(a) Suppose your principal objective is to maximize the selectivity of monochloroethane production relative to dichloroethane production. Would you design the reactor for a high or low conversion of ethane? Explain your answer. (*Hint:* If the reactor contents remained in the reactor long enough for most of the ethane in the feed to be consumed, what would the main product constituent probably be?) What additional processing steps would almost certainly be carried out to make the process economically sound?

(b) Take a basis of 100 mol C_2H_5Cl produced. Assume that the feed contains only ethane and chlorine and that all of the chlorine is consumed, and carry out a degree-of-freedom analysis based on atomic species balances.

(c) The reactor is designed to yield a 15% conversion of ethane and a selectivity of 14 mol C_2H_5Cl/mol $C_2H_4Cl_2$, with a negligible amount of chlorine in the product gas. Calculate the feed ratio (mol Cl_2/mol C_2H_6) and the fractional yield of monochloroethane.

(d) Suppose the reactor is built and started up and the conversion is only 14%. Chromatographic analysis shows that there is no Cl_2 in the product but another species with a molecular weight higher than that of dichloroethane is present. Offer a likely explanation for these results.

4.69. Ethanol can be produced commercially by the hydration of ethylene:

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

Some of the product is converted to diethyl ether in the side reaction

$$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$$

The feed to the reactor contains ethylene, steam, and an inert gas. A sample of the reactor effluent gas is analyzed and found to contain 43.3 mole% ethylene, 2.5% ethanol, 0.14% ether, 9.3% inerts, and the balance water.

(a) Take as a basis 100 mol of effluent gas, draw and label a flowchart, and do a degree-of-freedom analysis based on atomic species to prove that the system has zero degrees of freedom.[15]

(b) Calculate the molar composition of the reactor feed, the percentage conversion of ethylene, the fractional yield of ethanol, and the selectivity of ethanol production relative to ether production.

(c) The percentage conversion of ethylene you calculated should be very low. Why do you think the reactor would be designed to consume so little of the reactant? (*Hint:* If the reaction mixture remained in the reactor long enough to use up most of the ethylene, what would the main product constituent probably be?) What additional processing steps are likely to take place downstream from the reactor?

BIOENGINEERING →

4.70. Fermentation of sugars obtained from hydrolysis of starch or cellulosic biomass is an alternative to using petrochemicals as the feedstock in production of ethanol. One of the many commercial processes to do this[16] uses an enzyme to hydrolyze starch in corn to maltose (a disaccharide consisting of two glucose units) and oligomers consisting of several glucose units. A yeast culture then converts the maltose to ethyl alcohol and carbon dioxide:

$$C_{12}H_{22}O_{11} + H_2O\ (+\ \text{yeast}) \rightarrow 4C_2H_5OH + 4CO_2\ (+\ \text{yeast} + H_2O)$$

As the yeast grows, 0.0794 kg of yeast is produced for every kg ethyl alcohol formed, and 0.291 kg water is produced for every kg of yeast formed. For use as a fuel, the product from such a process must be around 99.5 wt% ethyl alcohol. Corn fed to the process is 72.0 wt% starch on a moisture-free basis and contains 15.5 wt% moisture. It is estimated that 101.2 bushels of corn can be harvested from an acre of corn, that each bushel is equivalent to 25.4 lb_m of corn, and that 6.7 kg of ethanol can be obtained from a bushel of corn. What acreage of farmland is required to produce 100,000 kg of ethanol product?

ENVIRONMENTAL →

What factors (economic and environmental) must be considered in comparing production of ethanol by this route with other routes involving petrochemical feedstocks?

4.71. Solid calcium fluoride (CaF_2) reacts with sulfuric acid to form solid calcium sulfate and gaseous hydrogen fluoride (HF). The HF is then dissolved in water to form hydrofluoric acid. A source of calcium fluoride is fluorite ore containing 96.0 wt% CaF_2 and 4.0% SiO_2.

In a typical hydrofluoric acid manufacturing process, fluorite ore is reacted with 93 wt% aqueous sulfuric acid, supplied 15% in excess of the stoichiometric amount. Ninety-five percent of the ore dissolves in the acid. Some of the HF formed reacts with the dissolved silica in the reaction

$$6HF + SiO_2(aq) \rightarrow H_2SiF_6(s) + 2H_2O(l)$$

The hydrogen fluoride exiting from the reactor is subsequently dissolved in enough water to produce 60.0 wt% hydrofluoric acid. Calculate the quantity of fluorite ore needed to produce a metric ton of aqueous hydrofluoric acid. Note: Some of the given data are not needed to solve the problem.

ENVIRONMENTAL →

4.72. A Claus plant converts gaseous sulfur compounds to elemental sulfur, thereby eliminating emission of sulfur into the atmosphere. The process can be especially important in the gasification of coal, which contains significant amounts of sulfur that is converted to H_2S during gasification. In the Claus process, the H_2S-rich product gas recovered from an acid-gas removal system following the gasifier is split, with one-third going to a furnace where the hydrogen sulfide is burned at 1 atm with a stoichiometric amount of air to form SO_2.

$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O$$

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[15] Your first attempt is likely to yield D.F. = −1, meaning that either (i) you counted one too many independent balances, (ii) you forgot to label one unknown variable, or (iii) the problem statement contains one redundant—and possibly inconsistent—process variable specification. Prove that (i) is actually the case. (Review the definition of independent balances in Section 4.7b.)

[16] "Grain Motor Fuel Alcohol Technical and Economic Assessment Study," Report to the U.S. Department of Energy, NTIS HCP/J6639-01, June 1979.

The hot gases leave the furnace and are cooled prior to being mixed with the remainder of the H_2S-rich gases. The mixed gas is then fed to a catalytic reactor where hydrogen sulfide and SO_2 react to form elemental sulfur.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

The coal available to the gasification process is 0.6 wt% sulfur, and you may assume that all of the sulfur is converted to H_2S, which is then fed to the Claus plant.

(a) Estimate the feed rate of air to the Claus plant in kg/kg coal.

(b) While the removal of sulfur emissions to the atmosphere is environmentally beneficial, identify an environmental concern that still must be addressed with the products from the Claus plant.

4.73. Chlorobenzene (C_6H_5Cl), an important solvent and intermediate in the production of many other chemicals, is produced by bubbling chlorine gas through liquid benzene in the presence of ferric chloride catalyst. In an undesired side reaction, the product is further chlorinated to dichlorobenzene, and in a third reaction the dichlorobenzene is chlorinated to trichlorobenzene.

The feed to a chlorination reactor consists of essentially pure benzene and a technical grade of chlorine gas (98 wt% Cl_2, the balance gaseous impurities with an average molecular weight of 25.0). The liquid output from the reactor contains 65.0 wt% C_6H_6, 32.0% C_6H_5Cl, 2.5% $C_6H_4Cl_2$, and 0.5% $C_6H_3Cl_3$. The gaseous output contains only HCl and the impurities that entered with the chlorine.

(a) You wish to determine (i) the percentage by which benzene is fed in excess, (ii) the fractional conversion of benzene, (iii) the fractional yield of monochlorobenzene, and (iv) the mass ratio of the gas feed to the liquid feed. Without doing any calculations, prove that you have enough information about the process to determine these quantities.

(b) Perform the calculations.

(c) Why would benzene be fed in excess and the fractional conversion kept low?

(d) What might be done with the gaseous effluent?

(e) It is possible to use 99.9% pure ("reagent-grade") chlorine instead of the technical grade actually used in the process. Why is this probably not done? Under what conditions might extremely pure reactants be called for in a commercial process? (*Hint:* Think about possible problems associated with the impurities in technical grade chemicals.)

4.74. The following two reactions take place in a gas-phase reactor:

$$\underset{\text{(A)}}{2CO_2} \rightleftharpoons \underset{\text{(B)}}{2CO} + \underset{\text{(C)}}{O_2}$$

$$\underset{\text{(C)}}{O_2} + \underset{\text{(D)}}{N_2} \rightleftharpoons \underset{\text{(E)}}{2NO}$$

If the system comes to equilibrium at 3000 K and 1 atm, the product gas mole fractions satisfy the relations

$$y_B^2 y_C = 0.1071 y_A^2 \qquad (1) \qquad\qquad y_E^2 = 0.01493 y_C y_D \qquad (2)$$

(a) Let $n_{A0}, \ldots, n_{E0}$ be the initial number of gram-moles of each species and ξ_{e1} and ξ_{e2} be the extents of reactions 1 and 2, respectively, at equilibrium (see Equation 4.6-7). Derive expressions for the mole fractions $y_A, y_B, \ldots, y_E$ in terms of $n_{A0}, n_{B0}, \ldots, n_{E0}$, ξ_{e1}, and ξ_{e2}. Then substitute in the equilibrium relations to derive two simultaneous equations for the two extents of reaction.

(b) One-third of a gram-mole each of CO_2, O_2, and N_2 are charged into a batch reactor and the reactor contents equilibrate at 3000 K and 1 atm. Without doing any calculations, prove that you have enough information to calculate the component mole fractions of the reactor contents at equilibrium.

(c) Create a spreadsheet and input the sets of values of n_{A0}, n_{B0}, n_{C0}, n_{D0}, and n_{E0} shown below, and two initial guesses for ξ_1 and ξ_2 (make them each 0.1). Then for each set, have the spreadsheet calculate n_A, n_B, n_C, n_D, n_E from Eq. (4.6-7); then n_{total} and y_A, y_B, y_C, y_D, and y_E; and then the squares of the left-hand side minus the right-hand side of Equations (1) and (2). Finally, use Solver to find the values of ξ_1 and ξ_2 that minimize the sum of those two squares. When you call Solver the

first time, click on "Options," and select "Use automatic scaling." Don't be surprised if you get negative extents of reaction, which can happen with reversible reactions.

n_{A0}	n_{B0}	n_{C0}	n_{D0}	n_{E0}
1/3	0	1/3	1/3	0
0	1/3	1/3	1/3	0
1/2	0	0	0	1/2
1/5	1/5	1/5	1/5	1/5

4.75. A catalytic reactor is used to produce formaldehyde from methanol in the reaction

$$CH_3OH \rightarrow HCHO + H_2$$

A single-pass conversion of 60.0% is achieved in the reactor. The methanol in the reactor product is separated from the formaldehyde and hydrogen in a multiple-unit process. The production rate of formaldehyde is 900.0 kg/h.

(a) Calculate the required feed rate of methanol to the process (kmol/h) if there is no recycle.

(b) Suppose the unreacted methanol is recovered and recycled to the reactor and the single-pass conversion remains 60%. Without doing any calculations, prove that you have enough information to determine the required fresh feed rate of methanol (kmol/h) and the rates (kmol/h) at which methanol enters and leaves the reactor. Then perform the calculations.

(c) The single-pass conversion in the reactor, X_{sp}, affects the costs of the reactor (C_r) and the separation process and recycle line (C_s). What effect would you expect an increased X_{sp} would have on each of these costs for a fixed formaldehyde production rate? (*Hint:* To get a 100% single-pass conversion you would need an infinitely large reactor, and lowering the single-pass conversion leads to a need to process greater amounts of fluid through both process units and the recycle line.) What would you expect a plot of ($C_r + C_s$) versus X_{sp} to look like? What does the design specification $X_{sp} = 60\%$ probably represent?

4.76. Methanol is produced by reacting carbon monoxide and hydrogen. A fresh feed stream containing CO and H_2 joins a recycle stream and the combined stream is fed to a reactor. The reactor outlet stream flows at a rate of 350 mol/min and contains 10.6 wt% H_2, 64.0 wt% CO, and 25.4 wt% CH_3OH. (Notice that those are percentages by mass, not mole percents.) This stream enters a cooler in which most of the methanol is condensed. The liquid methanol condensate is withdrawn as a product, and the gas stream leaving the condenser—which contains CO, H_2, and 0.40 mole% uncondensed CH_3OH vapor—is the recycle stream that combines with the fresh feed.

(a) Without doing any calculations, prove that you have enough information to determine (i) the molar flow rates of CO and H_2 in the fresh feed, (ii) the production rate of liquid methanol, and (iii) the single-pass and overall conversions of carbon monoxide. Then perform the calculations.

(b) After several months of operation, the flow rate of liquid methanol leaving the condenser begins to decrease. List at least three possible explanations of this behavior and state how you might check the validity of each one. (What would you measure and what would you expect to find if the explanation is valid?)

Equipment Encyclopedia
reactor, condenser, distillation column, absorption column

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4.77. Methane reacts with chlorine to produce methyl chloride and hydrogen chloride. Once formed, the methyl chloride may undergo further chlorination to form methylene chloride (CH_2Cl_2), chloroform, and carbon tetrachloride.

A methyl chloride production process consists of a reactor, a condenser, a distillation column, and an absorption column. A gas stream containing 80.0 mole% methane and the balance chlorine is fed to the reactor. In the reactor a single-pass chlorine conversion of essentially 100% is attained, the mole ratio of methyl chloride to methylene chloride in the product is 5:1, and negligible amounts of chloroform and carbon tetrachloride are formed. The product stream flows to the condenser. Two streams emerge from the condenser: the liquid condensate, which contains essentially all of the methyl chloride and methylene chloride in the reactor effluent, and a gas containing the methane and hydrogen chloride. The condensate goes to the distillation column in which the two component species are separated. The gas leaving the condenser flows to the absorption column where it contacts an aqueous solution. The solution absorbs essentially all of the HCl and none of the CH_4 in

the feed. The liquid leaving the absorber is pumped elsewhere in the plant for further processing, and the methane is recycled to join the fresh feed to the process (a mixture of methane and chlorine). The combined stream is the feed to the reactor.

(a) Choose a quantity of the reactor feed as a basis of calculation, draw and label a flowchart, and determine the degrees of freedom for the overall process and each single unit and stream mixing point. Then write in order the equations you would use to calculate the molar flow rate and molar composition of the fresh feed, the rate at which HCl must be removed in the absorber, the methyl chloride production rate, and the molar flow rate of the recycle stream. Do no calculations.

(b) Calculate the quantities specified in Part (a), either manually or with an equation-solving program.

(c) What molar flow rates and compositions of the fresh feed and the recycle stream are required to achieve a methyl chloride production rate of 1000 kg/h?

4.78. Ethylene oxide is produced by the catalytic oxidation of ethylene:

$$2C_2H_4 + O_2 \longrightarrow 2C_2H_4O$$

An undesired competing reaction is the combustion of ethylene:

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

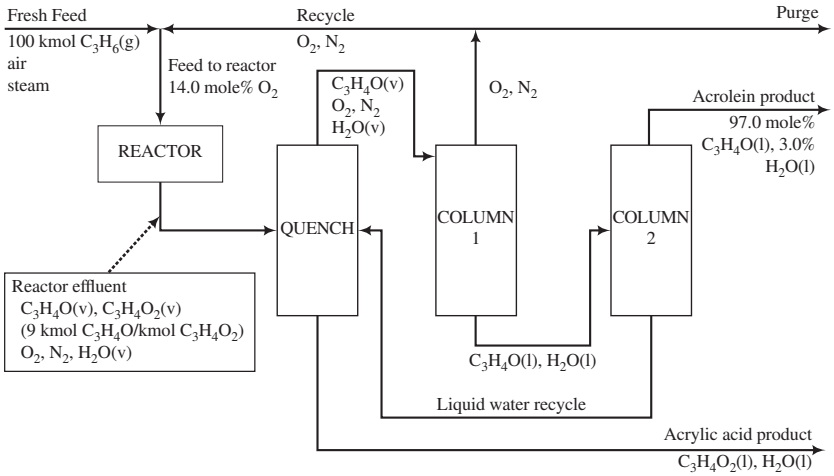
The feed to the reactor (*not* the fresh feed to the process) contains 3 moles of ethylene per mole of oxygen. The single-pass conversion of ethylene is 20%, and for every 100 moles of ethylene consumed in the reactor, 90 moles of ethylene oxide emerge in the reactor products. A multiple-unit process is used to separate the products: ethylene and oxygen are recycled to the reactor, ethylene oxide is sold as a product, and carbon dioxide and water are discarded.

(a) Assume a quantity of the reactor feed stream as a basis of calculation, draw and label the flowchart, perform a degree-of-freedom analysis, and write the equations you would use to calculate (i) the molar flow rates of ethylene and oxygen in the fresh feed, (ii) the production rate of ethylene oxide, and (iii) the overall conversion of ethylene. Do no calculations.

(b) Calculate the quantities specified in Part (a), either manually or with an equation-solving program.

(c) Calculate the molar flow rates of ethylene and oxygen in the fresh feed needed to produce 1 ton per hour of ethylene oxide.

***4.79.** Acrolein (C_3H_4O) is a specialty chemical intermediate used in the manufacture of acrylic acid ($C_3H_4O_2$) and the synthesis of methionine, an essential amino acid. It is generated via the catalytic oxidation of propylene with air in the presence of steam at a temperature in the range 350–450°C.[17] A flowchart of the process is shown below for an assumed basis of calculation of 100 kmol propylene fed.



* Adapted from a problem contributed by Jeffrey R. Seay of the University of Kentucky.

[17] Weigert, W. M. and Haschke, H. (1976). "Acrolein and Derivatives," in J. McKetta, ed., *Encyclopedia of Chemical Processing and Design*. New York: Marcel Dekker.

The molar ratios of propylene to oxygen to steam in the fresh feed to the reactor are 10:20:6.5. Of the propylene fed, 90.0% is converted to acrolein and the rest is converted to acrylic acid.

$$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O$$
$$C_3H_6 + \tfrac{3}{2}O_2 \rightarrow C_3H_4O_2 + H_2O$$

To meet the stoichiometric requirements of the process *and* remain outside of the flammable zone, the oxygen concentration entering the reactor is maintained at 14.0 mole%.

A water quench followed by a pair of separation columns is used to isolate and purify the acrolein product. In the quench tower, all of the acrylic acid from the reactor effluent is absorbed in liquid water recycled from Column 2. Of the water entering the quench tower in the reactor effluent and recycle streams, half emerges with the acrylic acid liquid stream and the other half emerges in the gas stream fed to Column 1.

The oxygen and nitrogen entering Column 1 emerge in the product stream leaving the top of the column, from which a fraction Z_p is taken off as purge while the remainder is recycled to the reactor. The acrolein and water entering Column 1 are recovered in a liquid stream leaving the bottom of Column 1 and sent to Column 2. The product stream from the top of Column 2 is a liquid mixture containing 97.0 mole% acrolein, which represents essentially all of the acrolein entering the column, and 3.0 mole% water. The product stream leaving the bottom of Column 2 is essentially pure liquid water and is the recycle stream fed to the quench tower.

(a) Completely label the flowchart for the process. Describe in your own words the purpose of each process unit.

(b) Perform a degree-of-freedom analysis for the system and write the equations you would solve to calculate the values of all unknown variables on the flowchart (including the purge fraction).

(c) Complete the solution.

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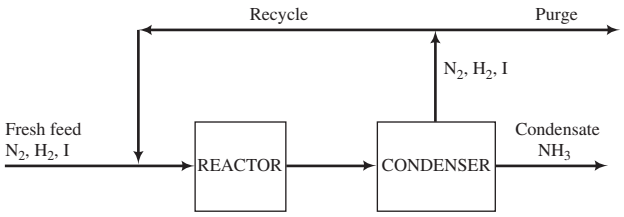
4.80. Methanol is synthesized from carbon monoxide and hydrogen in a catalytic reactor. The fresh feed to the process contains 32.0 mole% CO, 64.0% H_2, and 4.0% N_2. This stream is mixed with a recycle stream in a ratio 5 mol recycle/1 mol fresh feed to produce the feed to the reactor, which contains 13.0 mole% N_2. A low single-pass conversion is attained in the reactor. The reactor effluent goes to a condenser from which two streams emerge: a liquid product stream containing essentially all the methanol formed in the reactor, and a gas stream containing all the CO, H_2, and N_2 leaving the reactor. The gas stream is split into two fractions: one is removed from the process as a purge stream, and the other is the recycle stream that combines with the fresh feed to the reactor.

(a) Assume a methanol production rate of 100 kmol/h. Perform the DOF for the overall system and all subsystems to prove that there is insufficient information to solve for all unknowns.

(b) Briefly explain in your own words the reasons for including (i) the recycle stream and (ii) the purge stream in the process design.

4.81. The fresh feed to an ammonia production process contains nitrogen and hydrogen in stoichiometric proportion, along with an inert gas (I). The feed is combined with a recycle stream containing the same three species, and the combined stream is fed to a reactor in which a low single-pass conversion of nitrogen is achieved. The reactor effluent flows to a condenser. A liquid stream containing essentially all of the ammonia formed in the reactor and a gas stream containing all the inerts and the unreacted nitrogen and hydrogen leave the condenser. The gas stream is split into two fractions with the same composition: one is removed from the process as a purge stream, and the other is the recycle stream combined with the fresh feed. *In every stream containing nitrogen and hydrogen, the two species are in stoichiometric proportion.*



(a) Let x_{I0} be the mole fraction of inerts in the fresh feed, f_{sp} the single-pass conversion of nitrogen (and of hydrogen) in the reactor, and y_p the fraction of the gas leaving the condenser that is purged (mol purged/mol total). Taking a basis of 1 mol fresh feed, draw and fully label a process flowchart, incorporating x_{I0}, f_{sp}, and y_p in the labeling to the greatest possible extent. Then, assuming that the values of these three variables are given, write a set of equations for the total moles fed to the reactor (n_r), moles of ammonia produced (n_p), and overall nitrogen conversion (f_{ov}). Each equation should involve only one unknown variable, which should be circled.

(b) Solve the equations of Part (a) for $x_{I0} = 0.01$, $f_{sp} = 0.20$, and $y_p = 0.10$.

(c) Briefly explain in your own words the reasons for including (i) the recycle stream and (ii) the purge stream in the process design.

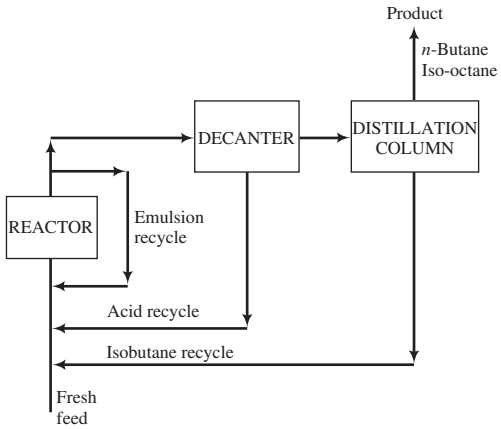
(d) Prepare a spreadsheet to perform the calculations of Part (a) for given values of x_{I0}, f_{sp}, and y_p. Test it with the values in Part (b). Then in successive rows of the spreadsheet, vary each of the three input variables two or three times, holding the other two constant. The first six columns and first five rows of the spreadsheet should appear as follows:

xio	fsp	yp	nr	np	fov
0.01	0.20	0.10			
0.05	0.20	0.10			
0.10	0.20	0.10			
0.01	0.30	0.10			

Summarize the effects on ammonia production (n_P) and reactor throughput (n_r) of changing each of the three input variables.

4.82. Iso-octane is produced in the reaction of isobutane and butylene in an emulsion with concentrated sulfuric acid:

$$i\text{-}C_4H_{10} + C_4H_8 \rightarrow i\text{-}C_8H_{18}$$



The fresh feed to the process flows at a rate of 60,000 kg/h and contains 25.0 mole% isobutane, 25.0% butylene, and 50.0% *n*-butane, which is chemically inert in this process. The fresh feed combines with three separate recycle streams, as shown in the flowchart, and the combined stream enters the reactor. Essentially all of the butylene fed to the reactor is consumed. A portion of the reactor effluent is recycled to the reactor inlet and the remainder passes to a decanter, in which the aqueous (sulfuric acid) and hydrocarbon phases are allowed to separate. The acid is recycled to the reactor, and the hydrocarbons pass to a distillation column.

The overhead from the column contains iso-octane and *n*-butane, and the bottoms product, which is recycled to the reactor, contains only isobutane. The stream entering the reactor contains 200 moles of isobutane per mole of butylene, and 2 kg of 91 wt% H_2SO_4(aq) per kg of hydrocarbon. The stream obtained by combining the fresh feed and isobutane recycle contains 5.0 moles of isobutane per mole of butylene.

You wish to determine the molar flow rates (kmol/h) of each component of the fresh feed, the product stream, and the emulsion, isobutane, and acid recycle streams.

(a) Draw and completely label a flowchart of the process, perform degree-of-freedom analyses on the overall process and subprocesses, and write the equations you would use to determine the required flow rates. (*Suggestion:* Begin by calculating the total molar flow rate of the fresh feed stream.)

(b) Perform the calculations.

(c) List the assumptions in this problem that are not likely to be fully satisfied in practice.

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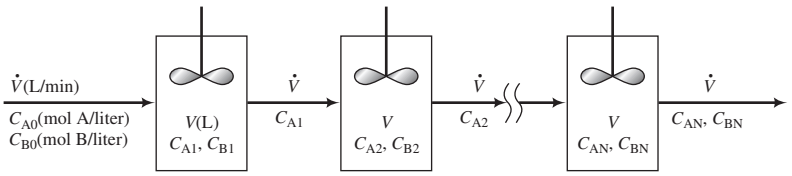
4.83. Ethyl acetate (A) undergoes a reaction with sodium hydroxide (B) to form sodium acetate and ethyl alcohol:

$$\underset{\text{(A)}}{CH_3COOC_2H_5} + \underset{\text{(B)}}{NaOH} \longrightarrow CH_3COONa + C_2H_5OH$$

The reaction is carried out at steady state in a series of stirred-tank reactors. The output from the *i*th reactor is the input to the $(i + 1)$st reactor. The volumetric flow rate between the reactors is constant at $\dot{V}$(L/min), and the volume of each tank is V(L).



The concentrations of A and B in the feed to the first tank are C_{A0} and C_{B0} (mol/L). The tanks are stirred sufficiently for their contents to be uniform throughout, so that C_A and C_B in a tank equal C_A and C_B in the stream leaving that tank. The rate of reaction is given by the expression

$$r\left(\frac{\text{mol A or B reacting}}{\text{min}\cdot\text{L}}\right) = kC_AC_B$$

where k[L/(mol·min)] is the *reaction rate constant*.

(a) Write a material balance on A in the *i*th tank, and show that it yields

$$C_{A,i-1} = C_{Ai} + k\tau C_{Ai}C_{Bi}$$

where $\tau = V/\dot{V}$ is the *mean residence time* in each tank. Then write a balance on B in the *i*th tank and subtract the two balances, using the result to prove that

$$C_{Bi} - C_{Ai} = C_{B0} - C_{A0}, \quad \text{all } i$$

(b) Use the equations derived in Part (a) to prove that

$$C_{A,i-1} = C_{Ai} + k\tau C_{Ai}(C_{Ai} + C_{B0} - C_{A0})$$

and from this relation derive an equation of the form

$$\alpha C_{Ai}^2 + \beta C_{Ai} + \gamma = 0$$

where α, β, and γ are functions of $k, C_{A0}, C_{B0}, C_{A,i-1}$, and τ. Then write the solution of this equation for C_{Ai}.

(c) Write a spreadsheet or computer program to calculate N, the number of tanks needed to achieve a fractional conversion $x_{AN} \geq x_{Af}$ at the outlet of the final reactor. Your program should implement the following procedure:

(i) Take as input values of k, $\dot{V}$, V, C_{A0} (mol/L), C_{B0}(mol/L), and x_{Af}.

(ii) Use the equation for C_{Ai} derived in Part (b) to calculate C_{A1}; then calculate the corresponding fractional conversion x_{A1}.

(iii) Repeat the procedure to calculate C_{A2} and x_{A2}, then C_{A3} and x_{A3}, continuing until $x_{Ai} \geq x_{Af}$.

Test the program supposing that the reaction is to be carried out at a temperature at which $k = 36.2$ L/(mol·min), and that the other process variables have the following values:

Feed concentration: $C_{A0} = 5.0$ g/L(= ??? mol/L)
$C_{B0} = 0.10$ molar(= ??? mol/L)
Throughput: $\dot{V} = 5000$ L/min
Tank volume: $V = 2000$ L

Use the program to calculate the required number of tanks and the final fractional conversion for the following values of the desired minimum final fractional conversion, x_{Af}: 0.50, 0.80, 0.90, 0.95, 0.99, 0.999. Briefly describe the nature of the relationship between N and x_{Af} and what probably happens to the process cost as the required final fractional conversion approaches 1.0. *Hint:* If you write a spreadsheet, it might appear in part as follows:

Spreadsheet for Problem 4.83						
k =	36.2		N	gamma	CA(N)	xA(N)
Vdot =	5000		1	−5.670E–02	2.791E–02	0.5077
V =	2000		2	−2.791E–02	1.512E–02	0.7333
CA0 =	0.0567		3	⋮	⋮	⋮
CB0 =	0.1000		⋮	⋮	⋮	⋮
alpha =	14.48		⋮	⋮	⋮	⋮
beta =	1.6270		⋮	⋮	⋮	⋮
			⋮	⋮	⋮	⋮

(d) Suppose a 95% conversion is desired. Use your program to determine how the required number of tanks varies as you increase (i) the rate constant, k; (ii) the throughput, $\dot{V}$; and (iii) the individual reactor volume, V. Then briefly explain why the results you obtain make sense physically.

4.84. A gas contains 75.0 wt% methane, 10.0% ethane, 5.0% ethylene, and the balance water.

(a) Calculate the *molar* composition of this gas on both a wet and a dry basis and the ratio (mol H_2O/mol dry gas).

(b) If 100 kg/h of this fuel is to be burned with 30% excess air, what is the required air feed rate (kmol/h)? How would the answer change if the combustion were only 75% complete?

4.85. Five liters of liquid *n*-hexane and 4 liters of liquid *n*-heptane are mixed and burned with 4000 gram moles of air. Not all of the hydrocarbons are burned in the furnace, and both CO and CO_2 are formed. If it is possible to do so without additional information, calculate the percent excess air supplied to the furnace; if more information is needed, state what it is and outline the calculation of the percent excess air.

4.86. Gasoline, which we will represent as having the properties of isooctane, is consumed by an idling automobile engine at a rate of 1 gal/h. A monitor in the garage where work is being done on the engine detects an accumulation of CO, indicating incomplete combustion of the gasoline. What does this information imply about the gasoline-to-air ratio being fed to the engine? If we assume that gasoline has the properties of isooctane, C_8H_{18}, estimate the feed rate (mol/h) of air for 10% excess oxygen fed to the engine?

4.87. A fuel gas produced by gasifying coal is to be burned with 20% excess air. The gas contains 50.0 mole% nitrogen and the balance carbon monoxide and hydrogen. A sample of the gas is passed through an infrared spectrometer, which registers a signal R that depends on the mole fraction of carbon monoxide in the sample, and a reading $R = 38.3$ is recorded.

Analyzer calibration data are as follows:

x(mol CO/mol)	0.05	0.10	0.40	0.80	1.00
R	10.0	17.0	49.4	73.6	99.7

A power law ($x = aR^b$) should be suitable for fitting the calibration data. Derive the equation relating x and R (use a graphical method), and then calculate the molar flow rate of air required for a fuel feed rate of 175 kmol/h, assuming that CO and H_2 are oxidized but N_2 is not.

4.88. Natural gas containing a mixture of methane, ethane, propane, and butane is burned in a furnace with excess air.

(a) One hundred kmol/h of a gas containing 94.4 mole% methane, 3.40% ethane, 0.60% propane, and 0.50% butane is to be burned with 17% excess air. Calculate the required molar flow rate of the air.

(b) Let

$\dot{n}_f$(kmol/h) = molar flow of the fuel gas
x_1, x_2, x_3, x_4 = mole fractions of methane, ethane, propane, and butane, respectively, in the fuel
P_{xs} = percent excess air
$\dot{n}_a$(kmol/h) = molar flow rate of the air fed to the furnace

Derive an expression for $\dot{n}_a$ in terms of the other variables. Check your formula with the results of Part (a).

(c) Suppose the feed rate and composition of the fuel gas are subject to periodic variations, and a process control computer is to be used to adjust the flow rate of air to maintain a constant percentage excess. A calibrated electronic flowmeter in the fuel gas line transmits a signal R_f that is directly proportional to the flow rate ($\dot{n}_f = \alpha R_f$), with a flow rate of 75.0 kmol/h yielding a signal $R_f = 60$. The fuel gas composition is obtained with an on-line gas chromatograph. A sample of the gas is injected into the gas chromatograph (GC), and signals A_1, A_2, A_3, and A_4, which are directly proportional to the moles of methane, ethane, propane, and butane, respectively, in the sample, are transmitted. (Assume the same proportionality constant for all species.) The control computer processes these data to determine the required air flow rate and then sends a signal R_a to a control valve in the air line. The relationship between R_a and the resulting air flow rate, $\dot{n}_a$, is another direct proportionality, with a signal $R_a = 25$ leading to an air flow rate of 550 kmol/h.

Write a spreadsheet or computer program to perform the following tasks:

(i) Take as input the desired percentage excess and values of R_f, A_1, A_2, A_3, and A_4.

(ii) Calculate and print out $\dot{n}_f$, x_1, x_2, x_3, x_4, $\dot{n}_a$, and R_a.

Test your program on the data given below, assuming that 15% excess air is required in all cases. Then explore the effects of variations in P_{xs} and R_f on $\dot{n}_a$ for the values of $A_1 - A_4$ given on the third line of the data table. Briefly explain your results.

R_f	A_1	A_2	A_3	A_4
62	248.7	19.74	6.35	1.48
83	305.3	14.57	2.56	0.70
108	294.2	16.61	4.78	2.11

(d) Finally, suppose that when the system is operating as described, stack gas analysis indicates that the air feed rate is consistently too high to achieve the specified percentage excess. Give several possible explanations.

4.89. An unknown paraffinic hydrocarbon is defined by the chemical formula C_xH_{2x+2}. The paraffin is burned with air, and there is no CO in the combustion products.

(a) Use a degree-of-freedom analysis to determine how many variables must be specified to determine the flow rates of all components entering and leaving the combustion unit. Express the fraction excess air as y and write elemental balances in terms of x, y, and the molar flow rate of C_xH_{2x+2}.

(b) Calculate the molar composition of the combustion product gas in terms of x for each of the following three cases: (i) theoretical air supplied ($y = 0$), 100% conversion of the paraffin; (ii) 20% excess air ($y = 0.2$), 100% conversion of the paraffin; (iii) 20% excess air, 90% conversion of the paraffin.

(c) Suppose $x = 3$ (i.e. the paraffin is propane). Assuming complete combustion of the hydrocarbon, what is the ratio of CO_2 to H_2O in the product gas? Use this result to suggest a method for determining the molecular formula of the paraffin.

4.90. Propane is burned completely with excess oxygen. The product gas contains 24.5 mole% CO_2, 6.10% CO, 40.8% H_2O, and 28.6% O_2.

(a) Calculate the percentage excess O_2 fed to the furnace.

(b) A student wrote the stoichiometric equation of the combustion of propane to form CO_2 and CO as

$$2C_3H_8 + \tfrac{17}{2}O_2 \longrightarrow 3CO_2 + 3CO + 8H_2O$$

According to this equation, CO_2 and CO should be in a ratio of 1/1 in the reaction products, but in the product gas of Part (a) they are in a ratio of 24.8/6.12. Is that result possible? (*Hint:* Yes.) Explain how.

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4.91. A mixture of 75 mole% methane and 25 mole% hydrogen is burned with 25% excess air. Fractional conversions of 90% of the methane and 85% of the hydrogen are achieved; of the methane that reacts, 95% reacts to form CO_2 and the balance reacts to form CO. The hot combustion product gas passes through a boiler in which heat transferred from the gas converts boiler feedwater into steam.

(a) Calculate the concentration of CO (ppm) in the stack gas.

(b) The CO in the stack gas is a pollutant. Its concentration can be decreased by increasing the percent excess air fed to the furnace. Think of at least two costs of doing so. (*Hint:* The heat released by the combustion goes into heating the combustion products; the higher the combustion product temperature, the more steam is produced.)

4.92. *n*-Pentane is burned with excess air in a continuous combustion chamber.

(a) A technician runs an analysis and reports that the product gas contains 0.270 mole% pentane, 5.3% oxygen, 9.1% carbon dioxide, and the balance nitrogen *on a dry basis*. Assume 100 mol of dry product gas as a basis of calculation, draw and label a flowchart, perform a degree-of-freedom analysis based on atomic species balances, and show that the system has –1 degree of freedom. Interpret this result.

(b) Use balances to prove that the reported percentages could not possibly be correct.

(c) The technician reruns the analysis and reports new values of 0.304 mole% pentane, 5.9% oxygen, 10.2% carbon dioxide, and the balance nitrogen. Verify that this result *could* be correct and, assuming that it is, calculate the percent excess air fed to the reactor and the fractional conversion of pentane.

(d) It was emphasized in Part (c) that the new composition *could* be correct. Explain why it isn't possible to say for sure; illustrate your response by considering a set of equations with −1 degree of freedom.

4.93. Liquid methanol is fed to a space heater at a rate of 12.0 L/h and burned with excess air. The product gas is analyzed and the following dry-basis mole percentages are determined: $CH_3OH = 0.45\%$, $CO_2 = 9.03\%$, and $CO = 1.81\%$.

(a) Draw and label a flowchart and verify that the system has zero degrees of freedom.

(b) Calculate the fractional conversion of methanol, the percentage excess air fed, and the mole fraction of water in the product gas.

SAFETY

(c) Suppose the combustion products are released directly into a room. What potential problems do you see and what remedies can you suggest?

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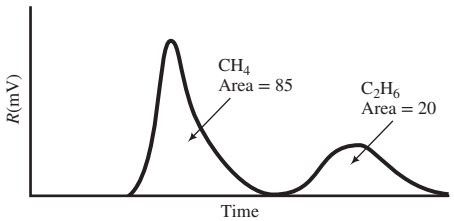
4.94. A gas containing methane, ethane, and carbon dioxide is analyzed with a gas chromatograph (GC) and flame ionization detector (FID): the GC separates the components of the gas, and the FID registers signals proportional to the amount of each hydrocarbon (but not CO_2) in its sample chamber.

The output of the FID is as follows:



The area under each peak is proportional to the number of carbon atoms in the sample, so that 1 mol of ethane would yield a peak with twice the area of a peak corresponding to 1 mol of methane.

This fuel is being burned with air in a continuous combustion chamber. The molar feed ratio of air to fuel was supposed to be 7:1, but you suspect the air flowmeter is not functioning properly. To check it, you take a 0.50-mol sample of the product gas and pass it through a condenser, which condenses essentially all of the water in the sample. The condensate (which can be assumed to be pure water) is weighed and found to have a mass of 1.134 g. The dry gas leaving the condenser is analyzed and found to contain no hydrocarbons, no CO, and 11.9% CO_2.

(a) Calculate the molar composition (component mole fractions) of the fuel gas and the desired percent excess air.

(b) Calculate the actual molar feed ratio of air to fuel and the actual percent excess air.

4.95. A mixture of propane and butane is burned with pure oxygen. The combustion products contain 47.4 mole% H_2O. After all the water is removed from the products, the residual gas contains 69.4 mole % CO_2 and the balance O_2.

(a) What is the mole percent of propane in the fuel?

(b) It now turns out that the fuel mixture may contain not only propane and butane but also other hydrocarbons. All that is certain is that there is no oxygen in the fuel. Use atomic balances to calculate the elemental molar composition of the fuel from the given combustion product analysis (i.e., what mole percent is C and what percent is H). Prove that your solution is consistent with the result of Part (a).

4.96. A fuel oil is analyzed and found to contain 85.0 wt% carbon, 12.0% elemental hydrogen (H), 1.7% sulfur, and the remainder noncombustible matter. The oil is burned with 20.0% excess air, based on complete combustion of the carbon to CO_2, the hydrogen to H_2O, and the sulfur to SO_2. The oil is burned completely, but 8% of the carbon forms CO. Calculate the molar composition of the stack gas.

4.97. The analysis of a coal indicates 75 wt% C, 17% H, 2% S, and the balance noncombustible ash. The coal is burned at a rate of 5000 kg/h, and the feed rate of air to the furnace is 50 kmol/min. All of the ash and

6% of the carbon in the fuel leave the furnace as a molten slag; the remainder of the carbon leaves in the stack gas as CO and CO_2; the hydrogen in the coal is oxidized to water, and the sulfur emerges as SO_2. The selectivity of CO_2 to CO production is 10:1.

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(a) Calculate the percent excess air fed to the reactor.

(b) Calculate the mole fractions of the gaseous pollutants—CO and SO_2—in the stack gas.

(c) Emitted sulfur dioxide by itself is a health hazard, but it is a more serious threat to the environment as a precursor to **acid rain.** Under the catalytic action of sunlight, the sulfur dioxide is oxidized to sulfur trioxide, which in turn combines with water vapor to form sulfuric acid, which eventually returns to earth as rainfall. Acid rain formed in this manner has caused extensive damage to forests, fields, and lakes in many parts of the world. For the furnace described above, calculate the rate of formation of sulfuric acid (kg/h) if all the emitted SO_2 is converted in the indicated manner.

(d) Access http://www.epa.gov/airmarkets/quarterlytracking.html to find the quarterly ARP (Acid Rain Program) SO_2 emissions of U.S. coal-fired power plants. How many coal-fired power plants exist in a state where your father or mother grew up? What are the total annual tons of SO_2 emissions from those plants according to the most recent reporting data? If there are none in your first chosen state, pick a neighboring state.

4.98. The composition of a coal is determined by a **proximate analysis.** The coal is first finely ground and air-dried. Samples of the dried coal are then subjected to several operations, with the sample weights being recorded before and after each operation. *Moisture content* is determined as the weight loss when a sample is held at 105°C in an oxygen-free atmosphere for roughly 2 h, added to the weight loss in the initial drying step. *Volatile matter* (primarily organic tars) is determined by holding a sample at 925°C in an oxygen-free atmosphere for 7 min and subtracting the moisture loss from the total weight loss. *Ash* (or *mineral matter*—oxides and sulfates of silicon, aluminum, iron, calcium, sulfur, and trace minerals) is the residue that remains after a sample has been heated to 800°C in an oxygen-containing atmosphere until all the organic matter has been burned away. *Fixed carbon* is what is present in coal besides moisture, volatile matter, and ash.

(a) Use the following proximate analysis data to determine the percentages by mass of moisture, fixed carbon, volatile matter, and ash in a coal:

$$1.207\ \text{g} \xrightarrow[25°\text{C, 12 h}]{\text{air-dry}} 1.147\ \text{g}$$

The remaining tests are performed on air-dried samples.

$$1.234\ \text{g} \xrightarrow[2\ \text{h}]{105°\text{C, N}_2} 1.204\ \text{g}$$

$$1.347\ \text{g} \xrightarrow[7\ \text{min}]{925°\text{C, N}_2} 0.811\ \text{g}$$

$$1.175\ \text{g} \xrightarrow[1\ \text{h}]{800°\text{C, O}_2} 0.111\ \text{g}$$

(b) If the mass ratio of C to H in the volatile matter is 6:1, calculate the gram-moles of air theoretically required to burn 1 metric ton of this coal.

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4.99. A fuel oil is fed to a furnace and burned with 25% excess air. The oil contains 87.0 wt% C, 10.0% H, and 3.0% S. Analysis of the furnace exhaust gas shows only N_2, O_2, CO_2, SO_2, and H_2O. The sulfur dioxide emission rate is to be controlled by passing the exhaust gas through a scrubber, in which most of the SO_2 is absorbed in an alkaline solution. The gases leaving the scrubber (all of the N_2, O_2, and CO_2, and some of the H_2O and SO_2 entering the unit) pass out to a stack. The scrubber has a limited capacity, however, so that a fraction of the furnace exhaust gas must be bypassed directly to the stack.

At one point during the operation of the process, the scrubber removes 90% of the SO_2 in the gas fed to it, and the combined stack gas contains 612.5 ppm (parts per million) SO_2 on a dry basis; that is, every million moles of dry stack gas contains 612.5 moles of SO_2. Calculate the fraction of the exhaust bypassing the scrubber at this moment.

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4.100. You have been sent by the Environmental Protection Agency to measure SO_2 emissions from a small industrial power plant. You withdraw and analyze a gas sample from the boiler stack and obtain the following composition: 75.66% N_2, 10.24% CO_2, 8.27% H_2O, 5.75% O_2, and 0.0825% SO_2. You show these figures to the plant superintendent next day, and she insists they must be wrong, since the fuel was a natural gas containing methane and ethane, and no sulfur. You ask if they ever burn another fuel, and the superintendent replies that they sometimes use a fuel oil but the plant log shows that they were not doing so when the measurements were made. You do some calculations and prove that the oil and not the gas must have been the fuel; the superintendent checks further and discovers that the plant log is in error and you are right.

(a) Calculate the mole ratio of carbon to hydrogen in the fuel, and use the result to prove that the fuel could not have been the natural gas.

(b) Calculate the *mass* ratio of carbon to hydrogen and the wt% of sulfur in the fuel, assuming that C, H, and S are the only elements present. Then use the results in conjunction with the ultimate fuel oil analyses in Table 24-6 of *Perry's Chemical Engineers' Handbook*[18] to deduce the most probable classification of the fuel oil.

4.101. Fuel oils contain primarily organic compounds and sulfur. The molar composition of the organic fraction of a fuel oil may be represented by the formula $C_pH_qO_r$; the mass fraction of sulfur in the fuel is x_S (kg S/kg fuel); and the percentage excess air, P_{xs}, is defined in terms of the theoretical air required to burn only the carbon and hydrogen in the fuel.

(a) For a certain high-sulfur No. 6 fuel oil, $p = 0.71$, $q = 1.1$, $r = 0.003$, and $x_S = 0.02$. Calculate the composition of the stack gas on a dry basis if this fuel is burned with 18% excess air, assuming complete combustion of the fuel to form CO_2, SO_2, and H_2O and expressing the SO_2 fraction as ppm (mol $SO_2/10^6$ mol dry gas).

(b) Create a spreadsheet to calculate the mole fractions of the stack gas components on a dry basis for specified values of p, q, r, x_S, and P_{xs}. The output should appear as follows:

Solution to Problem 4.101			
Run	1	2	. . .
p	0.71	0.71	. . .
q	1.1	1.1	. . .
r	0.003	0.003	. . .
xS	0.02	0.02	. . .
Pxs	18%	36%	. . .
y(CO2)	13.4%	. . .	. . .
y(O2)	. . .	. . .	. . .
y(N2)	. . .	. . .	. . .
ppm SO2	1165	. . .	. . .

[18] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008, p. 24-9.

(Rows below the last one shown can be used to calculate intermediate quantities.) Execute enough runs (including the two shown above) to determine the effect on the stack gas composition of each of the five input parameters. Then for the values of p, q, r, and x_S given in Part (a), find the minimum percentage excess air needed to keep the dry-basis SO_2 composition below 700 ppm. (Make this the last run in the output table.)

You should find that for a given fuel oil composition, increasing the percentage excess air decreases the SO_2 concentration in the stack gas. Explain why this should be the case.

ENVIRONMENTAL

(c) Someone has proposed using the relationship between P_{xs} and ppm SO_2 as the basis of a pollution control strategy. The idea is to determine the minimum acceptable concentration of SO_2 in the stack gas, then run with the percentage excess air high enough to achieve this value. Give several reasons why this is a poor idea.

CHAPTER 5

Single-Phase Systems

Most of the material balance problems in Chapter 4 could be solved entirely from information given in the problem statements. As you will come to discover, problems in process analysis are rarely so conveniently self-contained; before you can carry out a complete material balance on a process, you usually must determine various physical properties of the process materials and use these properties to derive additional relations among the system variables. The following methods can be used to determine a physical property of a process material:

Look It Up. When you need a value for a physical property of a substance—whether it be a density, vapor pressure, solubility, or heat capacity—there is a good chance that someone, somewhere has measured this property and published the result. Since experiments are usually costly and time consuming, a reliable source of physical property data is an invaluable asset in process analysis. Three excellent sources of data are the following:

Perry's Chemical Engineers' Handbook, 8th Edition, R. H. Perry and D. W. Green, Eds., McGraw-Hill, New York, 2008.

CRC Handbook of Chemistry and Physics, 95th Edition, D. Lide, Ed., Chemical Rubber Company, Boca Raton, FL, 2014.

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/) is an excellent source of on-line information regarding thermochemical, thermophysical, and other resources compiled by the National Institute of Standards and Technology.

If the desired information cannot be found in these references, the species in question can be looked up in the index of *Chemical Abstracts* in an effort to locate data in the open literature.

Estimate It. There are a relatively small number of atomic elements and a much larger but still countable number of molecular species of interest to chemical engineers. Chemical species can be combined into mixtures in an infinite number of ways, however, and it is clearly impossible to tabulate physical property data for even a small fraction of the possible combinations. Moreover, even when data are found they are likely to have been determined for conditions other than the ones for which you need them. Poling, Prausnitz, and O'Connell[1] summarize a large number of empirical correlations that express physical properties of a mixture in terms of the pure-component properties and the mixture composition. These correlations can be used to estimate physical properties when no data are available and to extrapolate available data to conditions other than the ones at which the data were obtained.

Measure It. When no information on a particular physical property of a substance can be found in the literature or when the property must be known with a precision greater than that provided by general estimation formulas, the only recourse is to determine the property experimentally. Information on experimental techniques for measuring physical properties can be found in any of numerous texts on experimental physical, organic, and analytical chemistry.

Density is a frequently needed physical property of a process fluid. For example, engineers often know volumetric flow rates ($\dot{V}$) of process streams from flowmeter readings

[1] B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th Edition, McGraw-Hill, New York, 2001.

but need to know mass flow rates ($\dot{m}$) or molar flow rates ($\dot{n}$) for material balance calculations. The factor needed to calculate $\dot{m}$ or $\dot{n}$ from $\dot{V}$ is the density of the stream. This chapter illustrates the uses of both tabulated data and estimation formulas for calculating densities. Section 5.1 concerns solids and liquids; Section 5.2 covers *ideal gases*, gases for which the ideal-gas equation of state ($PV = nRT$) is a good approximation; and Section 5.3 extends the discussion to nonideal gases.

5.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- Explain in your own words and without the use of jargon (a) the three ways of obtaining values of physical properties; (b) why some fluids are referred to as incompressible; (c) the "liquid volume additivity assumption" and the species for which it is most likely to be valid; (d) the term "equation of state"; (e) what it means to assume ideal-gas behavior; (f) what it means to say that the specific volume of an ideal gas at standard temperature and pressure is 22.4 L/mol; (g) the meaning of partial pressure; (h) why volume fraction and mole fraction for ideal gases are identical; (i) what the compressibility factor, z, represents, and what its value indicates about the validity of the ideal-gas equation of state; (j) why certain equations of state are referred to as cubic; and (k) the physical meaning of critical temperature and pressure (explain them in terms of what happens when a vapor either below or above its critical temperature is compressed).
- For a mixture of liquids with known composition, determine V (or $\dot{V}$) from a known m (or $\dot{m}$) or vice versa using (a) tabulated density data for the mixture and (b) pure-component densities and an assumption of volume additivity. Derive the density estimation formula for the second case (Equation 5.1-1).
- Given any three of the quantities P, V (or $\dot{V}$), n (or $\dot{n}$), and T for an ideal gas, (a) calculate the fourth either directly from the ideal-gas equation of state or by conversion from standard conditions; (b) calculate the density of the gas; and (c) test the assumption of ideality either by using a rule of thumb about the specific volume or by estimating a compressibility factor and seeing how much it differs from 1.
- Explain the meaning of "37.5 SCFH" (37.5 standard cubic feet per hour) and what it means to say that the flow rate of a gas stream at 120°F and 2.8 atm is 37.5 SCFH. (Why doesn't this statement specify the impossible condition that the gas is at two sets of temperatures and pressures simultaneously?) Calculate the true volumetric flow rate of that gas.
- Given the component partial pressures of an ideal-gas mixture and the total gas pressure, determine the mixture composition expressed in either mole fractions (or mole percents), volume fractions (or % v/v), or mass fractions (or % w/w).
- Carry out *PVT* calculations for a gas using (a) the truncated virial equation of state, (b) the van der Waals equation of state, (c) the SRK equation of state, and (d) the compressibility factor equation of state with either tabulated compressibility factors or a generalized compressibility chart for a single species and Kay's rule for a nonideal mixture of gases.
- Given a description of a process system in which a volumetric flow rate is either specified or requested for any process stream, (a) carry out the degree-of-freedom analysis, including density estimates for liquid and solid streams and equations of state for gas streams; (b) write the system equations and outline the procedure you would use to solve for all requested quantities; (c) carry out the calculations; (d) list all your assumptions (e.g., volume additivity for liquids or ideal-gas behavior) and state whether or not they are reasonable for the given process conditions.

5.1 LIQUID AND SOLID DENSITIES

Specific gravities of solids and liquids were discussed in Sections 3.1 and 3.2. Values for several substances at a single temperature are listed in Table B.1 in Appendix B, and more extensive tabulations can be found in *Perry's Chemical Engineers' Handbook*[2] on pp. 2-7 through 2-47 and 2-96 through 2-125.

When you heat a liquid or a solid it normally expands (i.e., its density decreases). In most process applications, however, it can be assumed with little error that solid and liquid densities are independent of temperature. Similarly, changes in pressure do not cause significant changes in liquid or solid densities; these substances are therefore termed **incompressible**.

Perry's Chemical Engineers' Handbook (pp. 2-96 and 2-97) lists densities of liquid water and mercury at different temperatures and gives expressions on pp. 2-134 through 2-136 that may be used to calculate densities for many other substances at different temperatures. Poling, Prausnitz, and O'Connell (see Footnote 1) present a number of methods to estimate the density of a liquid for which tabulated values are not available. Some of these estimation formulas are also given in *Perry's Chemical Engineers' Handbook* on pp. 2-497 through 2-504.

The most accurate way to determine the density of a mixture of liquids or a solution of a solid in a liquid is from experimental data. *Perry's Chemical Engineers' Handbook* provides data for mixtures and solutions of a number of substances on pp. 2-104 through 2-123 and lists additional sources of data on p. 2-104.

In the absence of data, the density $\overline{\rho}$ of a mixture of n liquids $(A_1, A_2, \ldots, A_n)$ can be estimated from the component mass fractions (x_i) and pure-component densities (ρ_i) in two ways. First, we might assume *volume additivity*—that is, if 2 mL of liquid A and 3 mL of liquid B are mixed, the resulting volume would be exactly 5 mL. Making this assumption and recognizing that component masses are always additive leads to the formula

$$\frac{1}{\overline{\rho}} = \sum_{i=1}^{n} \frac{x_i}{\rho_i} \tag{5.1-1}$$

Second, we might simply average the pure-component densities, weighting each one by the mass fraction of the component:

$$\overline{\rho} = \sum_{i=1}^{n} x_i \rho_i \tag{5.1-2}$$

(Equation 5.1-1 calculates the inverse of the mixture density, or the *specific volume* of the mixture, as the weighted average of the pure-component specific volumes.)

One of these estimation formulas might work better for some species and the other might work better for other species. For example, Figure 5.1-1 shows densities of both methanol–water and sulfuric acid–water mixtures at 20°C. The densities for each pair of components are obtained in three ways: from experimental data in *Perry's Chemical Engineers' Handbook* (p. 2-112 for sulfuric acid solutions and p. 2-116 for methanol solutions), using Equation 5.1-1, and using Equation 5.1-2. Equation 5.1-1 provides a slightly better estimate (i.e., values closer to the experimental data) for methanol and water, and Equation 5.1-2 provides a much better estimate for sulfuric acid and water.

Which method should you use? Equation 5.1-1 and the assumption of volume additivity work best for mixtures of liquid species with similar molecular structures (e.g., all straight-chain hydrocarbons of nearly equal molecular weight, such as *n*-pentane, *n*-hexane, and *n*-heptane). There are no general rules for when Equation 5.1-2 works better—all we can do is rely on empirical (experimental) findings.

[2] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008.

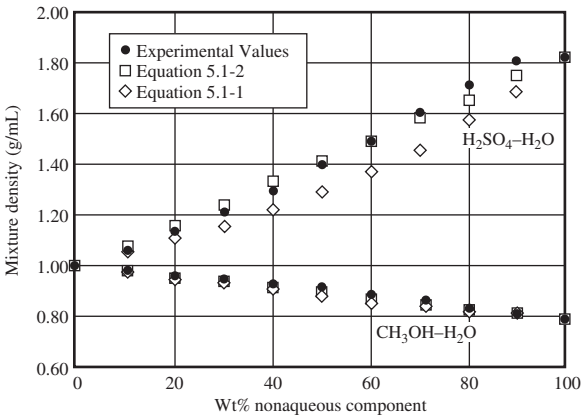


FIGURE 5.1-1 Experimental and estimated mixture densities. Experimental values from *Perry's Chemical Engineers' Handbook*, p. 2-112 for sulfuric acid–water and p. 2-116 for methanol–water, both at 20°C.

Test Yourself

(Answers, p. 656)

1. The specific gravity of water is 1.0000 at 4.0°C. A stream of water at 4°C has a mass flow rate of 255 g/s. What is its volumetric flow rate? If the stream temperature is raised to 75°C, does the mass flow rate change? How would you expect the volumetric flow rate to change? How would you calculate the volumetric flow rate at 75°C without actually measuring it?
2. The pressure equivalence $14.696\ \text{lb}_\text{f}/\text{in}^2 \Longleftrightarrow 760\ \text{mm Hg}$ is not complete—it should be stated as

$$14.696\ \text{lb}_\text{f}/\text{in}^2 \Longleftrightarrow 760\ \text{mm Hg at } 0°\text{C}$$

   Why is it technically necessary to state a temperature? Why is omitting the temperature not a serious mistake?
3. Suppose you mix m_1(g) of liquid A_1 with density ρ_1(g/cm^3), m_2(g) of liquid A_2 with density $\rho_2, \ldots,$ and m_n(g) of liquid A_n with density ρ_n. Assuming that the volumes are additive, show that the density of the mixture is given by Equation 5.1-1.

Example 5.1-1 Determination of a Solution Density

Determine the density in g/cm^3 of a 50 wt% aqueous solution of H_2SO_4 at 20°C, both by (1) looking up a tabulated value and (2) assuming volume additivity of the solution components.

Solution

1. ***Look It Up.*** *Perry's Chemical Engineers' Handbook*, pp. 2-112 and 2-113, tabulates specific gravities of sulfuric acid solutions. From this table,

$$\rho(50\%\ \text{H}_2\text{SO}_4,\ 20°\text{C}) = 1.3951\ \text{g/cm}^3$$

2. ***Estimate It.*** The pure-component densities are

$$\rho(\text{H}_2\text{O},\ 20°\text{C}) = 0.998\ \text{g/cm}^3\ (\textit{Handbook},\ \text{p. 2-96})$$
$$\rho(\text{H}_2\text{SO}_4,\ 18°\text{C}) = 1.834\ \text{g/cm}^3\ (\textit{Handbook},\ \text{p. 2-25})$$

   We will neglect the density change for H_2SO_4 between 18°C and 20°C, although *Perry's Chemical Engineers' Handbook*, p. 2-136, gives thermal expansion data for H_2SO_4 that could be used to make this minor correction. We then estimate from Equation 5.1-1:

$$1/\overline{\rho} = (0.500/0.998 + 0.500/1.834)\ \text{cm}^3/\text{g} = 0.7736\ \text{cm}^3/\text{g}$$
$$\Downarrow$$
$$\overline{\rho} = 1.29\ \text{g/cm}^3$$

The density estimated assuming volume additivity thus differs from the true density, given in Part (1), by $[(1.29 - 1.3951)/1.3951] \times 100\% = -7.3\%$. Alternatively, we could estimate the density from Equation 5.1-2:

$$\overline{\rho} = (0.500 \times 0.998 + 0.500 \times 1.834)\frac{\text{g}}{\text{cm}^3} = 1.42\ \text{g/cm}^3$$

This leads to an estimation error of $[(1.42 - 1.3951)/1.3951] \times 100\% = 1.5\%$. Clearly, the accuracy of Equation 5.1-2 is better in this instance than that of Equation 5.1-1.

5.2 IDEAL GASES

Looking up a density or specific volume at one temperature and pressure and using it at another temperature and pressure usually works well for a solid or a liquid, but not at all for a gas. An expression is needed for gases that relates specific volume to temperature and pressure, so that if any two of these quantities are known the third can be calculated.

Typical problems that require a PVT relationship for their solution include the following:

1. Propane at 120°C and 2.3 bar passes through a flowmeter that reads 250 L/min. What is the mass flow rate of the gas?
2. A pure hydrocarbon gas fills a two-liter vessel at 30°C with an absolute pressure of 25 atm. How many gram-moles of gas are contained in the vessel? If the mass of the gas is 60 g, what might the gas be?
3. A 20-ft^3 gas cylinder in your laboratory can hold pressures up to 400 atm. The Bourdon gauge on the cylinder reads 380 atm one morning when the temperature is 55°F. How high can the temperature go before it becomes advisable to move to a different laboratory?

An **equation of state** relates the molar quantity and volume of a gas to temperature and pressure. The simplest and most widely used of these relationships is the **ideal-gas equation of state** (the familiar $PV = nRT$), which, while approximate, is adequate for many engineering calculations involving gases at low pressures. However, some gases deviate from ideal behavior at nearly all conditions and all gases deviate substantially at certain conditions (notably at high pressures and/or low temperatures). In such cases it is necessary to use more complex equations of state for PVT calculations.

In this section we discuss the ideal-gas equation of state and show how it is applied to systems containing single gaseous substances and mixtures of gases. Section 5.3 outlines methods used for a single nonideal gas (by definition, a gas for which the ideal-gas equation of state does not work well) and for mixtures of nonideal gases.

5.2a The Ideal-Gas Equation of State

The ideal-gas equation of state can be derived from the kinetic theory of gases by assuming that gas molecules have a negligible volume, exert no forces on one another, and collide elastically with the walls of their container. The equation usually appears in the form

$$\boxed{PV = nRT} \quad \text{or} \quad \boxed{P\dot{V} = \dot{n}RT} \qquad \textbf{(5.2-1)}$$

where

P = *absolute* pressure of a gas
$V(\dot{V})$ = volume (volumetric flow rate) of the gas
$n(\dot{n})$ = number of moles (molar flow rate) of the gas
R = the *gas constant*, whose value depends on the units of P, V, n, and T
T = *absolute* temperature of the gas

The equation may also be written as

$$P\hat{V} = RT \tag{5.2-2}$$

where $\hat{V} = V/n$ (or $\dot{V}/\dot{n}$) is the **specific molar volume** of the gas.

A gas whose *PVT* behavior is well represented by Equation 5.2-1 is said to behave as an **ideal gas** or a **perfect gas.** The use of this equation does not require a knowledge of the gas species: *1 mol of an ideal gas at 0°C and 1 atm occupies 22.415 liters*, whether the gas is argon, nitrogen, a mixture of propane and air, or any other single species or mixture of gases.

The gas constant R has units of (pressure × volume)/(mole × temperature); moreover, since pressure times volume has units of energy (prove it), R may also be expressed in units of (energy)/(mole × temperature). Values of the gas constant expressed in various units are listed in the table on the inside back cover of this book.

The ideal-gas equation of state is an approximation. It works well under some conditions—generally speaking, at temperatures above about 0°C and pressures below about 1 atm—but at other conditions its use may lead to substantial errors. Here is a useful rule of thumb for when it is reasonable to assume ideal-gas behavior. Let X_{ideal} be a quantity calculated using the ideal-gas equation of state [$X = P$ (absolute), T (absolute), n or V] and ε be the error in the estimated value,

$$\varepsilon = \frac{X_{\text{ideal}} - X_{\text{true}}}{X_{\text{true}}} \times 100\%$$

An error of no more than about 1% may be expected if the quantity RT/P (the *ideal specific molar volume*) satisfies the following criterion:[3]

$$|\varepsilon| < 1\% \text{ if } \hat{V}_{\text{ideal}} = \frac{RT}{P} > 5 \text{ L/mol } (80 \text{ ft}^3\text{/lb-mole}) \quad \text{(diatomic gases)} \tag{5.2-3a}$$

$$> 20 \text{ L/mol } (320 \text{ ft}^3\text{/lb-mole}) \quad \text{(other gases)} \tag{5.2-3b}$$

Example 5.2-1 The Ideal-Gas Equation of State

One hundred grams of nitrogen is stored in a container at 23.0°C and 3.00 psig.

1. Assuming ideal-gas behavior, calculate the container volume in liters.
2. Verify that the ideal-gas equation of state is a good approximation for the given conditions.

Solution

1. The ideal-gas equation of state relates absolute temperature, absolute pressure, and the quantity of a gas in moles. We therefore first calculate

$$n = \frac{100.0 \text{ g}}{28.0 \text{ g/mol}} = 3.57 \text{ mol}$$

$$T = 296 \text{ K}$$

and (assuming $P_{\text{atm}} = 14.7$ psia) $P = 17.7$ psia. Then from the ideal-gas equation of state

$$V(\text{L}) = \frac{nRT}{P}$$

$$= \frac{(3.57 \text{ mol})(296 \text{ K}) \quad | \quad R(\text{L}\cdot\text{psia})}{17.7 \text{ psia} \quad | \quad (\text{mol}\cdot\text{K})}$$

[3] O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles.* Part I. Material and Energy Balances, 2nd Edition, John Wiley & Sons, New York, 1956, p. 67.

Unfortunately, the table of gas constants at the back of this book does not list the value of R with this particular set of units. In its absence, we use an available value and carry out the necessary additional unit conversions.

$$V = \frac{(3.57\ \text{mol})(296\ \text{K})}{17.7\ \text{psi}} \left| \frac{0.08206\ \text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right| \frac{14.7\ \text{psi}}{\text{atm}} = \boxed{72.0\ \text{L}}$$

2. To check the assumption of ideal-gas behavior for N_2 (a diatomic gas), we apply Criterion 5.3-a. Since we have already determined n and V_{ideal}, we can determine $\hat{V}_{\text{ideal}} = V_{\text{ideal}}/n$ rather than as RT/P. (Both calculations yield the same value, which you might want to verify for yourself.)

$$\hat{V}_{\text{ideal}} = \frac{V}{n} = \frac{72.0\ \text{L}}{3.57\ \text{mol}} = 20.2\ \text{L/mol} > 5\ \text{L/mol} \quad \checkmark$$

Since the calculated value of $\hat{V}_{\text{ideal}}$ exceeds the criterion value of 5 L/mol, the ideal-gas equation of state should yield an error of less than 1%.

Test Yourself

(Answers, p. 656)

1. What is an equation of state? What is the ideal-gas equation of state? At what conditions (high or low temperature, high or low pressure) does the ideal-gas equation provide the most accurate estimates?

2. Two gas cylinders have identical volumes and contain gases at identical temperatures and pressures. Cylinder A contains hydrogen and cylinder B contains carbon dioxide. Assuming ideal-gas behavior, which of the following variables differ for the two gases: (a) number of gram-moles, (b) number of molecules, (c) masses, (d) specific molar volumes (L/mol), (e) mass densities (g/L)? For each of the quantities that differ, which one is bigger and by how much? (Assume ideal-gas behavior.)

3. One hundred grams per hour of ethylene (C_2H_4) flows through a pipe at 1.2 atm and 70°C and 100 g/h of butene (C_4H_8) flows through a second pipe at the same temperature and pressure. Which of the following quantities differ for the two gases: (a) volumetric flow rate, (b) specific molar volume (L/mol), (c) mass density (g/L)? For each of the quantities that differ, which one is bigger and by how much? (Assume ideal-gas behavior.)

4. A gas is stored at $T = 200$ K and $P = 20$ atm. Show whether or not the ideal-gas equation of state would provide an estimate of the specific volume of the gas, $\hat{V}$(L/mol), within 1% of the true value.

The relationship between the density ρ (mass/volume), temperature, and pressure of an ideal gas can be obtained by first relating the specific molar volume, $\hat{V}$ (volume/mole), to the density. Using a specific set of units for illustration,

$$\hat{V}\left(\frac{\text{L}}{\text{mol}}\right) = \frac{\overline{M}\ (\text{g/mol})}{\rho\ (\text{g/L})}$$

where $\overline{M}$ is the average molecular weight of the gas (the molecular weight if the gas is a single species or Equation 3.3-7 for a mixture). Substituting $\hat{V} = \overline{M}/\rho$ into Equation 5.2-2 and solving for ρ yields

$$\rho = \frac{P\overline{M}}{RT} \qquad \textbf{(5.2-4)}$$

CREATIVITY EXERCISE

An unlabeled gas cylinder is equipped with a sensitive pressure gauge. Devise several experiments that could be used to estimate the molecular weight of the gas, using only equipment and materials likely to be found in the average home or purchasable at a neighborhood hardware store. (You may

have a sensitive balance if you need one, but you may not assume that the average home has its own chemistry laboratory.)

5.2b Standard Temperature and Pressure

Doing *PVT* calculations by substituting given values of variables into the ideal-gas equation of state is straightforward, but to use this method you must have on hand either a table of values of R with different units or a good memory. A way to avoid these requirements is to use *conversion from standard conditions*.

For an ideal gas at an arbitrary temperature T and pressure P,

$$PV = nRT \tag{5.2-1}$$

and for the same ideal gas at a specified reference temperature T_s and pressure P_s (referred to as *standard temperature and pressure*, or STP), we may write Equation 5.2-2 as

$$P_s \hat{V}_s = RT_s$$

The first equation divided by the second yields

$$\frac{PV}{P_s \hat{V}_s} = n\frac{T}{T_s} \tag{5.2-5}$$

(For a flowing stream, $\dot{n}$ and $\dot{V}$ would replace n and V in this equation.) Since the standard conditions (P_s, T_s, $\hat{V}_s = RT_s/P_s$) are known, Equation 5.2-5 may be used to determine V for a given value of n or vice versa. Note that when you use this method you do not need a value for R.

The standard conditions most commonly used are shown in Table 5.2-1. Standard temperature ($T_s = 0°C \Longrightarrow 273$ K) and standard pressure ($P_s = 1$ atm) are easy to remember. You should also commit to memory the following values of the standard specific molar volume:

$$\hat{V}_s = 22.4\ \frac{\text{m}^3(\text{STP})}{\text{kmol}} \Longleftrightarrow 22.4\ \frac{\text{L(STP)}}{\text{mol}} \Longleftrightarrow 359\ \frac{\text{ft}^3(\text{STP})}{\text{lb-mole}} \tag{5.2-6}$$

The term **standard cubic meters** (or **SCM**) is often used to denote m^3(STP), and **standard cubic feet** (or **SCF**) denotes ft^3(STP). A volumetric flow rate of 18.2 SCMH means 18.2 m^3/h at 0°C and 1 atm.

Caution: While standard temperature and pressure for most equation-of-state calculations have historically been 0°C and 1 atm, those values are by no means universal. The International Union of Pure and Applied Chemistry (IUPAC) uses 273.15 K and 100 kPa (0.986 atm or 14.505 psi), and some industries (such as the petroleum industry) have adopted different values. If you see a reference to standard temperature and pressure in a reported gas-law calculation, find out which values were assumed. (In this book it is always safe to assume 0°C and 1 atm.)

TABLE 5.2-1 Standard Conditions for Gases

System	T_s	P_s	V_s	n_s
SI	273 K	1 atm	0.022415 m^3	1 mol
CGS	273 K	1 atm	22.415 L	1 mol
U.S. customary	492°R	1 atm	359.05 ft^3	1 lb-mole

Example 5.2-2 Conversion from Standard Conditions

Butane (C_4H_{10}) at 360°C and 3.00 atm absolute flows into a reactor at a rate of 1100 kg/h. Calculate the volumetric flow rate of this stream using conversion from standard conditions.

Solution As always, molar quantities and absolute temperature and pressure must be used.

$$\dot{n} = \frac{1100\ \text{kg/h}}{58.1\ \text{kg/kmol}} = 19.0\ \text{kmol/h}$$
$$T = 633\ \text{K}, \qquad P = 3.00\ \text{atm}$$

From Equation 5.2-5

$$\frac{P\dot{V}}{P_s\hat{V}_s} = \dot{n}\frac{T}{T_s} \Longrightarrow \dot{V} = \dot{n}\hat{V}_s\frac{T}{T_s}\frac{P_s}{P}$$

$$\Downarrow$$

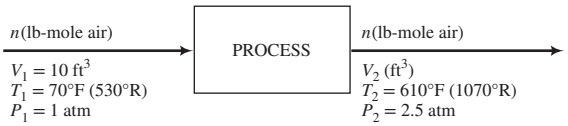
$$\dot{V} = \frac{19.0\ \text{kmol}}{\text{h}} \left| \frac{22.4\ \text{m}^3\text{(STP)}}{\text{kmol}} \right| \frac{633\ \text{K}}{273\ \text{K}} \left| \frac{1.00\ \text{atm}}{3.00\ \text{atm}} \right| = \boxed{329\ \frac{\text{m}^3}{\text{h}}}$$

You will frequently encounter problems that involve gases at two different states (sets of conditions)—for example, at the inlet and outlet of a process unit. A convenient way to determine an unknown variable (P, V, n, or T) of the gas at one of the states is to write the ideal-gas equation of state for both states and divide one equation by the other. Any variables that are the same at both points will cancel, leaving an equation containing only the variable you wish to determine and known quantities. Inherent in this approach is an assumption that the ideal-gas equation of state is valid at both sets of conditions.

Example 5.2-3 Effect of T and P on Volumetric Flow Rates

Ten cubic feet of air at 70°F and 1.00 atm is heated to 610°F and compressed to 2.50 atm. What volume does the gas occupy in its final state?

Solution Let 1 denote the initial state of the gas and 2 the final state. Note that $n_1 = n_2$ (the number of moles of the gas does not change). Assume ideal-gas behavior.



$$\left.\begin{aligned} P_2V_2 &= nRT_2 \\ P_1V_1 &= nRT_1 \end{aligned}\right\} \Longrightarrow \frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1}$$

$$\Longrightarrow V_2 = V_1\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right) = \frac{10.0\ \text{ft}^3}{} \left| \frac{1.00\ \text{atm}}{2.50\ \text{atm}} \right| \frac{1070°\text{R}}{530°\text{R}} = \boxed{8.08\ \text{ft}^3}$$

You may on occasion be told that the flow rate of a gas stream is, say, 23.8 SCMH [or m^3(STP)/h] at 150°C and 2.5 atm. This looks like a contradiction: How can a gas be at standard temperature and pressure (0°C and 1 atm) *and* at 150°C and 2.5 atm? The answer is that it can't—the gas is *not* at standard temperature and pressure. A flow rate specified in the given manner (23.8 SCMH) is not the true volumetric flow rate of the stream at its actual temperature and pressure (150°C and 2.5 atm) but the flow rate that would be obtained *if* the stream were brought from its

actual conditions to standard temperature and pressure. From the given value of 23.8 SCMH, you could (a) calculate the molar flow rate (kmol/h) by dividing 23.8 m^3/h by 22.4 m^3(STP)/kmol, or (b) calculate the true volumetric flow rate (m^3/h) by multiplying 23.8 m^3/h by (423 K/273 K)(1 atm/2.5 atm). (Convince yourself of both of these claims.)

Example 5.2-4 Standard and True Volumetric Flow Rates

Equipment Encyclopedia
flowmeter
@
www.wiley.com/college/felder

The flow rate of a methane stream at 285°F and 1.30 atm is measured with an orifice meter. The calibration chart for the meter indicates that the flow rate is 3.95×10^5 SCFH. Calculate the molar flow rate and the true volumetric flow rate of the stream.

Solution Recall that SCFH means ft^3(STP)/h.

$$\dot{n} = \frac{3.95 \times 10^5 \text{ ft}^3\text{(STP)}}{\text{h}} \left| \frac{1 \text{ lb-mole}}{359 \text{ ft}^3\text{(STP)}} \right. = \boxed{1.10 \times 10^3 \text{ lb-moles/h}}$$

Note that to calculate the molar flow rate from a standard volumetric flow rate, you don't need to know the actual gas temperature and pressure.

The true volumetric flow rate of the methane is calculated using the method illustrated in Example 5.2-3, only now we are bringing the gas from standard conditions ($T_1 = 492°R$, $P_1 = 1.0$ atm, $\dot{V}_1 = 3.95 \times 10^5$ ft^3/h) to actual conditions ($T_2 = 745°R$, $P_2 = 1.30$ atm, $\dot{V}_2 = ?$). We therefore obtain

$$\dot{V}_2 = \dot{V}_1 \left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right) = (3.95 \times 10^5 \text{ ft}^3\text{/h})\left(\frac{745°R}{492°R}\right)\left(\frac{1.00 \text{ atm}}{1.30 \text{ atm}}\right) = \boxed{4.60 \times 10^5 \text{ ft}^3\text{/h}}$$

Test Yourself

(Answers, p. 656)

1. What are standard temperature and pressure? What are the values of $\hat{V}_s$ in SI, CGS, and U.S. customary units?
2. What happens to the volume of an ideal gas when you double the pressure at a fixed temperature? When you double the temperature at a fixed pressure?
3. What happens to the density of a fixed quantity of an ideal gas when you raise the temperature at a fixed pressure? When you raise the temperature at a fixed volume?
4. The volumetric flow rate of an ideal gas is given as 35.8 SCMH. The temperature and pressure of the gas are −15°C and 1.5 atm. Is the actual volumetric flow rate of the gas (a) <35.8 m^3/h, (b) 35.8 m^3/h, (c) >35.8 m^3/h, or (d) indeterminate without additional information?

5.2c Ideal-Gas Mixtures

Suppose n_A moles of substance A, n_B moles of B, n_C moles of C, and so on, are contained in a volume V at a temperature T and total pressure P. The **partial pressure** p_A and **pure-component volume** v_A of A in the mixture are defined as follows:

$\boldsymbol{p_A}$: the pressure that would be exerted by n_A moles of A alone in the same total volume V at the same temperature T.

$\boldsymbol{v_A}$: the volume that would be occupied by n_A moles of A alone at the total pressure P and temperature T of the mixture.

Suppose next that each of the individual mixture components and the mixture as a whole behave in an ideal manner. (This is the definition of an **ideal-gas mixture**.) If there are n moles of all species in the volume V at pressure P and temperature T, then

$$PV = nRT$$

In addition, from the definition of partial pressure,

$$p_A V = n_A RT$$

Dividing the second equation by the first yields

$$\frac{p_A}{P} = \frac{n_A}{n} = y_A \qquad \text{(the mole fraction of A in the gas)}$$

or

$$\boxed{p_A = y_A P} \tag{5.2-7}$$

That is, *the partial pressure of a component in an ideal-gas mixture is the mole fraction of that component times the total pressure*.[4] Moreover, since $y_A + y_B + \cdots = 1$,

$$p_A + p_B + \cdots = (y_A + y_B + \cdots)P = P \tag{5.2-8}$$

or, *the partial pressures of the components of an ideal-gas mixture add up to the total pressure (Dalton's law)*.

A similar series of calculations can be performed for pure-component volumes:

$$Pv_A = n_A RT$$
$$\Big\Downarrow \text{ Divide by } PV = nRT$$
$$\frac{v_A}{V} = \frac{n_A}{n} = y_A$$

or

$$\boxed{v_A = y_A V} \tag{5.2-9}$$

and

$$v_A + v_B + \cdots = V \qquad \text{(Amagat's law)}$$

The quantity v_A/V is the **volume fraction** of A in the mixture, and 100 times this quantity is the **percentage by volume** (% v/v) of this component. As shown above, *the volume fraction of a substance in an ideal-gas mixture equals the mole fraction of this substance*. Stating, for example, that an ideal-gas mixture contains 30% CH_4 and 70% C_2H_6 by volume (or 30% v/v CH_4 and 70% v/v C_2H_6) is equivalent to specifying 30 mole% CH_4 and 70 mole% C_2H_6.

Test Yourself

(Answers, p. 656)

1. A cylinder containing a mixture of N_2 and O_2 is taken from the basement to the top of a 50-story building. Assuming that the temperature remains constant, which of the following properties of the gas change during the ascent? (a) mass, (b) weight, (c) absolute pressure, (d) gauge pressure, (e) partial pressure of N_2, (f) pure-component volume of O_2, (g) density, (h) specific molar volume.
2. An ideal-gas mixture at 10 bar absolute and 200°C in a 100-m^3 tank contains 50 mole% H_2 and 50 mole% N_2. What is the partial pressure of H_2? What is the pure-component volume of H_2? What would happen to p_{H_2} and v_{H_2} if the temperature were raised?
3. An ideal-gas mixture at 10 atm absolute contains 50 wt% H_2 and 50 wt% N_2. Is the partial pressure of H_2 less than, equal to, or greater than 5 atm?

[4] Equation 5.2-7 is often used as the definition of the partial pressure. For an ideal-gas mixture, the definition given and Equation 5.2-7 are equivalent; for a nonideal gas the concept of partial pressure has little utility.

Example 5.2-5 Material Balances on an Evaporator-Compressor

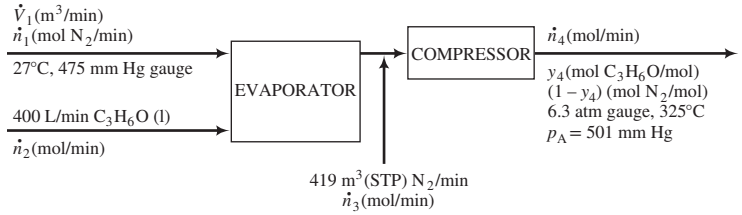
Liquid acetone (C_3H_6O) is fed at a rate of 400 L/min into a heated chamber, where it evaporates into a nitrogen stream. The gas leaving the heater is diluted by another nitrogen stream flowing at a measured rate of 419 m^3(STP)/min. The combined gases are then compressed to a total pressure $P = 6.3$ atm (gauge) at a temperature of 325°C. The partial pressure of acetone in this stream is $p_A = 501$ mm Hg. Atmospheric pressure is 763 mm Hg.

1. What is the molar composition of the stream leaving the compressor?
2. What is the volumetric flow rate of the nitrogen entering the evaporator if the temperature and pressure of this stream are 27°C and 475 mm Hg gauge?

Solution

Basis: Given Feed Rates

Assume ideal-gas behavior. Let $\dot{n}_1, \dot{n}_2, \ldots$ (mol/min) be the molar flow rates of each stream.



You should be able to examine the flowchart and see exactly how the solution will proceed.

1. Perform a degree-of-freedom analysis for the system and verify that the problem can be solved.
2. Calculate $\dot{n}_2$ (from the given volumetric flow rate and a tabulated density of liquid acetone), $\dot{n}_3$ (from the ideal-gas equation of state), and y_4 ($= p_A/P$).
3. Calculate $\dot{n}_4$ (overall acetone balance), $\dot{n}_1$ (overall mass balance), and $\dot{V}_1$ (ideal-gas equation of state).

Degree-of-Freedom Analysis

6 unknowns ($\dot{V}_1, \dot{n}_1, \dot{n}_2, \dot{n}_3, \dot{n}_4, y_4$)
−1 specific gravity relationship ($\dot{n}_2$)
−2 molecular balances (overall, C_3H_6O)
−1 ideal-gas equation of state ($\dot{V}_1$)
−1 partial pressure relationship (y_4)
−1 ideal-gas equation of state ($\dot{n}_3$)
0 degrees of freedom

Calculate Molar Flow Rate of Acetone

From Table B.1 in Appendix B, the density of liquid acetone is 0.791 g/cm^3 (791 g/L), so that

$$\dot{n}_2 = \frac{400\ \text{L}}{\text{min}} \left| \frac{791\ \text{g}}{\text{L}} \right| \frac{1\ \text{mol}}{58.08\ \text{g}} = 5450\ \frac{\text{mol}\ C_3H_6O}{\text{min}}$$

Determine Mole Fractions from Partial Pressures

In the stream leaving the compressor,

$$\frac{p_A}{P} = y_4 \left(\frac{\text{mol}\ C_3H_6O}{\text{mol}} \right)$$

$$P = P_{\text{gauge}} + P_{\text{atm}} = \frac{6.3\ \text{atm}}{} \left| \frac{760\ \text{mm Hg}}{1\ \text{atm}} \right. + 763\ \text{mm Hg} = 5550\ \text{mm Hg}$$

so that

$$y_4 = \frac{501 \text{ mm Hg}}{5550 \text{ mm Hg}} = 0.0903 \frac{\text{mol } C_3H_6O}{\text{mol}}$$
$$1 - y_4 = 0.9097 \frac{\text{mol } N_2}{\text{mol}}$$

Calculate $\dot{n}_3$ from PVT Information $\dot{n}_3 = \dfrac{419 \text{ m}^3\text{(STP)}}{\text{min}} \left| \dfrac{1 \text{ mol}}{0.0224 \text{ m}^3\text{(STP)}} \right. = 18{,}700 \dfrac{\text{mol}}{\text{min}}$

Overall Mole Balance on Acetone $\dot{n}_2 = \dot{n}_4 y_4$

$\Downarrow$ $\dot{n}_2 = 5450$ mol/min, $y_4 = 0.0903$

$\dot{n}_4 = 60{,}400$ mol/min

Overall Mole Balance $\dot{n}_1 + \dot{n}_2 + \dot{n}_3 = \dot{n}_4$

$\Downarrow$ $\dot{n}_2 = 5450$ mol/min, $\dot{n}_3 = 18{,}700$ mol/min, $\dot{n}_4 = 60{,}400$ mol/min

$\dot{n}_1 = 36{,}200$ mol/min

$\Downarrow$ Ideal-gas equation of state, $T_1 = 27°\text{C}$ (300 K), $P_1 = 475$ mm Hg gauge (1238 mm Hg)

$$\dot{V}_1 = \dot{n}_1 \frac{V_s}{n_s} \frac{T_1}{T_s} \frac{P_s}{P_1}$$
$$= \frac{36{,}200 \text{ mol}}{\text{min}} \left| \frac{0.0224 \text{ m}^3}{1 \text{ mol}} \right| \frac{300 \text{ K}}{273 \text{ K}} \left| \frac{760 \text{ mm Hg}}{1238 \text{ mm Hg}} \right.$$

$\Downarrow$

$$\dot{V}_1 = 550 \text{ m}^3 \text{ N}_2\text{/min}$$

5.3 EQUATIONS OF STATE FOR NONIDEAL GASES

The ideal gas is the basis of the simplest and most convenient equation of state: solving it is trivial, regardless of which variable is unknown, and the calculation is independent of the species of the gas and is the same for single species and mixtures. Its shortcoming is that it can be seriously inaccurate. At a sufficiently low temperature and/or a sufficiently high pressure, a value of $\hat{V}$ predicted with the ideal-gas equation could be off by a factor of two or three or more in either direction. Making things worse, the predicted value for one species at a given temperature and pressure could be much too high, that for another species at the same T and P could be much too low, and that for a third species could be quite close to the true value.

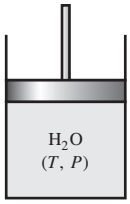
In this section we introduce several more complex but more accurate equations of state for single species: the *virial equation*, the *van der Waals equation*, and the *Soave–Redlich–Kwong equation*. In Section 5.4 we introduce another approach to nonideal gas analysis that makes use of the *law of corresponding states* and *compressibility factors*, and we describe *Kay's rule*, a method for performing PVT calculations on gas mixtures.

5.3a Critical Temperature and Pressure

How well or poorly the ideal-gas equation of state fits PVT data for a species often depends on the values of the system temperature and pressure relative to two physical properties of the species—the **critical temperature** (T_c) and **critical pressure** (P_c). Values of these *critical constants* can be

looked up in Table B.1 and in most standard chemical reference handbooks. Let us first consider their physical significance and then see how they are used in nonideal-gas calculations.

Suppose a quantity of water is kept in a closed piston-fitted cylinder.



The cylinder temperature is first set to a specified value with the cylinder pressure low enough for all the water to be vapor; then the water is compressed at constant temperature by lowering the piston until a drop of liquid water appears (i.e., until condensation occurs). The pressure at which condensation begins (P_{cond}) and the densities of the vapor (ρ_v) and of the liquid (ρ_l) at that point are noted, and the experiment is then repeated at several progressively higher temperatures. The following results might be obtained (observe the pattern for the three observed variables as T increases):

Run	T(°C)	P_{cond}(atm)	ρ_v(kg/m^3)	ρ_l(kg/m^3)
1	25.0	0.0329	0.0234	997.0
2	100.0	1.00	0.5977	957.9
3	201.4	15.8	8.084	862.8
4	349.8	163	113.3	575.0
5	373.7	217.1	268.1	374.5
6	374.15	218.3	315.5	315.5
7	>374.15	*No condensation occurs!*		

Notice what happens. At 25°C, water condenses at a very low pressure, and the density of the liquid is more than four orders of magnitude greater than that of the vapor. At higher temperatures, the condensation pressure increases and the densities of the vapor and liquid at condensation approach each other. At 374.15°C, the densities of the two phases are virtually equal, and above that temperature no phase separation is observed, no matter how high the pressure is raised.

In general, *the highest temperature at which a species can coexist in two phases (liquid and vapor) is the* **critical temperature** *of that species, T_c, and the corresponding pressure is the* **critical pressure**, P_c. A substance at T_c and P_c is said to be at its **critical state**. The above experiment demonstrates and Table B.1 confirms that, for water, $T_c = 374.15$°C and $P_c = 218.3$ atm.

The terms "gas" and "vapor" are often used interchangeably, but there is a technical difference between them that you are now in a position to understand. A **vapor** is a gaseous species below its critical temperature, and a **gas** is a species above its critical temperature at a pressure low enough for the species to be more like a vapor than a liquid (i.e., a density closer to 1 g/L than 1000 g/L). You can condense a vapor by compressing it isothermally, but while you can make a gas denser and denser by compressing, it isothermally you will never achieve a separation into two phases. Substances at temperatures above T_c and pressures above P_c are referred to as **supercritical fluids**.

Test Yourself

(Answers, p. 656)

The critical temperature and pressure of isopropanol (isopropyl alcohol) are $T_c = 508.8$ K and $P_c = 53.0$ atm.

1. Isopropanol is in a gaseous state at $T = 400$ K and $P = 1$ atm. Would it be classified as a vapor or a gas?

2. Isopropanol is compressed isothermally at 400 K until at pressure P_a a liquid phase forms. The vapor and liquid densities at that point are, respectively, ρ_{va} and ρ_{la}. In a second experiment, isopropanol is compressed at 450 K until condensation occurs, at which point the pressure and vapor and liquid densities are P_b, ρ_{vb}, and ρ_{lb}. What are the relationships (>, =, <, or?) between (a) P_a and P_b, (b) ρ_{va} and ρ_{vb}, and (c) ρ_{la} and ρ_{lb}?
3. If isopropanol at 550 K and 1 atm is compressed isothermally to 100 atm, will a condensate form? What term might you use to refer to the fluid at its initial condition? At its final condition?

5.3b Virial Equations of State

A **virial equation of state** expresses the quantity $P\hat{V}/RT$ as a power series in the inverse of specific volume:

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \cdots \tag{5.3-1}$$

where B, C, and D are functions of temperature and are known as the second, third, and fourth virial coefficients, respectively. This equation of state has a theoretical basis in statistical mechanics but procedures for estimating the coefficients are not well developed, especially for those beyond B. Note that the ideal-gas equation of state is obtained if $B = C = D = \cdots = 0$.

Simple approximations to Equation 5.3-1 can be useful because they are relatively easy to manipulate and there may be limited information on third and subsequent virial coefficients. For example, truncating after the second virial coefficient yields

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} \tag{5.3-2}$$

A further approximation substitutes $\hat{V} = RT/P$ (i.e., the ideal-gas equation of state) into the right-hand side of Equation 5.3-2 to give

$$\frac{P\hat{V}}{RT} = 1 + \frac{BP}{RT} \tag{5.3-3}$$

The latter equation can be solved easily for any of the three variables P, $\hat{V}$, or T.

Poling et al. (see Footnote 1) caution against using this equation for polar compounds (asymmetrical compounds with a nonzero dipole moment, such as water). The following procedure may be used to estimate $\hat{V}$ or P for a given T for a nonpolar species (one with a dipole moment close to zero, such as hydrogen and oxygen and all other molecularly symmetrical compounds).

- Look up the critical temperature and pressure (T_c and P_c) for the species of interest in Table B.1 or elsewhere. Also look up the **Pitzer acentric factor**, ω, a parameter that reflects the geometry and polarity of a molecule. Table 5.3-1 lists values of ω for selected compounds, and a more complete list can be found in Poling et al. (see Footnote 1).
- Calculate the **reduced temperature**, $T_r = T/T_c$.
- Estimate B using the following equations:

$$B_0 = 0.083 - \frac{0.422}{T_r^{1.6}} \tag{5.3-4}$$

$$B_1 = 0.139 - \frac{0.172}{T_r^{4.2}} \tag{5.3-5}$$

$$B = \frac{RT_c}{P_c}(B_0 + \omega B_1) \tag{5.3-6}$$

TABLE 5.3-1 Pitzer Acentric Factors
(Values with * were in the 4th edition of the reference in Footnote 1.)

Compound	Acentric Factor, ω
Ammonia	0.257
Argon	−0.002
Carbon dioxide	0.225
Carbon monoxide	0.045
Chlorine*	0.073
Ethane	0.099
Ethylene	0.087
Hydrogen sulfide	0.090
Methane	0.011
Methanol	0.565
Nitrogen	0.037
Oxygen*	0.021
Propane	0.152
Sulfur dioxide*	0.251
Water	0.344

- Substitute into Equation 5.3-3 the values of B and whichever of the variables P and $\hat{V}$ is known and solve for the other variable.

Example 5.3-1 The Truncated Virial Equation

Two gram-moles of nitrogen is placed in a three-liter tank at −150.8°C. Estimate the tank pressure using the ideal-gas equation of state and then using the virial equation of state truncated after the second term. Taking the second estimate to be correct, calculate the percentage error that results from the use of the ideal-gas equation at the system conditions.

Solution $T = (-150.8 + 273.2)\,\text{K} = 122.4\,\text{K}$, and $\hat{V} = 3.00\,\text{L}/2.00\,\text{mol} = 1.50\,\text{L/mol}$. From the ideal-gas equation of state,

$$P_{\text{ideal}} = \frac{RT}{\hat{V}} = \frac{0.08206\,\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \left| \begin{array}{c|c|c} 123\,\text{K} & \dfrac{1\,\text{mol}}{1.50\,\text{L}} \end{array} \right. = \boxed{6.73\,\text{atm}}$$

The procedure for using the virial equation is as follows:

- Table B.1 $\Longrightarrow (T_c)_{N_2} = 126.2\,\text{K}$, $(P_c)_{N_2} = 33.5\,\text{atm}$
  Table 5.3-1 $\Longrightarrow \omega_{N_2} = 0.040$
- $T_r = \dfrac{T}{T_c} = \dfrac{122.4\,\text{K}}{126.2\,\text{K}} = 0.970$
- Equation 5.3-4 $\Longrightarrow B_0 = 0.083 - \dfrac{0.422}{0.970^{1.6}} = -0.36$

  Equation 5.3-5 $\Longrightarrow B_1 = 0.139 - \dfrac{0.172}{0.970^{4.2}} = -0.056$

  Equation 5.3-6 $\Longrightarrow B = \dfrac{\left(0.08206\,\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(126.2\,\text{K})}{33.5\,\text{atm}}[-0.36 + 0.040(-0.056)]$

  $= -0.112\,\text{L/mol}$

- From a rearrangement of Equation 5.3-3, $P = \dfrac{RT}{\hat{V} - B}$, so that

$$P = \frac{\left(0.08206 \dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(122.4\ \text{K})}{(1.50 + 0.112)\dfrac{\text{L}}{\text{mol}}} = \boxed{6.23\ \text{atm}}$$

The error in the pressure calculated using the ideal-gas equation of state is

$$\varepsilon = \frac{P_{\text{ideal}} - P}{P} \times 100\% = \boxed{8.0\%\ \text{error}}$$

5.3c Cubic Equations of State

A number of analytical *PVT* relationships are referred to as **cubic equations of state** because, when expanded, they yield third-order equations for the specific volume. The **van der Waals equation of state** is the earliest of these expressions, and it remains useful for discussing deviations from ideal behavior.

$$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2} \tag{5.3-7}$$

where

$$a = \frac{27R^2T_c^2}{64P_c} \qquad b = \frac{RT_c}{8P_c}$$

In the van der Waals derivation, the term $a/\hat{V}^2$ accounts for attractive forces between molecules and b is a correction accounting for the volume occupied by the molecules themselves.[5]

Poling, Prausnitz, and O'Connell (see Footnote 1) discuss other important cubic equations of state including the **Redlich–Kwong, Soave–Redlich–Kwong (SRK)**, and **Peng–Robinson** equations. These equations are empirical but have proved remarkably robust in describing a wide variety of systems. Here we will use the SRK expression to illustrate the general characteristics of cubic equations of state.

The SRK equation of state is

$$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)} \tag{5.3-8}$$

where the parameters a, b, and α are empirical functions of the critical temperature and pressure (T_c and P_c from Table B.1), the Pitzer acentric factor (ω from Table 5.3-1), and the system temperature. The following correlations are used to estimate these three parameters:

$$a = 0.42747\,\frac{(RT_c)^2}{P_c} \tag{5.3-9}$$

$$b = 0.08664\,\frac{RT_c}{P_c} \tag{5.3-10}$$

$$m = 0.48508 + 1.55171\omega - 0.1561\omega^2 \tag{5.3-11}$$

$$T_r = T/T_c \tag{5.3-12}$$

$$\alpha = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2 \tag{5.3-13}$$

[5] An interesting discussion of the role of a and b is in the text of the lecture Johannes D. van der Waals gave upon receiving the Nobel Prize for his work in developing his equation of state (http://nobelprize.org/nobel_prizes/physics/laureates/1910/waals-lecture.html).

The complexity of using the SRK equation of state can vary depending on which of the three variables (P, $\hat{V}$, T) are known. We suggest the following procedure:

1. For given species, look up T_c, P_c, and the Pitzer acentric factor ω (Table 5.3-1 for selected species). Calculate a, b, and m from Equations 5.3-9, 5.3-10, and 5.3-11.
2. If T and $\hat{V}$ are known, evaluate T_r from Equation 5.3-12 and α from Equation 5.3-13, and solve Equation 5.3-8 for P.
3. If T and P are known, enter Equation 5.3-8 and all known values in Excel's Solver, and solve for $\hat{V}$. (Alternatively, use *Goal Seek* in Excel, as in Example 5.3-3.)
4. If P and $\hat{V}$ are known, enter Equations 5.3-8, 5.3-11 for T_r, 5.3-13 for α, and all known values in Excel's Solver, and solve for T.

Example 5.3-2 The SRK Equation of State

A gas cylinder with a volume of 2.50 m^3 contains 1.00 kmol of carbon dioxide at $T = 300$ K. Use the SRK equation of state to estimate the gas pressure in atm.

Solution The specific molar volume is calculated as

$$\hat{V} = \frac{V}{n} = \frac{2.5\ \text{m}^3}{1.00\ \text{kmol}} \left| \frac{10^3\ \text{L}}{1\ \text{m}^3} \right| \frac{1\ \text{kmol}}{10^3\ \text{mol}} = 2.50\ \text{L/mol}$$

From Table B.1, $T_c = 304.2$ K and $P_c = 72.9$ atm, and from Table 5.3-1, $\omega = 0.225$. The parameters in the SRK equation of state are evaluated using Equations 5.3-9 through 5.3-13:

$$\text{Equation 5.3-9} \Longrightarrow a = 0.42747 \frac{\{[0.08206\ \text{L·atm/(mol·K)}](304.2\ \text{K})\}^2}{72.9\ \text{atm}}$$
$$= 3.654\ \text{L}^2\text{·atm/mol}^2$$
$$\text{Equation 5.3-10} \Longrightarrow b = 0.08664 \frac{[0.08206\ \text{L·atm/(mol·K)}](304.2\ \text{K})}{72.9\ \text{atm}}$$
$$= 0.02967\ \text{L/mol}$$
$$\text{Equation 5.3-11} \Longrightarrow m = 0.8263$$
$$\text{Equation 5.3-12} \Longrightarrow T_r = 0.986$$
$$\text{Equation 5.3-13} \Longrightarrow \alpha = 1.0115$$

The SRK equation (5.3-8) can now be solved for the tank pressure:

$$P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)}$$
$$= \frac{[0.08206\ \text{L·atm/(mol·K)}](300\ \text{K})}{[(2.50 - 0.02967)\text{L/mol}]} - \frac{1.0115(3.654\ \text{L}^2\text{·atm/mol}^2)}{(2.50\ \text{L/mol})[(2.50 + 0.02967)\text{L/mol}]}$$
$$= \boxed{9.38\ \text{atm}}$$

Use of the ideal-gas equation of state leads to an estimated pressure of 9.85 atm (*verify*), a deviation of 5% from the more accurate SRK-determined value.

Evaluation of a system volume from a given temperature and pressure using a cubic equation of state requires a trial-and-error procedure. As illustrated by the next example, a spreadsheet is ideally suited to solving problems of this type.

Example 5.3-3 Estimation of Volumes Using the SRK Equation of State

A stream of propane at temperature $T = 423$ K and pressure P (atm) flows at a rate of 100.0 kmol/h. Use the SRK equation of state to estimate the volumetric flow rate of the stream for $P = 0.7$ atm, 7 atm, and 70 atm. In each case, calculate the percentage differences between the predictions of the SRK equation and the ideal-gas equation of state.

Solution The calculation of $\hat{V}$(L/mol) proceeds as follows: the SRK equation of state is written in the form

$$f(\hat{V}) = P - \frac{RT}{\hat{V} - b} + \frac{\alpha a}{\hat{V}(\hat{V} + b)} = 0$$

the values of T_c, P_c, and ω are looked up; a, b, and α are calculated from the given formulas; specified values of T and P are substituted; and the value of $\hat{V}$ for which $f(\hat{V}) = 0$ is found by trial and error. The percentage difference between $\hat{V}_{SRK}$ and $\hat{V}_{ideal}(= RT/P)$ is

$$D(\%) = \frac{\hat{V}_{ideal} - \hat{V}_{SRK}}{\hat{V}_{SRK}} \times 100\%$$

Once $\hat{V}$ is known for a given P, the volumetric flow rate corresponding to a molar flow rate of 100.0 kmol/h is obtained as

$$\dot{V}(\text{m}^3/\text{h}) = \frac{\hat{V}(\text{L})}{(\text{mol})} \left| \frac{10^3 \text{ mol}}{1 \text{ kmol}} \right| \frac{1 \text{ m}^3}{10^3 \text{ L}} \left| \frac{100.0 \text{ kmol}}{\text{h}} \right. = 100.0\ \hat{V}(\text{L/mol})$$

In Figure 5.3-1 we show one of many possible spreadsheet configurations that might be created to perform these calculations, along with the formulas entered into selected cells. The critical constants of propane

FIGURE 5.3-1 Spreadsheet for Example 5.3-3.

	A	B	C	D	E	F
1	**Example 5.3-3**					
2						
3	Tc =	369.9	Pc =	42.0	omega =	0.152
4	a =	9.3775	b =	0.06262	m =	0.7173
5	T =	423	Tr =	1.14355	alpha =	0.903
6						
7	P	Vhat ideal	Vhat	f(Vhat)	D	Vdot
8	(atm)	(L/mol)	(L/mol)	(atm)	(%)	(m3/h)
9	0.7	49.59	49.41	1.6E–5	0.37	4941
10	7	4.959	4.775	9.9E–6	3.9	477
11	70	0.4959	0.2890	9.2E–5	72	28.9

[B4] = 0.42747*(0.08206*B3)^2/D3
[D4] = 0.08664*0.08206 * B3/D3
[F4] = 0.48508+1.55171*F3–0.1561*F3^2
[D5] = B5/B3
[F5] = (1+F4*(1–SQRT(D5)))^2
[B9] = 0.08206*$B$5/A9
[C9] = 49.588
[D9] = A9–0.08206*$B$5/(C9–$D$4)+$F$5*$B$4/(C9*(C9+$D$4))
[E9] = 100*(B9–C9)/C9
[F9] = 100*C9

($T_c = 369.9$ K and $P_c = 42.0$ atm) come from Table B.1 and the Pitzer acentric factor ($\omega = 0.152$) comes from Table 5.3-1. Notice that the ideal-gas equation of state works very well at 0.7 atm and reasonably well at 7 atm, but for 70 atm the differences between the two estimates of $\hat{V}$ are considerable.

When the spreadsheet is constructed, the displayed contents of Rows 1, 3–5, 7, and 8 are entered exactly as shown except for the given formulas in Cells B4, D4, F4, D5, and F5. After the cell contents of Row 9 have been entered they are copied into Rows 10 and 11, and the pressures in Column A are then changed to their desired values. The entries in Cells C9–C11 (the initial guesses for $\hat{V}$) are the values copied from the adjacent cells in Column B (the values obtained using the ideal-gas equation of state). The correct values are then obtained by trial and error; for example, the value in Cell C9 would be varied until the value in Cell D9 is sufficiently close to zero, and similarly for Rows 10 and 11. The search is conveniently done using the spreadsheet's Goal Seek tool. If you are not experienced in the use of spreadsheets, it might be useful to construct this one and attempt to reproduce the given results.

Remember that the SRK equation of state (and every other equation of state) is itself an approximation. Referring back to the preceding example, a published study provides experimental data for the *PVT* behavior of propane.[6] The data indicate that at 423 K and 70 atm, the value of $\hat{V}$ is 0.2579 L/mol. The percentage error in the SRK estimate ($\hat{V} = 0.2890$ L/mol) is a far from insignificant 12%, and that in the ideal-gas estimate ($\hat{V} = 0.4959$ L/mol) is 92%.

All equations of state have parameters obtained by fitting empirical expressions to experimental *PVT* data. The fit may be excellent in the temperature and pressure ranges where the data were obtained but poor elsewhere. You should always try to ascertain the region of validity of any equation of state you intend to use. At conditions far removed from this region, you have no assurance of the accuracy of the equation.

Test Yourself

(Answers, p. 656)

1. Why is the SRK equation of state called a *cubic equation of state?*
2. What physical properties of a species do you have to look up in order to use the SRK equation of state? Where can you find values of these properties in this text?
3. The SRK equation of state is to be used to determine one of the variables T, P, and $\hat{V}$ from given values of the other two. Rank the following problems from easiest to most difficult: (a) given T and P, find $\hat{V}$; (b) given T and $\hat{V}$, find P; and (c) given P and $\hat{V}$, find T.
4. Explain in your own words why estimates obtained using an equation of state may be inaccurate and when you need to be particularly skeptical of them.

5.4 THE COMPRESSIBILITY-FACTOR EQUATION OF STATE

The **compressibility factor** of a gaseous species is defined as the ratio

$$z = \frac{P\hat{V}}{RT} \tag{5.4-1}$$

If the gas is ideal, $z = 1$. The extent to which z differs from 1 is a measure of the extent to which the gas is behaving nonideally. Equation 5.4-1 may be rearranged to form the **compressibility-factor equation of state**,

$$P\hat{V} = zRT \tag{5.4-2a}$$

or since $\hat{V} = V/n$ for a fixed quantity of gas and $\dot{V}/\dot{n}$ for a flowing stream,

$$PV = znRT \tag{5.4-2b}$$

$$P\dot{V} = z\dot{n}RT \tag{5.4-2c}$$

[6] R. D. Gray, N. H. Rent, and D. Zudkevitch, *AIChE Journal*, **16**, 991(1970).

It would be convenient if the compressibility factor at a single temperature and pressure were the same for all gases, so that a single chart or table of $z(T, P)$ could be used for all *PVT* calculations. Nature is not that accommodating, unfortunately; for example, z for nitrogen at 0°C and 100 atm is 0.9848 while z for carbon dioxide at the same temperature and pressure is 0.2020. Consequently, to use tabulated z values for all *PVT* calculations as in the preceding example, you would have to measure compressibilities as functions of temperature and pressure separately for every chemical species. Equations of state such as the van der Waals and the Soave–Redlich–Kwong equations were developed to avoid having to compile the massive volumes of z data that would be involved in such an effort.

One approach to using the compressibility-factor equation of state would be to determine z experimentally as a function of T and P for different chemical species and substitute it into Equation 5.4-2a, 5.4-2b, or 5.4-2c in process calculations. While such tabulations can be found for some common species, the immense amount of experimental work that would be required to do it for most species makes that approach impractical.

An alternative method uses the *law of corresponding states* to estimate z, and then substitutes z into the compressibility-factor equation of state. The basis for the law is the observation that the values of certain physical properties of gases—including the compressibility factor—depend to a great extent on the proximity of the gas temperature and pressure (T and P) to the critical temperature (T_c) and critical pressure (P_c) of the gas species. The law states that the compressibility factor of any gas at a specific value of *reduced temperature,* T/T_c, and *reduced pressure,* P/P_c, has approximately the same value for all species. A single **generalized compressibility chart**[7] showing z as a function of (T_r, P_r) may therefore be prepared and used to estimate compressibility factors.

Figure 5.4-1 shows a generalized compressibility chart for those species having a critical compressibility factor of 0.27.[8] Conditions for both gases and liquids are illustrated, although in our discussions here we only consider estimation of z for gases. Note the increasing deviations from ideal-gas behavior as pressures approach P_c (i.e., when $P_r \to 1$).

Figures 5.4-2 through 5.4-4 are expansions of various regions of Figure 5.4-1. The parameter V_r^{ideal} is introduced in these figures to eliminate the need for trial-and-error calculations in problems where either temperature or pressure is unknown. This parameter is defined in terms of the ideal critical volume[9] as

$$V_r^{\text{ideal}} = \frac{\hat{V}}{\hat{V}_c^{\text{ideal}}} = \frac{\hat{V}}{RT_c/P_c} = \frac{P_c\hat{V}}{RT_c} \tag{5.4-3}$$

Figure 5.4-1 covers a very wide spectrum of reduced pressures, and it is difficult to read the value of z with much precision in some pressure ranges. Figures 5.4-2, 5.4-3, and 5.4-4 expand the chart for low, medium, and high reduced pressures, respectively, adding considerable precision in those ranges. If P (and thus P_r) is known, the appropriate chart to use is easy to identify; if P is to be determined from the compressibility-factor equation of state and known values of T_r and V_r, finding the right chart may be a little harder.

The procedure for using the generalized compressibility chart for *PVT* calculations is as follows:

1. Determine the critical temperature, T_c, and critical pressure, P_c, of the species either by looking it up [e.g., in Table B.1 or with the APEx functions Tcrit("Species") and Pcrit("Species")] or using

[7] L. C. Nelson and E. F. Obert, *Trans. ASME,* **76**, 1057(1954).

[8] An extension of the generalized charts that provides somewhat greater accuracy also allows for a dependence of $z(T, P)$ on z_c, the compressibility factor at the critical point, which generally varies between 0.25 and 0.29.

[9] $\hat{V}_c^{\text{ideal}} = RT_c/P_c$ is the specific molar volume that would be calculated by the ideal-gas equation of state for temperature T_c and pressure P_c. It has no physical significance for the gas in question, unlike T_c, P_c, and the *critical volume* $\hat{V}_c$, another property of the gas.

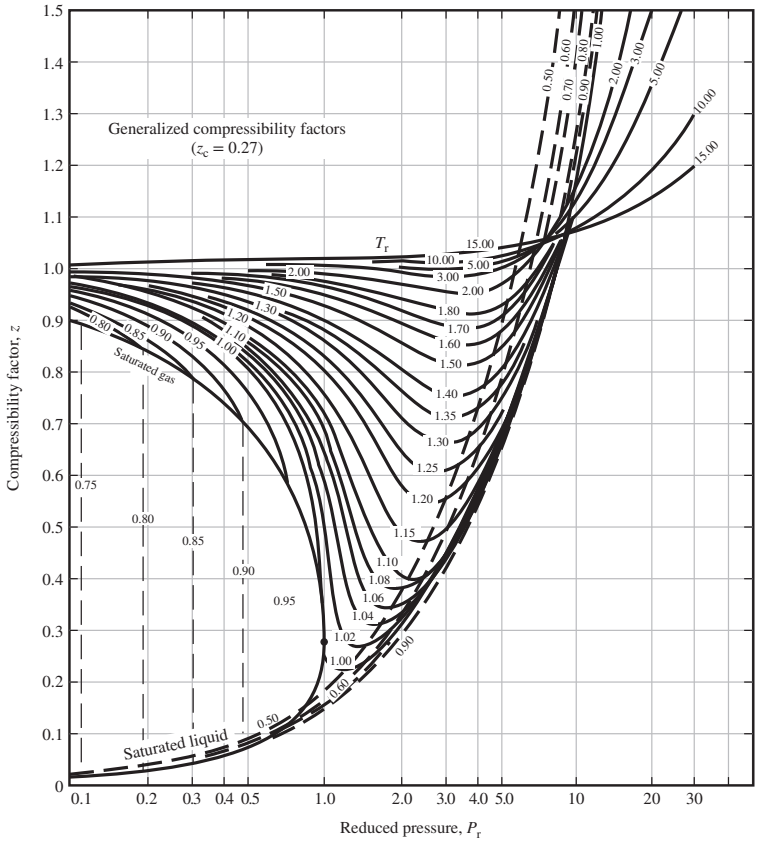


FIGURE 5.4-1
(Reprinted with permission from *Chemical Process Principles Charts*, 2nd Edition, by O. A. Hougen, K. M. Watson, and R. A. Ragatz, John Wiley & Sons, New York, 1960.)

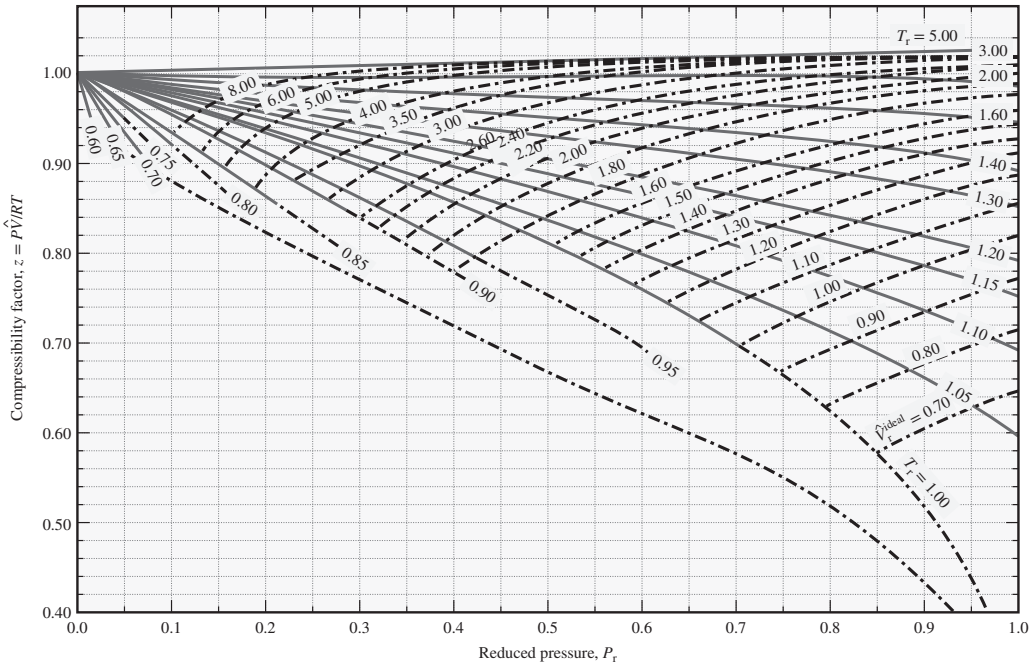


FIGURE 5.4-2
Generalized compressibility chart, low pressures. (Based on Footnote 7.)

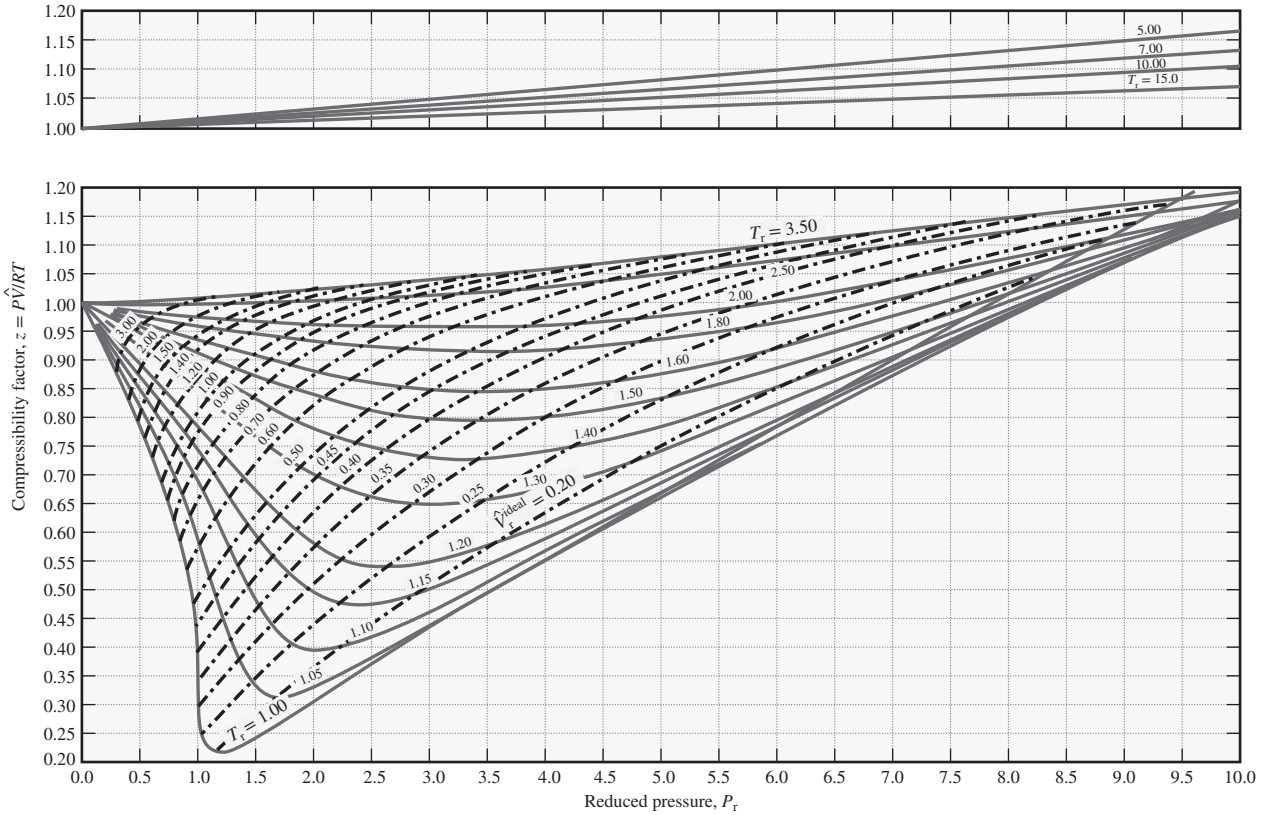


FIGURE 5.4-3 Generalized compressibility chart, medium pressures. (Based on Footnote 7.)

an estimation procedure such as those illustrated by Poling et al. (see Footnote 1) or described on pp. 2-468 through 2-471 of *Perry's Chemical Engineers' Handbook* (see Footnote 2).

2. If the gas is either hydrogen or helium, determine *adjusted critical constants* from the empirical formulas

$$T_c^a = T_c + 8\ \text{K} \tag{5.4-4}$$

$$P_c^a = P_c + 8\ \text{atm} \tag{5.4-5}$$

These equations are known as **Newton's corrections**.

3. Calculate reduced values of the two known variables (temperature and pressure, temperature and volume, or pressure and volume) using the definitions

$$T_r = \frac{T}{T_c} \tag{5.4-6}$$

$$P_r = \frac{P}{P_c} \tag{5.4-7}$$

$$V_r^{\text{ideal}} = \frac{P_c \hat{V}}{RT_c} \tag{5.4-8}$$

Don't forget to perform whatever unit conversions may be necessary to make the calculated reduced variables dimensionless. If the gas is H_2 or He, substitute for T_c and P_c the adjusted values of these quantities calculated in Step 2. *All temperatures and pressures used in these calculations must be absolute.*

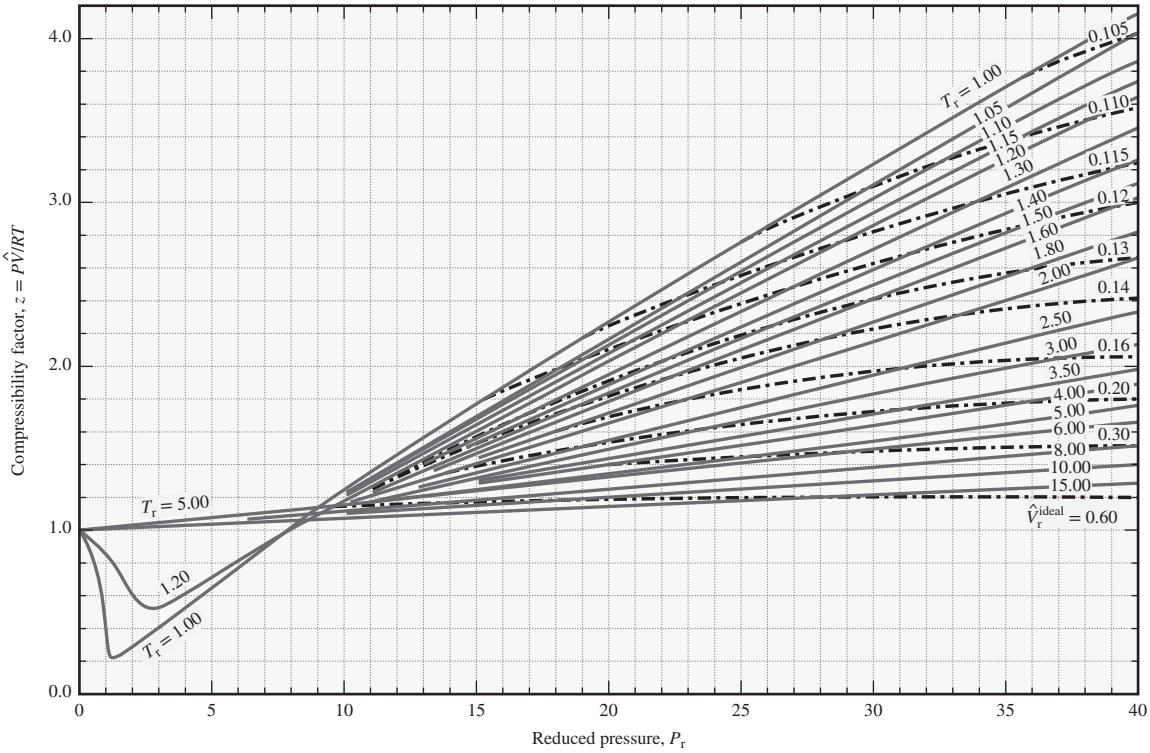


FIGURE 5.4-4 Generalized compressibility chart, high pressures. (Based on Footnote 7.)

4. Use the compressibility charts to determine the compressibility factor, and then solve for the unknown variable from the compressibility-factor equation of state (Equation 5.4-2).

The compressibility-factor equation of state used in conjunction with the generalized compressibility chart is not generally as accurate as a multiple-constant equation of state for *PVT* calculations under highly nonideal conditions. Furthermore, it lacks precision and cannot readily be adapted to computer calculations. Its advantages include relative computational simplicity and (as will be shown) adaptability to multicomponent gas mixtures.

Example 5.4-1 The Generalized Compressibility Chart

One hundred gram-moles of nitrogen is contained in a 5.00-liter vessel at −20.6°C. Estimate the pressure in the cylinder.

Solution From Table B.1, the critical temperature and pressure of nitrogen are

$$T_c = 126.2\ \text{K}, \quad P_c = 33.5\ \text{atm}$$

The reduced temperature and volume are calculated from Equations 5.4-6 and 5.4-8 as

$$T_r = \frac{T}{T_c} = \frac{(-20.6 + 273.2)\ \text{K}}{126.2\ \text{K}} = 2.00$$

$$V_r^{ideal} = \frac{\hat{V}P_c}{RT_c} = \frac{\dfrac{5\ \text{L}}{100\ \text{mol}} \left| \dfrac{33.5\ \text{atm}}{126.2\ \text{K}} \right| \dfrac{\text{mol}\cdot\text{K}}{0.08206\ \text{L}\cdot\text{atm}}}{} = 0.161$$

From Figure 5.4-4, the intersection of $T_r = 2$ and $V_r^{ideal} = 0.161$ occurs at approximately $z = 1.77$. From Equation 5.4-2a, we can now calculate

$$P = \frac{zRT}{\hat{V}} = \frac{1.77 \left| \frac{0.08206\ \text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right| 252.6\ \text{K}}{0.05\ \text{L/mol}} = \boxed{734\ \text{atm}}$$

Note: You could also read the value of P_r at the intersection and calculate $P = P_r P_c$; however, it is generally more precise to calculate unknown variables by first determining z and then using the equation of state, as was done above.

Test Yourself

(Answers, p. 656)

1. Suppose you need to know the volume that would be occupied by 10 kmol of H_2 at −190°C and 300 atm. Would you consider it reasonable to use a value calculated from the ideal-gas equation of state? How would you use the generalized compressibility chart for this calculation?
2. Why would a chart such as that in Figure 5.4-1 be useless if T and P were the chart parameters?
3. What is the law of corresponding states, and how does it provide a basis for the generalized compressibility chart?

5.4a Nonideal-Gas Mixtures

Whether an analytical or graphical correlation is used to describe nonideal-gas behavior, difficulties arise when the gas contains more than one species. Consider, for example, the SRK equation of state (Equation 5.3-8): How would you estimate the parameters a, b, and α if the gas consisted of methane, carbon dioxide, and nitrogen? **Mixture rules** developed for such circumstances are summarized by Poling et al. (see Footnote 1). We will illustrate *PVT* calculations for mixtures with a simple rule developed by Kay[10] that utilizes the generalized compressibility charts.

Kay's rule estimates *pseudocritical properties* of mixtures as simple averages of pure-component critical constants:[11]

Pseudocritical Temperature:
$$T'_c = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + \cdots \quad \textbf{(5.4-9)}$$

Pseudocritical Pressure:
$$P'_c = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + \cdots \quad \textbf{(5.4-10)}$$

where y_A, y_B, . . . are mole fractions of species A, B, . . . in the mixture. Assuming that the system temperature T and pressure P are known, the pseudocritical properties can be used to estimate the *pseudoreduced temperature and pressure* of the mixture:

Pseudoreduced Temperature:
$$T'_r = T/T'_c \quad \textbf{(5.4-11)}$$

Pseudoreduced Pressure:
$$P'_r = P/P'_c \quad \textbf{(5.4-12)}$$

The compressibility factor for a gas mixture, z_m, can now be estimated from the compressibility charts and the pseudoreduced properties, and $\hat{V}$ for the mixture can be calculated as

$$\hat{V} = \frac{z_m RT}{P} \quad \textbf{(5.4-13)}$$

[10] W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014(1936).

[11] The pseudocritical constants are simply empirical parameters that have been found useful for correlating the physical properties of a mixture. Unlike T_c and P_c for a single component, T'_c and P'_c have no physical significance.

As with single-component gases, if you know $\hat{V}$ and either T or P, you can estimate the ideal pseudoreduced volume $\hat{V}_r^{ideal} = \hat{V}P'_c/RT'_c$ and use the other known reduced property to determine the unknown temperature or pressure from the compressibility chart.

Like the theory of corresponding states on which it is based, Kay's rule provides only approximate values of the quantities it is used to calculate. It works best when used for mixtures of nonpolar compounds whose critical temperatures and pressures are within a factor of two of one another. Poling et al. (see Footnote 1) provide more complex but more accurate mixing rules for systems that do not fall into this category.

Test Yourself

(Answers, p. 656)

What is Kay's rule? How would you use it to calculate the specific molar volume of an equimolar mixture of gases at a given temperature and pressure? For what types of gases would you have the greatest confidence in the answer?

Example 5.4-2 Kay's Rule

A mixture of 75% H_2 and 25% N_2 (molar basis) is contained in a tank at 800 atm and −70°C. Estimate the specific volume of the mixture in L/mol using Kay's rule.

Solution

Critical Constants: From Table B.1:

H_2: $T_c = 33$ K

$T_c^a = (33 + 8)$ K = 41 K (Newton's correction: Equation 5.4-4)

$P_c = 12.8$ atm

$P_c^a = (12.8 + 8)$ atm = 20.8 atm (Newton's correction: Equation 5.4-5)

N_2: $T_c = 126.2$ K

$P_c = 33.5$ atm

Pseudocritical Constants: From Equations 5.4-9 and 5.4-10:

$$T'_c = y_{H_2}(T_c^a)_{H_2} + y_{N_2}(T_c)_{N_2} = 0.75 \times 41\text{ K} + 0.25 \times 126.2\text{ K} = 62.3\text{ K}$$
$$P'_c = y_{H_2}(P_c^a)_{H_2} + y_{N_2}(P_c)_{N_2} = 0.75 \times 20.8\text{ atm} + 0.25 \times 33.5\text{ atm} = 24.0\text{ atm}$$

Reduced Conditions: $T = (-70 + 273)$ K = 203 K, $P = 800$ atm

$$T'_r = \frac{T}{T'_c} = \frac{203\text{ K}}{62.3\text{ K}} = 3.26$$
$$P'_r = \frac{P}{P'_c} = \frac{800\text{ atm}}{24.0\text{ atm}} = 33.3$$

Mixture Compressibility: From Figure 5.4-4:

$$z_m(T'_r = 3.26, P'_r = 33.3) = 1.86$$

Calculation of Specific Volume: $P\hat{V} = z_m RT$

$$\Downarrow$$

$$\hat{V}\left(\frac{\text{L}}{\text{mol}}\right) = \frac{z_m T(\text{K})}{P(\text{atm})} \times R\left(\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right) = \frac{(1.86)(203)(0.08206)}{800}\frac{\text{L}}{\text{mol}}$$
$$= \boxed{0.0387\ \frac{\text{L}}{\text{mol}}}$$

5.5 SUMMARY

Problems often arise that call for determining the value of one of the four variables P, T, V, and n (or $\dot{V}$ and $\dot{n}$) for a process material from known values of the other three.

- If the material is a solid or liquid and consists of a single species, look up the specific gravity or density in Table B.1 or one of the references on p. 216. As a first approximation, assume that the tabulated value is independent of temperature and pressure. For a more refined estimate, find and apply a correlation for the dependence of the density on temperature.
- If the material is a liquid mixture, either find a table of mixture density as a function of composition or assume volume additivity and estimate the mixture density from either Equation 5.1-1 or Equation 5.1-2. If the material is a dilute liquid solution, either find a table of mixture density as a function of composition or take the density to be that of the pure solvent.
- If the material is a gas, the ideal-gas equation of state ($PV = nRT$) may provide a reasonable approximation for *PVT* calculations. The equation works best at low pressures (on the order of 1 atm or less) and high temperatures (generally not much lower than 0°C). A rule of thumb is that the ideal-gas equation provides reasonable estimates if RT/P is greater than 5 L/mol for diatomic gases and greater than 20 L/mol for other gases.
- *Standard temperature and pressure* (STP) are generally defined as 0°C and 1 atm. These values and the corresponding *standard specific volume,* $\hat{V}_s = 22.4\ \text{L(STP)/mol} \Longrightarrow 359\ \text{ft}^3\text{(STP)/lb-mole}$, can be used in conjunction with Equation 5.2-5 for *PVT* calculations on ideal gases.
- The *partial pressure* of a component in an ideal-gas mixture is $y_i P$, where y_i is the mole fraction of the component and P is the total absolute pressure. The component partial pressures add up to the total pressure.
- The volume percent of a component in an ideal-gas mixture (%v/v) is the same as the mole percent of that component. If the gas mixture is nonideal, the volume percent has no useful meaning.
- The *critical temperature* T_c of a species is the highest temperature at which isothermal compression of the species vapor results in the formation of a separate liquid phase, and the *critical pressure* is the pressure at which that phase forms. Isothermal compression of a species above its critical temperature—a *gas* (as opposed to *vapor*) or *supercritical fluid*—results in a fluid of increasing density but not a separate liquid phase.
- If process conditions are such that the ideal-gas equation of state is a poor approximation, a more complex species-specific equation of state must be used. Most such equations, including the *Soave-Redlich-Kwong (SRK)* equation of state, contain adjustable parameters that depend on the critical temperature and pressure of the species and possibly other factors that depend on the molecular geometry and polarity of the species.
- An alternative to using quadratic equations of state (such as the truncated virial equation) and cubic equations of state (such as the SRK equation) is to use the *compressibility-factor equation of state:* $PV = znRT$. The compressibility factor z, defined as the ratio $P\hat{V}/RT$, equals 1 if the gas behaves ideally. For some species it may be looked up in a table (e.g., in *Perry's Chemical Engineers' Handbook*) or, more generally, estimated from the generalized compressibility charts (Figures 5.4-1 through 5.4-4).
- The basis of the generalized compressibility charts is the *law of corresponding states*, an empirical rule stating that the compressibility factor of a species at a given temperature and pressure depends primarily on the *reduced temperature* and *reduced pressure,* $T_r = T/T_c$ and $P_r = P/P_c$. Once you have determined these quantities, you may use the charts to determine z and then substitute the value in the compressibility-factor equation of state and solve for whichever variable is unknown.
- To perform *PVT* calculations for non-ideal gas mixtures, you may use *Kay's rule*. Determine *pseudocritical constants* (temperature and pressure) by weighting the critical constants for each mixture component by the mole fraction of that component in the mixture; then calculate the reduced temperature and pressure and the compressibility factor as before.
- Remember that every equation of state for nonideal gases is an approximation, often based on fitting adjustable parameters to experimental *PVT* data. Be skeptical of every value you estimate, especially if you are using an equation of state beyond the range of conditions for which it was developed.
- If a *PVT* calculation is part of a material balance problem and a volume (or volumetric flow rate) is either given or required for a process stream, label both n (or $\dot{n}$) and V (or $\dot{V}$) on the flowchart and count a density relationship (for solids and liquids) or an equation of state (for gases) as an additional relation in the degree-of-freedom analysis.

PROBLEMS

Note: *Unless otherwise specified, all pressures given in these problems are absolute.*

5.1. A liquid mixture containing 40.0 wt% *n*-octane and the balance *n*-decane flows into a tank mounted on a balance. The mass in kg indicated by the scale is plotted against time. The data fall on a straight line that passes through the points ($t = 3$ min, $m = 150$ kg) and ($t = 10$ min, $m = 250$ kg).

(a) Estimate the volumetric flow rate of the liquid mixture.

(b) What does the empty tank weigh?

5.2. Sulfuric acid is used in the synthesis and processing of countless chemicals and metals and is the electrolyte in common lead-acid batteries. It is used in various strengths, ranging from concentrated (100%) to dilute, so being able to estimate its concentration from a simple measurement of specific gravity is quite useful.

Suppose you prepare a solution that is 30.0 wt% H_2SO_4 in water and intend to confirm the concentration by comparing the specific gravity of the solution to a value obtained from the literature. You carefully add 30.0 g of H_2SO_4 to 70.0 g of water (you know that rapidly adding acid to water or water to concentrated acid can lead to dangerous splatters of liquid) and allow the resulting mixture to equilibrate at 20°C.

SAFETY

(a) From the specific gravities in Table B.1, estimate the volumes of water and sulfuric acid that have been blended, and then estimate the density of the 30.0 wt% sulfuric acid solution, assuming the volumes are additive. Why are the values of pure-component specific gravities different from those in Example 5.1-1, and what is the effect of these differences on the total volume of the mixture?

(b) *Perry's Chemical Engineers' Handbook* (p. 2-112) gives the specific gravity of sulfuric acid as a function of both acid concentration and temperature. The value for 30.0 wt% sulfuric acid at 20°C is given as 1.2185. Estimate the volume of the 30.0 wt% solution prepared as described by the above process.

(c) What volume of 40.0 wt% sulfuric acid at 25°C (SG = 1.2991) must be added to 100.0 g of the 30.0-wt% solution to produce a solution that is 35.0 wt% sulfuric acid?

5.3. When a liquid or a gas occupies a volume, it may be assumed to fill the volume completely. On the other hand, when solid particles occupy a volume, there are always spaces (voids) among the particles. The **porosity** or **void fraction** of a bed of particles is the ratio (void volume)/(total bed volume). The **bulk density** of the solids is the ratio (mass of solids)/(total bed volume), and the **absolute density** of the solids has the usual definition (mass of solids)/(volume of solids).

Suppose 600.0 g of a crushed ore is placed in a graduated cylinder, filling it to the 184 cm^3 level. One hundred cm^3 of water is then added to the cylinder, whereupon the water level is observed to be at the 233.5 cm^3 mark. Calculate the porosity of the dry particle bed, the bulk density of the ore in this bed, and the absolute density of the ore.

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5.4. The volume of a steady-state crystallizer is 85,000 L, and the solids fraction in the unit and the exiting stream is 0.35; that is, there are 0.35 kg of crystals per kg of slurry (the crystal-solution mixture). The density of the solution is 1.1 g/mL and that of the crystals is 2.3 g/mL. The production rate of crystals from the crystallizer is 19.5 kg crystals/min. Estimate the volumetric flow rate of slurry from the crystallizer and the *drawdown time* of the crystallizer (the time it would take to empty the crystallizer if the feed were discontinued).

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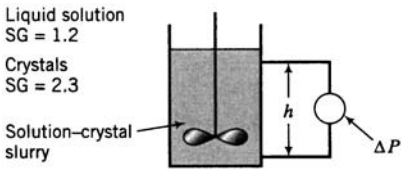
5.5. Two liquid streams are flowing at constant rates into a mixer. One is benzene, which flows at a measured rate of 20.0 L/min, and the other is toluene. The blended mixture enters a storage tank (inner diameter = 5.5 m) equipped with a sight gauge. During an interval in which no liquid leaves the storage tank, the liquid level in the tank is observed to increase by 0.15 meters over a one-hour period. Calculate the flow rate of toluene into the mixer (L/min) and the composition of the tank contents (wt% benzene).

5.6. A slurry contains crystals of copper sulfate pentahydrate [$CuSO_4 \cdot 5H_2O$(s), specific gravity = 2.3] suspended in an aqueous copper sulfate solution (liquid SG = 1.2). A sensitive transducer is used to measure the pressure difference, ΔP(Pa), between two points in the sample container separated by a vertical distance of h meters. The reading is in turn used to determine the mass fraction of crystals in the slurry, x_c(kg crystals/kg slurry).



(a) Derive an expression for the transducer reading, ΔP(Pa), in terms of the overall slurry density, ρ_{sl}(kg/m^3), assuming that the equation used to calculate the pressure head in Chapter 3 ($P = P_0 + \rho gh$) is valid for this two-phase system.

(b) Validate the following expression relating the overall slurry density to the liquid and solid crystal densities (ρ_l and ρ_c) and the mass fraction of crystals in the slurry:

$$\frac{1}{\rho_{sl}} = \frac{x_c}{\rho_c} + \frac{(1 - x_c)}{\rho_l}$$

(*Suggestion:* Insert units for all variables.)

(c) Suppose 175 kg of the slurry is placed in the sample container with $h = 0.200$ m and a transducer reading $\Delta P = 2775$ Pa is obtained. Calculate (i) ρ_{sl}, (ii) x_c, (iii) the total slurry volume, (iv) the mass of crystals in the slurry, (v) the mass of anhydrous copper sulfate ($CuSO_4$ without the water of hydration) in the crystals, (vi) the mass of liquid solution, and (vii) the volume of liquid solution.

(d) Prepare a spreadsheet to generate a calibration curve of x_c versus ΔP for this device. Take as inputs ρ_c(kg/m^3), ρ_l(kg/m^3), and h(m), and calculate ΔP(Pa) for $x_c = 0.0, 0.05, 0.10, \ldots, 0.60$. Run the program for the parameter values in this problem ($\rho_c = 2300$, $\rho_l = 1200$, and $h = 0.200$). Then plot x_c versus ΔP (have the spreadsheet program do it, if possible), and verify that the value of x_c corresponding to $\Delta P = 2775$ Pa on the calibration curve corresponds to the value calculated in Part (c).

(e) Derive the expression in Part (b). Take a basis of 1 kg of slurry [x_c (kg), V_c (m^3) crystals, $(1 - x_c)$(kg), V_l (m^3) liquid], and use the fact that the volumes of the crystals and liquid are additive.

5.7. Magnesium sulfate has a number of uses, some of which are related to the ability of the anhydrate form to remove water from air and others based on the high solubility of the heptahydrate ($MgSO_4 \cdot 7H_2O$) form, also known as Epsom salt. The densities of the anhydrate and heptahydrate crystalline forms are 2.66 and 1.68 g/mL, respectively.

Suppose you wish to form a 20.0 wt% $MgSO_4$ aqueous solution by simply pouring crystals of one of the forms into a tank of water while the temperature is held constant at 30°C. The specific gravity of the 20.0 wt% solution at 30°C is 1.22. Answer the following questions for both forms of the $MgSO_4$ crystals:

(a) What volume of water should be in the tank before crystals are added if the final product is to be 1000 kg of the 20 wt% solution?

(b) Suppose the tank diameter is 0.30 m. What is the height of liquid in the tank before the crystals are added?

(c) What is the height of the water in the tank after addition of the crystals but before they begin to dissolve?

(d) What is the height of liquid in the tank after all the $MgSO_4$ has dissolved?

5.8. Use the ideal-gas equation of state to estimate the molar volume in m^3/mol and the density of air in kg/m^3 at 40°C and a gauge pressure of 3.0 atm.

5.9. One gram-mole of methyl chloride vapor is contained in a vessel at 100°C and 10 atm.

(a) Use the ideal-gas equation of state to estimate the system volume.

(b) Suppose the actual volume of the vessel is 2.8 liters. What percentage error results from assuming ideal-gas behavior?

5.10. The pressure gauge on a 20.0 m^3 tank of nitrogen at 25°C reads 10.0 bar. Estimate the mass of nitrogen in the tank by (a) direct solution of the ideal-gas equation of state and (b) conversion from standard conditions. (See Example 5.2-2.)

5.11. From the standard conditions given in Table 5.2-1, calculate the value of the gas constant R in (a) atm·m^3/(kmol·K) and (b) torr·ft^3/(lb-mole·°R).

SAFETY

*__5.12.__ After being purged with nitrogen, a low-pressure tank used to store flammable liquids is at a total pressure of 0.03 psig.

(a) If the purging process is done in the morning when the tank and its contents are at 55°F, what will be the pressure in the tank when it is at 85°F in the afternoon?

(b) If the maximum design gauge pressure of the tank is 8 inches of water, has the design pressure been exceeded?

(c) Speculate on the purpose of purging the tank with nitrogen.

* Adapted from a problem developed as part of the AIChE Safety and Chemical Engineering Education (SAChE) program, Volume 2 (S-5).

5.13. The volume of a **dry box** (a closed chamber with dry nitrogen flowing through it) is 2.0 m^3. The dry box is maintained at a slight positive gauge pressure of 10 cm H_2O and room temperature (25°C). If the contents of the box are to be replaced every five minutes, calculate the required mass flow rate of nitrogen in g/min by (a) direct solution of the ideal-gas equation of state and (b) conversion from standard conditions. You may assume the gas in the dry box is well mixed.

5.14. A stream of air enters a 7.50-cm ID pipe with a velocity of 60.0 m/s at 27°C and 1.80 bar (gauge). At a point downstream, the air flows through a 5.00 cm ID pipe at 60°C and 1.53 bar (gauge). What is the average velocity of the gas at this point.

5.15. The label has come off a cylinder of gas in your laboratory. You know only that one species of gas is contained in the cylinder, but you do not know whether it is hydrogen, oxygen, or nitrogen. To find out, you evacuate a 5-liter flask, seal it and weigh it, then let gas from the cylinder flow into it until the gauge pressure equals 1.00 atm. The flask is reweighed, and the mass of the added gas is found to be 13.0 g. Room temperature is 27°C, and barometric pressure is 1.00 atm. What is the gas?

5.16. A gas cylinder filled with nitrogen at standard temperature and pressure has a mass of 37.289 g. The same container filled with carbon dioxide at STP has a mass of 37.440 g. When filled with an unknown gas at STP, the container mass is 37.062 g. Calculate the molecular weight of the unknown gas, and then state its probable identity.

5.17. In the Pixar film, *Up*, Carl Fredrickson turns his house into a makeshift airship using helium balloons.
(a) Neglecting the force required to remove the house from its foundation, how many spherical balloons, each having a 9.5-inch diameter and an interior gas pressure of 1.05 atm, would Carl have to tie to his house for it to float? Assume that the house weighs 1.00×10^5 lb_f, and that atmospheric pressure and temperature are 1.0 atm and 25°C.
(b) The original version of this problem assumed that the pressure in the balloons also was 1.0 atm. Why must the balloon pressure be greater than that?

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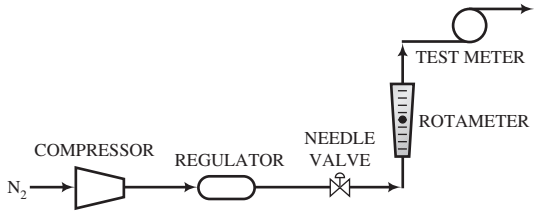
5.18. A nitrogen rotameter is calibrated by feeding N_2 from a compressor through a pressure regulator, a needle valve, the rotameter, and a **dry test meter**, a device that measures the total volume of gas that passes through it. A water manometer is used to measure the gas pressure at the rotameter outlet. A flow rate is set using the needle valve, the rotameter reading, ϕ, is noted, and the change in the dry gas meter reading (ΔV) for a measured running time (Δt) is recorded.



The following calibration data are taken on a day when the temperature is 23°C and barometric pressure is 763 mm Hg.

ϕ	Δt(min)	ΔV(L)
5.0	10.0	1.50
9.0	10.0	2.90
12.0	5.0	2.00

(a) Prepare a calibration chart of ϕ versus $\dot{V}_{std}$, the flow rate in standard cm^3/min equivalent to the actual flow rate at the measurement conditions.
(b) Suppose the rotameter–valve combination is to be used to set the flow rate to 0.010 mol N_2/min. What rotameter reading must be maintained by adjusting the valve?

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5.19. The flow rate required to yield a specified reading on an orifice meter varies inversely as the square root of the fluid density; that is, if a fluid with density ρ_1(g/cm^3) flowing at a rate $\dot{V}_1$ (cm^3/s) yields a meter reading ϕ, then the flow rate of a fluid with density ρ_2 required to yield the same reading is

$$\dot{V}_2 = \dot{V}_1(\rho_1/\rho_2)^{1/2}$$

(a) An orifice meter has been calibrated with nitrogen at 25°C and 758 mm Hg, but it now has methane flowing through it at 50°C and 1800 mm Hg. Applying the nitrogen calibration to the reading indicates that the flow rate is 21 L/min. Estimate the true volumetric flow rate of the methane.

(b) Repeat Part (a) but suppose the stream contains 10.0 mole% CO_2 and 5.0 mole% ethane in addition to methane.

BIOENGINEERING

5.20. A device has been designed to measure the flow rate of carbon dioxide evolved from a fermentation reactor. The reactor is sealed except for a tube that allows the generated CO_2 to bubble through a soap solution and into a vertical glass tube with an internal diameter of 1.2 cm. On leaving the soap solution, the bubbles form thin soap films stretched across the tube and pushed through the tube by the CO_2. Ambient temperature and pressure are 27°C and 755 mm Hg. It takes the films 7.4 s to traverse the 1.2 m between two calibration marks on the tube.

(a) Sketch the apparatus.

(b) What is the rate of generation of CO_2 in mol/min?

(c) A more refined analysis of the system takes into account that the gas leaving the fermentation reactor contains water with a partial pressure of 26.7 mm Hg. Calculate the percentage error in Part (b) using this new information.

5.21. A stream of air (21 mole% O_2, the rest N_2) flowing at a rate of 10.0 kg/h is mixed with a stream of CO_2. The CO_2 enters the mixer at a rate of 20.0 m^3/h at 150°C and 1.5 bar. What is the mole percent of CO_2 in the product stream?

5.22. The lift L (upward force) associated with flow across an airplane wing can be approximated from the expression $L = C\rho u^2 A$, where C is a coefficient that depends on wing characteristics, ρ is the density of air, u is the velocity of air across the wing, and A is the wing area. The maximum weight of a new Boeing 737-900 at takeoff is 187,700 lb_f. Estimate the ratio of takeoff speeds in New Orleans, where the average barometric pressure is 14.69 psia, to that in Mexico City, where the average barometric pressure is 11.2 psia. Assume the temperatures at both locations are the same.

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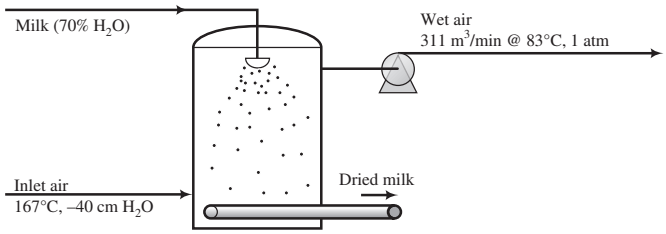
5.23. **Spray drying** is a process in which a liquid containing dissolved or suspended solids is injected into a chamber through a spray nozzle or centrifugal disk atomizer. The resulting mist is contacted with hot air, which evaporates most or all of the liquid, leaving the dried solids to fall to a conveyor belt at the bottom of the chamber.



Powdered milk is produced in a spray dryer 6 m in diameter by 6 m high. Air enters at 167°C and −40 cm H_2O. The milk fed to the atomizer contains 70% water by mass, all of which evaporates. The outlet gas contains 12 mole% water and leaves the chamber at 83°C and 1 atm (absolute) at a rate of 311 m^3/min.

(a) Calculate the production rate of dried milk and the volumetric flow rate of the inlet air. Estimate the upward velocity of air (m/s) at the bottom of the dryer.

(b) Engineers often face the challenge of what to do to a process when demand for a product increases (or decreases). Suppose in the present case production must be doubled. (i) Why is it unlikely that the flow rates of feed and air can simply be increased to achieve the new production rate? (ii) An obvious option is to buy another dryer like the existing one and operate the two in parallel. Give two advantages and two disadvantages of this option. (iii) Still another possibility is to buy a larger dryer to replace the original unit. Give two advantages and two disadvantages of doing so. Estimate the approximate dimensions of the larger unit.

5.24. Many references give the specific gravity of gases with reference to air. For example, the specific gravity of carbon dioxide is 1.53 relative to air at the same temperature and pressure. Show that this value is correct as long as the ideal-gas equation of state applies.

SAFETY

5.25. Lewis[12] describes the hazards of breathing air containing appreciable amounts of an *asphyxiant* (a gas that has no specific toxicity but, when inhaled, excludes oxygen from the lungs). When the mole percent of the asphyxiant in the air reaches 50%, marked symptoms of distress appear, and at 75% death occurs in a matter of minutes.

A small storage room whose dimensions are 2 m × 1.5 m × 3 m contains a number of expensive and dangerous chemicals. To prevent unauthorized entry, the door to the room is always locked and can be opened with a key from either side. A cylinder of liquid carbon dioxide is stored in the room. The valve on the cylinder is faulty and some of the contents have escaped over the weekend. The room temperature is 25°C.

(a) If the concentration of CO_2 reaches the lethal 75 mole% level, what would be the mole percent of O_2?

(b) How much CO_2 (kg) is present in the room when the lethal concentration is reached? Why would more than that amount have to escape from the cylinder for this concentration to be reached?

(c) Describe a set of events that could result in a fatality in the given situation. Suggest at least two measures that would reduce the hazards associated with storage of this seemingly harmless substance.

5.26. A stream of air at 35°C and a gauge pressure of 0.5 atm (Stream 1) flows into a pipe passing through a heater, emerges at 87°C and 0.2 atm (gauge), and splits into two streams. Stream 2 passes out of the system, and Stream 3 goes through another heater and emerges at 180°C and 0.1 atm (gauge). Flowmeters mounted in all three streams show readings of 3120 L/min (Stream 1), 1940 L/min (Stream 2), and 3420 L/min (Stream 3).

(a) Show that the system is not functioning properly.

(b) Speculate on several possible causes of the malfunction, and state how you would check each one.

5.27. A tank in a room at 19°C is initially open to the atmosphere on a day when the barometric pressure is 102 kPa. A block of dry ice (solid CO_2) with a mass of 15.7 kg is dropped into the tank, which is then sealed. The reading on the tank pressure gauge initially rises very quickly, then much more slowly, eventually reaching a value of 3.27 MPa. Assume T_{final} = 19°C.

(a) How many moles of air were in the tank initially? Neglect the volume occupied by CO_2 in the solid state, and assume that a negligible amount of CO_2 escapes prior to the sealing of the tank.

(b) Estimate the percentage error made by neglecting the volume of the block of dry ice placed in the tank. (The specific gravity of solid carbon dioxide is approximately 1.56.)

(c) What is the final density (g/L) of the gas in the tank?

(d) Explain the observed variation of pressure with time. More specifically, what is happening in the tank during the initial rapid pressure increase and during the later slow pressure increase?

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5.28. In **froth flotation**, air is bubbled through an aqueous solution or slurry to which a foaming agent (soap) has been added. The air-soap bubbles carry finely dispersed solids and hydrophobic materials such as grease and oil to the surface where they can be skimmed off in the foam.

An ore-containing slurry is to be processed in a froth flotation tank at a rate of 300 tons/h. The slurry consists of 20.0 wt% solids (the ore, SG = 1.2) and the remainder an aqueous solution with a density close to that of water. Air is *sparged* (blown through a nozzle designed to produce small bubbles) into the slurry at a rate of 40.0 ft^3(STP)/1000 gal of slurry. The entry point of the air is 10 ft below the slurry surface. The tank contents are at 75°F and the barometric pressure is 28.3 inches of Hg. The sparger design is such that the average bubble diameter on entry is 2.0 mm.

(a) What is the volumetric flow rate of the air at its entering conditions?

(b) By what percentage does the average bubble diameter change between the entry point and the slurry surface?

SAFETY

*__5.29.__ Air in industrial plants is subject to contamination by many different chemicals, and companies must monitor ambient levels of hazardous species to be sure they are below limits specified by the National Institute for Occupational Safety and Health (NIOSH). In *personal breathing-zone sampling* (as opposed to area sampling), workers wear devices that periodically collect air samples less than 10 inches away from their noses. Breathing-zone sampling and analysis methods for hundreds of species are set forth in the *NIOSH Manual of Analytical Methods*.[13] For benzene, NIOSH specifies a

[12] R. J. Lewis, *Hazardous Chemicals Desk Reference*, 6th Edition, John Wiley & Sons, New York, 2008, p. 98.

* Adapted from a problem contributed by Ed Burroughs of the National Institute for Occupational Safety and Health.

[13] http://www.cdc.gov/niosh/docs/2003-154/.

recommended exposure limit (REL) of 0.1 ppm *time-weighted average* exposure (TWA), and the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) is 1.0 ppm TWA.

A worker in a petroleum refinery has a personal breathing-zone sampler for benzene clipped to her shirt collar. Following the NIOSH prescription, air is pumped through the sampler at a rate of 0.200 L/min by a small battery-operated pump attached to the worker's belt. The sampler contains an adsorbent that removes essentially all of the benzene from the air passing through it. After several hours, the sampler is removed and sent to a lab for analysis, and the worker puts on a fresh sampler. On a particular day when the temperature is 21°C and barometric pressure is 730 mm Hg, samples are collected during a 4-h period before lunch and a 3.5-h period after lunch. The analytical laboratory reports 0.17 mg of benzene in the first sample and 0.23 mg in the second.

(a) Calculate the average benzene concentration, C_B(ppm), in the worker's breathing zone during each sampling period, where 1 ppm = 1 mol $C_6H_6/10^6$ mol air.

(b) The worker's TWA is the average concentration of benzene in her breathing zone during the eight hours of her shift. It is calculated by multiplying C_B in each sampling period by the time of that period, summing the products over all periods during the shift, and dividing by the total time of the shift. Assume that the worker's exposure during the unsampled 30 minutes was zero, and calculate her TWA.

(c) If the worker's exposure is above the recommended limits, what actions might the company take?

SAFETY

5.30.[14] A few decades ago benzene was thought to be a harmless chemical with a somewhat pleasant odor and was widely used as a cleaning solvent. It has since been found that chronic exposure to benzene can cause health problems such as anemia and possibly leukemia. Benzene has an OSHA *permissible exposure level* (PEL) of 1.0 ppm (part per million on a molar basis, equivalent to a mole fraction of 1.0×10^{-6}) averaged over an 8-hour period.

The safety engineer in a plant wishes to determine whether the benzene concentration in a laboratory exceeds the PEL. One Monday at 9 a.m., 1 p.m., and 5 p.m., she collects samples of room air (33°C, 99 kPa) in evacuated 2-liter stainless steel containers. To collect a sample she opens the container valve, allows room air to enter until the container pressure equals atmospheric pressure, and then charges clean dry helium into the container until the pressure reaches 500 kPa. Next, she takes the containers to an analytical laboratory in which the temperature is 23°C, leaves them there for a day, and then feeds gas from each container to a gas chromatograph (GC) until the pressure in the container is reduced to 400 kPa. In the order in which they were collected, the samples that pass through the GC are found to contain 0.656 μg (microgram), 0.788 μg, and 0.910 μg of benzene, respectively.

(a) What were the concentrations of benzene (ppm on a molar basis) in the original room air at the three collection times? (Assume ideal-gas behavior.) Is the average concentration below the PEL?

(b) Why did the engineer add helium to the container after collecting the room air sample? Why did she wait a day before analyzing the container contents?

(c) Why might a finding that the average benzene concentration is below the PEL not necessarily mean that the laboratory is safe insofar as exposure to benzene is concerned? Give several reasons, including possible sources of error in the sampling and analysis procedure. (Among other things, note the day on which the samples were taken.)

BIOENGINEERING

**5.31.* Bread is typically made by first dissolving preserved yeast (a microscopic biological organism that consumes sugars and emits CO_2 as a waste product) in water, then adding other ingredients, including flour, sugar, fat (usually butter or shortening), and salt. After the ingredients are combined, the dough is "kneaded," or mixed to promote the formation of a protein network from two proteins (gliadin and glutenin)[15] present in wheat flour. This network is what strengthens the dough and allows it to stretch elastically without breaking. The dough is then allowed to rise in a process called "proofing," in which the yeast consumes sugar and releases CO_2, which inflates air

[14] From D. A. Crowl, D. W. Hubbard, and R. M. Felder, *Problem Set: Stoichiometry*, Center for Chemical Process Safety, New York, 1993.

[*] Adapted from a problem contributed by David Silverstein of the University of Kentucky.

[15] These proteins combine with water to form gluten, which gives the dough elasticity and strength. Approximately 6% of the U.S. population exhibits slight sensitivity to gluten, and 1% must adhere to a gluten-free diet to address celiac disease.

pockets in the dough that are subsequently filled with air. Finally the dough is baked; the gas pockets expand due to the temperature rise and evaporation of water, the starches from the flour are dehydrated (dried), and the yeast dies.

A good French bread has an open, porous structure. The pores must be stabilized by the protein network until the bread is dried sufficiently to hold its shape. The bread collapses if the protein network fails prematurely.

(a) Rouille et al.[16] investigated the influence of ingredients and mixing conditions on the quality of frozen French bread dough. Each loaf was initially formed roughly as a cylinder with a mass of 150 g (including essentially no CO_2), a diameter of 2.0 cm, and a length of 25.0 cm. Determine the specific volume of a bread dough proofed for two hours at 28°C from which 1.20 cm^3 gas/min per 100 g dough evolves as bubbles within the dough. State your assumptions.

(b) During proofing, the increases in volume of a series of control loaves were monitored along with the mass of CO_2 evolved. Rupture of the protein network during proofing can be detected when the volume of the dough no longer increases at the same rate as the production of CO_2 from the yeast. Data from one of these experiments are shown in the table below. Plot the specific volumes of CO_2 (per 100 g dough) and dough as a function of time. If the preferred proofing time is such that the dough achieves 70% of its total volume before collapse, specify the proper proofing time for this formula.

(c) The referenced study found that the parameter with the most significant influence on dough quality was mixing time, with an extended mixing time producing a stronger protein network. Why might extended mixing times not be desirable in commercial production of bread?

(d) Suggest causes for the following undesirable bread-baking outcomes: (i) a flat, dense loaf; (ii) an overly large loaf.

(e) Suggest why the period during which the dough rises is called "proofing." Remember that yeast is a biological organism.

t(min)	0	20	40	60	80	100	120	140	160	180	200	220	240
ΔV(cm^3 dough)	0	0	20	60	80	115	155	198	247	305	322	334	336
gas evolved (g CO_2)	0.0	37.2	63.2	68.8	126.3	192.7	234.8	315.8	385.4	515.0	578.1	657.5	745.0

5.32. A balloon 20 m in diameter is filled with helium at a gauge pressure of 2.0 atm. A man is standing in a basket suspended from the bottom of the balloon. A restraining cable attached to the basket keeps the balloon from rising. The balloon (not including the gas it contains), the basket, and the man have a combined mass of 150 kg. The temperature is 24°C that day, and the barometer reads 760 mm Hg.

(a) Calculate the mass (kg) and weight (N) of the helium in the balloon.

(b) How much force is exerted on the balloon by the restraining cable? (*Recall:* The buoyant force on a submerged object equals the weight of the fluid—in this case, the air—displaced by the object. Neglect the volume of the basket and its contents.)

(c) Calculate the initial acceleration of the balloon when the restraining cable is released.

(d) Why does the balloon eventually stop rising? What would you need to know to calculate the altitude at which it stops?

(e) Suppose at its point of suspension in midair the balloon is heated, raising the temperature of the helium. What happens and why?

5.33. The Cookenwythe Gas Company pumps propane gas to the nearby Noxious Chemicals, Inc., polypropylene production plant. The gas is metered at the Noxious plant at 400 m^3/h at 4.7 atm gauge and 30°C. The pressure at the Cookenwythe plant is 8.5 atm gauge, and the temperature is also 30°C. Noxious pays Cookenwythe at the rate of \$0.60/kg C_3H_8.

One dark night Sebastian Goniff, a Noxious engineer who is really a spy for the Rancid Plastics Corporation—Noxious's principal competitor and a bunch of really rotten guys—puts into effect his plan to divert propane from the Cookenwythe–Noxious line into an underground pipe that leads to a

[16] J. Rouille, A. Le Bail, and P. Courcoux, *J. Food Engr.*, **43**(4), 197–203 (2000).

secret Rancid tank-truck loading station in the middle of a nearby abandoned garbage dump. To cover the operation, Goniff obtains a broken pressure gauge that is stuck at 4.7 atm and substitutes it for the gauge at the Noxious plant. He adjusts the gas pressure regulator so that the real gauge pressure is 1.8 atm, instructs his associate in the field via mobile phone to open the Rancid line gradually, and tells him to hold it when the flowmeter at Noxious reads 400 m^3/h. To the unsuspecting Noxious meter reader, the flow rate and pressure would therefore appear to be normal.

The plan goes according to schedule until the associate smells gas, suspects a leak near the valve, and lights a match to see if he can pinpoint the location.

(a) What should the flowmeter read at the Cookenwythe end of the pipeline?
(b) How much does Noxious pay Cookenwythe each month?
(c) What flow rate of propane (kg/h) should the Rancid trucks be prepared to handle?
(d) What happened?

5.34. An ideal-gas mixture contains 35% helium, 20% methane, and 45% nitrogen by volume at 2.00 atm absolute and 90°C. Calculate (a) the partial pressure of each component, (b) the mass fraction of methane, (c) the average molecular weight of the gas, and (d) the density of the gas in kg/m^3.

SAFETY →

5.35. The *lower flammability limit* (LFL) and the *upper flammability limit* (UFL) of propane in air at 1 atm are, respectively, 2.3 mole% C_3H_8 and 9.5 mole% C_3H_8.[17] If the mole percent of propane in a propane–air mixture is between 2.3% and 9.5%, the gas mixture will burn explosively if exposed to a flame or spark; if the percentage is outside these limits, the mixture is safe—a match may burn in it but the flame will not spread. If the percentage of propane is below the LFL, the mixture is said to be too *lean* to ignite; if it is above the UFL, the mixture is too *rich* to ignite.

(a) Which would be safer to release into the atmosphere—a fuel–air mixture that is too lean or too rich to ignite? Explain.
(b) A mixture of propane in air containing 4.03 mole% C_3H_8 is fed to a combustion furnace. If there is a problem in the furnace, the mixture is diluted with a stream of pure air to make sure that it cannot accidentally ignite. If propane enters the furnace at a rate of 150 mol C_3H_8/s in the original fuel–air mixture, what is the minimum molar flow rate of the diluting air?
(c) The actual diluting air molar flow rate is specified to be 130% of the minimum value. Assuming the fuel mixture (4.03 mole% C_3H_8) enters the furnace at the same rate as in Part (b) at 125°C and 131 kPa and the diluting air enters at 25°C and 110 kPa, calculate the ratio (m^3 diluting air)/(m^3 fuel gas) and the mole percent of propane in the diluted mixture.
(d) Give several possible reasons for feeding air at a value greater than the calculated minimum rate.

BIOENGINEERING →

5.36. An adult takes about 12 breaths per minute, inhaling roughly 500 mL of air with each breath. The molar compositions of the inspired and expired gases are as follows:

Species	Inspired Gas (%)	Expired Gas (%)
O_2	20.6	15.1
CO_2	0.0	3.7
N_2	77.4	75.0
H_2O	2.0	6.2

The inspired gas is at 24°C and 1 atm, and the expired gas is at body temperature and pressure (37°C and 1 atm). Nitrogen is not transported into or out of the blood in the lungs, so that $(N_2)_{in} = (N_2)_{out}$.

(a) Calculate the masses of O_2, CO_2, and H_2O transferred from the pulmonary gases to the blood or vice versa (specify which) per minute.
(b) Calculate the volume of air exhaled per milliliter inhaled.
(c) At what rate (g/min) is this individual losing weight by merely breathing?
(d) The rate at which oxygen is transferred from the air in the lungs to the blood is roughly proportional to $\left[(p_{O_2})_{air} - (p_{O_2})_{blood}\right]$, where $(p_{O_2})_{blood}$ is a quantity related to the concentration of oxygen in the blood. Compared to regions where atmospheric pressure is 14.7 psia, what effect

[17] See Problem 4.17 for definitions and source of data.

does the atmospheric pressure in Denver, which is approximately 12.1 psi, have on the transport rate and breathing rate? How does the body adjust to address this condition?

BIOENGINEERING

*5.37. When a human takes a breath, the inhaled air flows through the nostrils and trachea before splitting into two primary bronchial tubes. The primary tubes further split to form smaller tubes, and eventually the air passages end in sacs, called *alveoli*. In the alveoli, oxygen and carbon dioxide are exchanged with the blood. The typical trachea is 2 cm in diameter; the right primary bronchial tube has a diameter of 12 mm and that of the left is 10.0 mm. The average adult takes 12 breaths per minute, with each breath taking in about 0.5 L of air at ambient conditions, which may be taken to be 1.0 atm and 25°C. The velocities of air in the two bronchial tubes are related by the approximation

$$\frac{u_L}{u_R} = \left(\frac{D_R}{D_L}\right)^{0.5}$$

where u_L and u_R are velocities in the left and right bronchial tubes and D_L and D_R are the diameters of the left and right tubes, respectively. The temperature of the air in the bronchial tubes may be assumed to have reached 37°C. Recognizing that half of a breathing cycle is exhaling, estimate the mass flow rates and the velocities of air flowing through the trachea and each of the primary bronchial tubes.

BIOENGINEERING

** 5.38. During your summer vacation, you plan an epic adventure trip to scale Mt. Kilimanjaro in Tanzania. Dehydration is a great danger on such a climb, and it is essential to drink enough water to make up for the amount you lose by breathing.

(a) During your pre-trip physical, your physician measured the average flow rate and composition of the gas you exhaled (expired air) while performing light activity. The results were 11.36 L/min at body temperature (37°C) and 1 atm, 17.08 mole% oxygen, 3.25% carbon dioxide, 6.12 mole% H_2O, and the balance nitrogen. The ambient (inspired) air contained 1.67 mole% water and a negligible amount of carbon dioxide. Calculate the rate of mass lost through the breathing process (kg/day) and the volume of water in liters you would have to drink per day just to replace the water lost in respiration. Consider your lungs to be a continuous steady-state system, with input streams being inspired air and water and CO_2 transferred from the blood and output streams being expired air and O_2 transferred to the blood. Assume no nitrogen is transferred to or from the blood.

(b) You made the trip to Tanzania and completed the climb to Uhuru Peak, the summit of Kilimanjaro, at an altitude of 5895 meters above sea level. The ambient temperature and pressure there averaged −9.4°C and 360 mm Hg, and the air contained 0.46 mole% water. The molar flow rate of your expired air was roughly the same as it had been at sea level, and the expired air contained 14.86% O_2, 3.80% CO_2, and 13.20% H_2O. Calculate the rate of mass lost (g/day) through breathing and water you would have to drink (L/day) just to replace the water lost in respiration.

(c) The equality of the molar flow rates of expired air at sea level and at Uhuru Peak is due to a cancellation of effects, one of which would tend to increase the rate at higher altitudes and the other to decrease it. What are those effects? (*Hint:* Use the ideal-gas equation of state in your solution, and think about how the oxygen concentration at a high altitude would likely affect your breathing rate.)

5.39. As everyone who has used a fireplace knows, when a fire burns in a furnace, a **draft**, or slight vacuum, is induced that causes the hot combustion gases and entrained particulate matter to flow up and out of the stack. The reason is that the hot gas in the stack is less dense than air at ambient temperature, leading to a lower hydrostatic head inside the stack than at the furnace inlet. The **theoretical draft** $D(N/m^2)$ is the difference in these hydrostatic heads; the **actual draft** takes into account pressure losses undergone by the gases flowing in the stack.

Let $T_s(K)$ be the average temperature in a stack of height $L(m)$ and T_a the ambient temperature, and let M_s and M_a be the average molecular weights of the gases inside and outside the stack. Assume that the pressures inside and outside the stack are both equal to atmospheric pressure, $P_a(N/m^2)$. (In fact, the pressure inside the stack is normally a little lower.)

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* This problem is adapted from A. Saterbak, L. V. McIntire, and K.-Y. San, *Bioengineering Fundamentals*, Pearson Prentice Hall, Upper Saddle River, 2007.

** Adapted from a problem contributed by Stephanie Farrell of Rowan University.

(a) Use the ideal-gas equation of state to prove that the theoretical draft is given by the expression

$$D(\text{N/m}^2) = \frac{P_a L g}{R}\left(\frac{M_a}{T_a} - \frac{M_s}{T_s}\right)$$

(b) Suppose the gas in a 53-m stack has an average temperature of 655 K and contains 18 mole% CO_2, 2% O_2, and 80% N_2 on a day when barometric pressure is 755 mm Hg and the outside temperature is 294 K. Calculate the theoretical draft (cm H_2O) induced in the furnace.

BIOENGINEERING

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5.40. A spray-drying operation similar to that described in Problem 5.23 is used by the pharmaceutical industry. Acetaminophen is an *active pharmaceutical ingredient* (API) that can be produced in powdered form by spray drying. A mixture of the API containing 75 wt% water is fed to an atomizer in a dryer where it is brought into contact with hot air that enters the dryer at 220°C and 6.0 bar. All of the water is evaporated. The outlet gas contains 8.1 mole% water and leaves the dryer chamber at 80°C and 1.0 atm absolute with a flow rate of 513.6 m^3/h. Calculate the production rate of powdered API and the volumetric flow rate of inlet air.

SAFETY

5.41. Phosgene (CCl_2O) is a colorless gas that was used as an agent of chemical warfare in World War I. It has the odor of new-mown hay (which is a good warning if you know the smell of new-mown hay).

Pete Brouillette, an innovative chemical engineering student, came up with what he believed was an effective new process that utilized phosgene as a starting material. He immediately set up a reactor and a system for analyzing the reaction mixture with a gas chromatograph. To calibrate the chromatograph (i.e., to determine its response to a known quantity of phosgene), he evacuated a 15.0 cm length of tubing with an outside diameter of 0.635 cm and a wall thickness of 0.559 mm, and then connected the tube to the outlet valve of a cylinder containing pure phosgene. The idea was to crack the valve, fill the tube with phosgene, close the valve, feed the tube contents into the chromatograph, and observe the instrument response.

What Pete hadn't thought about (among other things) was that the phosgene was stored in the cylinder at a pressure high enough for it to be a liquid. When he opened the cylinder valve, the liquid rapidly flowed into the tube and filled it. Now he was stuck with a tube full of liquid phosgene at a pressure the tube was not designed to support. Within a minute he was reminded of a tractor ride his father had once given him through a hayfield, and he knew that the phosgene was leaking. He quickly ran out of the lab, called campus security, and told them that a toxic leak had occurred, that the building had to be evacuated, and the tube removed and disposed of properly. Personnel in air masks shortly appeared, took care of the problem, and then began an investigation that is still continuing.

(a) Show why one of the reasons phosgene was an effective weapon is that it would collect in low spots soldiers often mistakenly entered for protection.

(b) Pete's intention was to let the tube equilibrate at room temperature (23°C) and atmospheric pressure. How many gram-moles of phosgene would have been contained in the sample fed to the chromatograph if his plan had worked?

(c) The laboratory in which Pete was working had a volume of 2200 ft^3, the specific gravity of liquid phosgene is 1.37, and Pete had read somewhere that the maximum "safe" concentration of phosgene in air is 0.1 ppm (0.1×10^{-6} mol CCl_2O/mol air). Would the "safe" concentration have been exceeded if all the liquid phosgene in the tube had evaporated into the room? Even if the limit would not have been exceeded, give several reasons why the lab would still have been unsafe.

(d) List several things Pete did (or failed to do) that made his experiment unnecessarily hazardous.

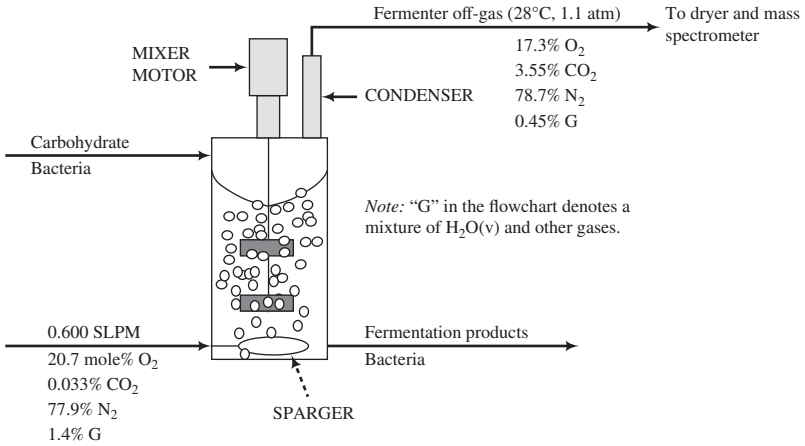
BIOENGINEERING

5.42.* **Fermentation is a biochemical process in which a carbohydrate—such as the sugar glucose—is converted by bacteria or yeast to an organic compound—such as ethanol—and carbon dioxide. The process is best known for its use in making beer, wine, and other alcoholic beverages, but it is also used to produce a wide range of other industrially important chemicals.

The diagram below shows a continuous fermentation process. An aqueous solid–liquid slurry containing a carbohydrate and bacteria enters a stirred tank where it undergoes fermentation. Fermentation products, including species condensed from the off-gas, and bacteria are withdrawn

* Adapted from a problem contributed by Claire Komives of San Jose State University.

from the tank. A mixer with multiple rotating impellers keeps the solids in the tank suspended in the liquid. An air stream enters the fermenter through a sparger (something like an inverted shower head) designed to produce small bubbles that rise through the mixture and remove the CO_2 formed in the reaction. Some of the oxygen in the air fed to the fermenter is consumed by the bacteria. The gas products go through a condenser, which condenses most of the water and returns it to the fermenter, and the uncondensed off-gas goes to a dryer and then to a mass spectrometer, where its composition is determined. The flow rate of the air feed is measured to be 0.600 SLPM (liters per minute at standard temperature and pressure) and the measured compositions of the air and the off-gas are shown on the diagram. The off-gas is at 28°C and 1.1 atm.



(a) Describe in your own words the purpose of this process and the functions of the mixer, the air, and the sparger.

(b) In a small laboratory fermenter, the mass of the broth in the tank is 0.58 kg, and the broth density is 1.05 kg/L. Calculate the carbon dioxide evolution rate (CER) and the oxygen uptake rate (OUR) in mmol/(h·L), where the volume unit in the denominator refers to the volume of broth in the tank. Also, calculate the off-gas volumetric flow rate in L/min.

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5.43. A distillation column is being used to separate methanol and water at atmospheric pressure. The column temperature varies from approximately 65°C at the top to 100°C at the bottom. Liquid enters the top of the column and flows down to the bottom; vapor is generated in a reboiler at the bottom of the column, flows upward, and leaves at the top. The molar flow rate of vapor up the column may be assumed to be constant from top to bottom. The vapor velocity is kept below 5.0 ft/s to keep the vapor from entraining liquid (suspending and carrying away liquid droplets).

(a) Where in the column is the greatest risk of liquid entrainment? Explain your answer.

(b) Assuming that the liquid flowing down the column and the column internals (equipment inside the column) occupy a negligible fraction of the column cross-sectional area, estimate the minimum column diameter if the vapor flow rate is 25.0 lb-mole/min.

(c) Suppose the column is constructed with a diameter 10% greater than that determined in Part (b). What are the vapor velocities at the top and bottom of the column if the vapor molar flow rate in both locations is 25.0 lb-mole/min? How much can the vapor molar flow rate be increased without causing liquid entrainment?

(d) There is a need to increase process throughput, which would require the vapor molar flow rate to be doubled. It has been suggested that increasing the pressure in the column would allow that to be done without risking excessive liquid entrainment. Again applying a vapor velocity limit of 5 ft/s, what would the new pressure be?

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5.44. A fuel gas containing 86% methane, 8% ethane, and 6% propane by volume flows to a furnace at a rate of 1450 m^3/h at 15°C and 150 kPa (gauge), where it is burned with 8% excess air. Calculate the required flow rate of air in SCMH (standard cubic meters per hour).

5.45. Ethane at 25°C and 1.1 atm (abs) flowing at a rate of 100 mol/s is burned with 20% excess oxygen at 175°C and 1.1 atm (abs). The combustion products leave the furnace at 800°C and 1 atm.

(a) What is the volumetric flow rate of oxygen (L/s) fed to the furnace?

(b) What should the volumetric flow rate of the combustion products be? State all assumptions you make.

(c) The volumetric flow rate of the combustion products is measured and found to be different from the value calculated in Part (b). Assuming that no mistakes were made in the calculation, what could be going on that could lead to the discrepancy? Consider assumptions made in the calculations and things that can go wrong in a real system.

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5.46. The flow of air to a gas-fired boiler furnace is controlled by a computer. The fuel gases used in the furnace are mixtures of methane (A), ethane (B), propane (C), *n*-butane (D), and isobutane (E). At periodic intervals the temperature, pressure, and volumetric flow rate of the fuel gas are measured, and voltage signals proportional to the values of these variables are transmitted to the computer. Whenever a new feed gas is used, a sample of the gas is analyzed and the mole fractions of each of the five components are determined and read into the computer. The desired percent excess air is then specified, and the computer calculates the required volumetric flow rate of air and transmits the appropriate signal to a flow-control valve in the air line.

The linear proportionalities between the input and the output signals and the corresponding process variables may be determined from the following calibration data:

Fuel Temperature:	$T = 25.0°C$,	$R_T = 14$
	$T = 35.0°C$,	$R_T = 27$
Fuel Pressure:	$P_{gauge} = 0$ kPa,	$R_P = 0$
	$P_{gauge} = 20.0$ kPa,	$R_P = 6$
Fuel Flow Rate:	$V_f = 0$ m^3/h,	$R_f = 0$
	$V_f = 2.00 \times 10^3$ m^3/h,	$R_f = 10$
Air Flow Rate:	$V_a = 0$ m^3(STP)/h,	$R_a = 0$
	$V_a = 1.0 \times 10^5$ m^3(STP)/h,	$R_a = 25$

(a) Create a spreadsheet or write a program to read in values of R_f, R_T, R_P, the fuel gas component mole fractions x_A, x_B, x_C, x_D, and x_E, and the percent excess air PX, and to calculate the required value of R_A.

(b) Run your program for the following data.

R_f	R_T	R_P	x_A	x_B	x_C	x_D	x_E	PX
7.25	23.1	7.5	0.81	0.08	0.05	0.04	0.02	15%
5.80	7.5	19.3	0.58	0.31	0.06	0.05	0.00	23%
2.45	46.5	15.8	0.00	0.00	0.65	0.25	0.10	33%

BIOENGINEERING

*5.47. The bacteria *acetobacter aceti* convert ethanol to acetic acid in the presence of oxygen according to the reaction

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$$

In a continuous fermentation process, ethanol enters the top of the fermenter at a rate of 145 kg/h, and the air fed to the bottom of the fermenter is 25% in excess of the amount required to consume all of the ethanol. A gas stream containing nitrogen and unreacted oxygen leaves the top of the fermenter, and a liquid stream containing acetic acid, water, and 10% of the entering ethanol leaves the bottom. Assume that none of the ethanol, water, and acetic acid in the reactor is vaporized. The fermenter operates at 30°C, maintains a liquid (SG = 0.95) height of 4.5 m, and is open to the atmosphere (i.e., the pressure at the top of the fermenter is 1 atm).

* This problem is adapted from A. Saterbak, L. V. McIntire, and K.-Y. San, *Bioengineering Fundamentals*, Pearson Prentice Hall, Upper Saddle River, 2007.

(a) What is the volumetric flow rate of air as it enters the bottom of the fermenter? What is the volumetric flow rate of gas leaving the top of the fermenter?

(b) Assume a linear relationship between the fraction of oxygen reacted and the position of gas bubbles rising through the liquid in the fermenter: for example, half of the oxygen reacted is consumed in the bottom half of the fermenter. At the vertical midpoint of the fermenter, the average bubble diameter is 1.5 mm. What is the average bubble diameter at the entry point of the air and as the gas leaves the liquid at the top of the fermenter?

Exploratory Exercises—Research and Discover

(c) What difference does the bubble size make in the design and operation of the fermenter? (*Hint:* What is the surface area of a sphere?)

(d) *Acetobacter aceti* are *gram-negative* bacteria. What does this mean, and why is it important?

5.48. The oxidation of nitric oxide

$$NO + \tfrac{1}{2}\,O_2 \rightleftharpoons NO_2$$

takes place in an isothermal batch reactor. The reactor is charged with a mixture containing 20.0 volume percent NO and the balance air at an initial pressure of 380 kPa (absolute).

(a) Assuming ideal-gas behavior, determine the composition of the mixture (component mole fractions) and the final pressure (kPa) if the conversion of NO is 90%.

(b) Suppose the pressure in the reactor eventually equilibrates (levels out) at 360 kPa. What is the equilibrium percent conversion of NO? Calculate the reaction equilibrium constant at the prevailing temperature, $K_p[(\text{atm})^{-0.5}]$, defined as

$$K_p = \frac{(p_{NO_2})}{(p_{NO})(p_{O_2})^{0.5}}$$

where p_i(atm) is the partial pressure of species i (NO_2, NO, O_2) at equilibrium.

(c) Assuming that K_p depends only on temperature, estimate the final pressure and composition in the reactor if the feed ratio of NO to O_2 and the initial pressure are the same as in Part (a), but the feed to the reactor is pure O_2 instead of air.

(d) Replace the partial pressures in the expression for K_p, and use the result to explain how reactor pressure influences the conversion of NO to NO_2.

5.49. Monochlorobenzene (M) is produced commercially by the direct catalytic chlorination of benzene (B) at 40°C and 120 kPa absolute. In the process, dichlorobenzene (D) is generated as a co-product:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$
$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$$

Liquid and gas streams leave the reactor. The liquid contains 49.2 wt% M, 29.6% D, and the remainder unreacted B. The gas, which is sent to a treatment facility, contains 92%(v/v) HCl and 8% unreacted chlorine. Assume ideal-gas behavior.

(a) What volume of gas leaves the reactor (m^3/kg B fed)?

(b) The pipe through which the gas is to flow is sized so that the gas velocity is no greater than 10 m/s. Derive an expression relating pipe diameter d_p (cm) to benzene feed rate $\dot{m}_{B0}$ (kg B/min).

(c) In 2004, the demand for monochlorobenzene was projected to increase by 6%/year through the year 2007.[18] What factors were contributing to the increased demand when the projection was made?

MATERIALS

5.50.[19] In *chemical vapor deposition* (CVD), a semiconducting or insulating solid material is formed in a reaction between a gaseous species and a species adsorbed on the surface of silicon *wafers* (disks about 10 cm in diameter and 1 mm thick). The coated wafers are subjected to further processing to produce the microelectronic chips in computers and most other electronic devices in use today.

[18] http://www.icis.com/Articles/2005/12/02/570444/chemical-profile-chlorobenzene.html.

[19] Based on a problem in H. S. Fogler, *Elements of Chemical Reaction Engineering*, 2nd Edition, Prentice Hall, Englewood Cliffs, NJ, 1992, p. 323.

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CVD reactor
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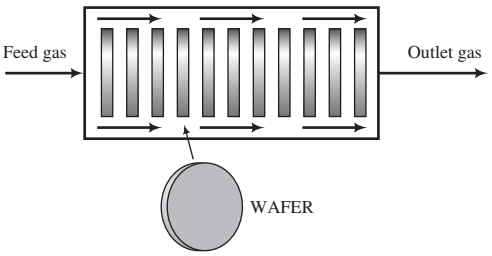
In one such process, silicon dioxide (MW = 60.06, SG = 2.67) is formed in the reaction between gaseous dichlorosilane (DCS) and adsorbed nitrous oxide:

$$SiH_2Cl_2(g) + 2N_2O(ads) \rightarrow SiO_2(s) + 2N_2(g) + 2HCl(g)$$

A mixture of DCS and N_2O flows through a "boat reactor"—a horizontal pipe in which 50 to 100 silicon wafers about 12 cm in diameter and 1 mm thick are set upright along the reactor length, with about 20 mm separation between each wafer. A side view of the reactor is shown below:



The feed gas enters the reactor at a rate of 3.74 SCMM (standard cubic meters per minute) and contains 22.0 mole% DCS and the balance N_2O. In the reactor, the gas flows around the wafers, DCS and N_2O diffuse into the spaces between the wafers, N_2O is adsorbed on the wafer surfaces, and the adsorbed N_2O reacts with gaseous DCS. The silicon dioxide formed remains on the surface, and the nitrogen and hydrogen chloride go into the gas phase and eventually leave the reactor with the unconsumed reactants. The temperature and absolute pressure in the reactor are constant at 900°C and 604 millitorr.

(a) The percentage conversion of DCS at a certain axial position (distance along the length of the reactor) is 60%. Calculate the volumetric flow rate (m^3/min) of gas at this axial position.

(b) The rate of deposition of silicon dioxide per unit area of wafer surface is given by the formula

$$r\left(\frac{\text{mol SiO}_2}{\text{m}^2 \cdot \text{s}}\right) = 3.16 \times 10^{-8} p_{DCS} p_{N_2O}^{0.65}$$

where p_{DCS} and p_{N_2O} are the partial pressures of DCS and N_2O in millitorr. What is r at the axial position in the reactor where the DCS conversion is 60%?

(c) Consider a wafer located at the axial position determined in Part (b). How thick is the silicon dioxide layer on that wafer after two hours of reactor operation, assuming that gas diffusion is rapid enough at the low reactor pressure for the composition of the gas (and hence the component partial pressures) to be uniform over the wafer surface? Express your answer in angstroms, where 1 Å $= 1.0 \times 10^{-10}$ m. (*Hint:* You can calculate the rate of growth of the SiO_2 layer in Å/min from r and properties of SiO_2 given in the problem statement.) Would the thickness be greater or less than this value at an axial position closer to the reactor entrance? Briefly explain your answer.

5.51. A gas turbine power plant receives a shipment of hydrocarbon fuel whose composition is uncertain but may be represented by the expression C_xH_y. The fuel is burned with excess air. An analysis of the product gas gives the following results on a moisture-free basis: 10.5%(v/v) CO_2, 5.3% O_2, and 84.2% N_2.

(a) Determine the molar ratio of hydrogen to carbon in the fuel (r), where $r = y/x$, and the percentage excess air used in the combustion.

(b) What is the air-to-fuel ratio (m^3 air/kg of fuel) if the air is fed to the power plant at 30°C and 98 kPa?

(c) The specific gravity of the fuel (a petroleum product) is 0.85. Estimate the ratio standard cubic feet of gas fed to the turbine per barrel of fuel.

Exploratory Exercise—Research and Discover

(d) What are the issues associated with using oil as a fuel as opposed to natural gas? Consider two factors: (i) the complete composition of typical fuel oils and their resulting emissions, and (ii) the availability and global distribution of the two fuel sources.

5.52. Liquid hydrazine (SG = 0.82) undergoes a family of decomposition reactions that can be represented by the stoichiometric expression

$$3N_2H_4 \rightarrow 6xH_2 + (1 + 2x)N_2 + (4 - 4x)NH_3$$

(a) For what range of values of x is this equation physically meaningful?
(b) Plot the volume of product gas [V(L)] at 600°C and 10.0 bar absolute that would be formed from 50.0 liters of liquid hydrazine as a function of x, covering the range of x values determined in Part (b).
(c) Speculate on what makes hydrazine a good propellant.

SAFETY

5.53.[20] Chemicals are stored in a laboratory with volume $V(\text{m}^3)$. As a consequence of poor laboratory practices, a hazardous species, A, enters the room air (from inside the room) at a constant rate $\dot{m}_A$(g A/h). The room is ventilated with clean air flowing at a constant rate $\dot{V}_{air}(\text{m}^3/\text{h})$. The average concentration of A in the room air builds up until it reaches a steady-state value $C_{A,r}(\text{g A/m}^3)$.

(a) List at least four situations that could lead to A getting into the room air.
(b) Assume that the A is perfectly mixed with the room air and derive the formula

$$\dot{m}_A = \dot{V}_{air} C_A$$

(c) The assumption of perfect mixing is never justified when the enclosed space is a room (as opposed to, say, a stirred reactor). In practice, the concentration of A varies from one point in the room to another: it is relatively high near the point where A enters the room air and relatively low in regions far from that point, including the ventilator outlet duct. If we say that $C_{A,duct} = kC_A$, where $k < 1$ is a nonideal mixing factor (generally between 0.1 and 0.5, with the lowest value corresponding to the poorest mixing), then the equation of Part (b) becomes

$$\dot{m}_A = k\dot{V}_{air} C_A$$

Use this equation and the ideal-gas equation of state to derive the following expression for the average mole fraction of A in the room air:

$$y_A = \frac{\dot{m}_A}{k\dot{V}_{air}} \frac{RT}{M_A P}$$

where M_A is the molecular weight of A.
(d) The *permissible exposure level* (PEL) for styrene ($M = 104.14$) defined by the U.S. Occupational Safety and Health Administration is 50 ppm (molar basis).[21] An open storage tank in a polymerization laboratory contains styrene. The evaporation rate from this tank is estimated to be 9.0 g/h. Room temperature is 20°C. Assuming that the laboratory air is reasonably well mixed (so that $k = 0.5$), calculate the minimum ventilation rate (m^3/h) required to keep the average styrene concentration at or below the PEL. Then give several reasons why working in the laboratory might still be hazardous if the calculated minimum ventilation rate is used.
(e) Would the hazard level in the situation described in Part (d) increase or decrease if the temperature in the room were to increase? (Increase, decrease, no way to tell.) Explain your answer, citing at least two effects of temperature in your explanation.

5.54. Propylene is hydrogenated in a batch reactor:

$$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$$

Equimolar amounts of propylene and hydrogen are fed into the reactor at 25°C and a total absolute pressure of 32.0 atm. The reactor temperature is raised to 235°C and held constant thereafter until the reaction is complete. The propylene conversion at the beginning of the isothermal period is 53.2%. You may assume ideal-gas behavior for this problem, although at the high pressures involved this assumption constitutes an approximation at best.
(a) What is the final reactor pressure?
(b) What is the percentage conversion of propylene when $P = 35.1$ atm?
(c) Construct a graph of pressure versus fractional conversion of propylene covering the isothermal period of operation. Use the graph to confirm the results in Parts (a) and (b). (Suggestion: Use a spreadsheet.)

[20] From D. A. Crowl, D. W. Hubbard, and R. M. Felder, *Problem Set: Stoichiometry*, Center for Chemical Process Safety, New York, 1993.

[21] R. J. Lewis, *Hazardous Chemicals Desk Reference*, 6th Edition, John Wiley & Sons, New York, 2008, p. 1281.

5.55. A natural gas contains 95 wt% CH_4 and the balance C_2H_6. Five hundred cubic meters per hour of this gas at 40°C and 1.1 bar is to be burned with 25% excess air. The air flowmeter is calibrated to read the volumetric flow rate at standard temperature and pressure. What should the meter read (in SCMH) when the flow rate is set to the desired value?

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5.56. A stream of hot dry nitrogen flows through a process unit that contains liquid acetone. A substantial portion of the acetone vaporizes and is carried off by the nitrogen. The combined gases leave the recovery unit at 205°C and 1.1 bar and enter a condenser in which a portion of the acetone is liquefied. The remaining gas leaves the condenser at 10°C and 40 bar. The partial pressure of acetone in the feed to the condenser is 0.100 bar, and that in the effluent gas from the condenser is 0.379 bar. Assume ideal-gas behavior.

(a) Calculate for a basis of 1 m^3 of gas fed to the condenser the mass of acetone condensed (kg) and the volume of gas leaving the condenser (m^3).

(b) Suppose the volumetric flow rate of the gas leaving the condenser is 20.0 m^3/h. Calculate the rate (kg/h) at which acetone is vaporized in the solvent recovery unit.

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5.57. Ammonia is one of the chemical constituents of industrial waste that must be removed in a treatment plant before the waste can safely be discharged into a river or estuary. Ammonia is normally present in wastewater as aqueous ammonium hydroxide ($NH_4^+OH^-$). A two-part process is frequently carried out to accomplish the removal. Lime (CaO) is first added to the wastewater, leading to the reaction

$$CaO + H_2O \rightarrow Ca^{2+} + 2(OH^-)$$

The hydroxide ions produced in this reaction drive the following reaction to the right, resulting in the conversion of ammonium ions to dissolved ammonia:

$$NH_4^+ + OH^- \rightleftharpoons NH_3(g) + H_2O(l)$$

Air is then contacted with the wastewater, stripping out the ammonia.

(a) One million gallons per day of alkaline wastewater containing 0.03 mole NH_3/mole ammonia-free H_2O is fed to a stripping tower that operates at 68°F. Air at 68°F and 21.3 psia contacts the wastewater countercurrently as it passes through the tower. The feed ratio is 300 ft^3 air/gal wastewater, and 93% of the ammonia is stripped from the wastewater. Calculate the volumetric flow rate of the gas leaving the tower and the partial pressure of ammonia in this gas.

(b) Briefly explain in terms a first-year chemistry student could understand how this process works. Include the equilibrium constant for the second reaction in your explanation.

Exploratory Exercise—Research and Discover

(c) This problem is an illustration of challenges associated with addressing undesirable releases into the environment; namely, in developing a process to prevent dumping ammonia into a waterway, the release is instead made to the atmosphere. Suppose you are to write an article for a newspaper on the installation of the process described in the beginning of this problem. Explain why the company is installing the two-part process, and then explain the ultimate fate of the ammonia. Take one of two positions—either that the release is harmless or that it jeopardizes the environment in the vicinity of the plant. Since this is a newspaper article, it cannot be more than 800 words.

5.58. You have purchased a gas cylinder that is supposed to contain 5.0 mole% Cl_2 (±0.1%) and 95% air. The experiments you have been running are not giving reasonable results, and you suspect that the chlorine concentration in the gas cylinder is incorrect.

To check this hypothesis, you bubble gas from the suspicious cylinder through 2.0 L of an aqueous NaOH solution (12.0 wt% NaOH, SG = 1.13) for exactly one hour. The inlet gas is metered at a gauge pressure of 510 mm H_2O and a temperature of 23°C. Prior to entering the vessel, the gas passes through a flowmeter that indicates a flow rate of 2.00 L/min. At the conclusion of the experiment, a sample of the residual NaOH solution is analyzed and the results show that the NaOH content has been reduced by 23%. What is the concentration of Cl_2 in the cylinder gas? (Assume the Cl_2 is completely consumed in the reaction $Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$.)

ALTERNATIVE ENERGY

*5.59. The current global reliance on fossil fuels for heating, transportation, and electric power generation raises concerns regarding the release of CO_2 and CH_4, which are greenhouse gases thought to lead to climate

* Adapted from a problem contributed by W. James Frederick of Table Mountain Consulting.

change, and NO, which contributes to smog. One potential solution to these problems is to produce transportation fuels from renewable biomass.

You have been asked to evaluate a proposed process for converting forest residues to alcohols that may be used as transportation fuels. In the first stage of the process, steam and dry wood from hybrid poplar trees (which grow between five and eight feet a year and can be harvested roughly every five years) are fed to a gasifier in which the biomass is converted to light gases in the following reactions:

$$C + H_2O \rightarrow CO + H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$C + CO_2 \rightarrow 2CO$$
$$C + 2H_2 \rightarrow CH_4$$
$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The effluents from the reactor are a gas stream containing H_2, CO, CO_2, CH_4, and H_2O, and a solid char stream that contains only carbon and hydrogen. The char is discarded and the gases go through additional steps in which the hydrogen and carbon monoxide are converted to mixed alcohols. This problem only concerns the gasifier.

Data:

- Elemental composition of biomass: 51.9 mass% C, 6.3% H, and 41.8% O
- Pressure and temperature of entering steam: 155°C, 4.4 atm
- Feed ratio of steam to biomass: 1.1 kg steam/kg biomass
- Yield and dry-basis composition of product gas: 1.35 kg dry gas/kg biomass at 700°C, 1.2 atm; 50.7 mol% H_2, 23.8% CO, 18.0% CO_2, 7.5% CH_4

(a) Taking a basis of 100 kg of biomass fed, draw and completely label a flowchart for the gasifier incorporating the given data, labeling the volumes of the steam fed and the gases produced. Perform a degree-of-freedom analysis.
(b) Calculate the mass and mass composition of the char and the volumes of the steam feed and product gas streams.
(c) List advantages and possible drawbacks of using biomass rather than petroleum as a fuel source.

5.60. Two humid gas streams are combined in a heated mixing chamber. The first stream contains 23.5 mole% ethane and 76.5% ethylene on a dry basis and enters the chamber at 25°C and 105 kPa at a rate of 125 L/min. The second stream is humid air, which enters at 75°C and 115 kPa at a rate of 355 L/min. The product stream emerges at 65°C and 1.00 atm. A *hygrometer* is used to measure the water contents of the two feed streams and the combined product stream. The calibration curve for the hygrometer is a straight line on a semilog plot of y (mole fraction of water) versus R (hygrometer reading), which passes through the points ($y = 10^{-4}$, $R = 5$) and ($y = 0.2$, $R = 90$). The following readings are recorded.

Hydrocarbon Feed Stream:	$R = 86.0$
Air Feed Stream:	$R = 12.8$

(a) Derive an expression for $y(R)$.
(b) Calculate the volumetric flow rate of the product stream and the molar composition of the product gas on a dry basis.
(c) Calculate the partial pressure of water in the product gas and the hygrometer reading for this stream.

5.61. Most of the concrete used in the construction of buildings, roads, dams, and bridges is made from **Portland cement**, a substance obtained by pulverizing the hard, granular residue (*clinker*) from the roasting of a mixture of clay and limestone and adding other materials to modify the setting properties of the cement and the mechanical properties of the concrete.

The charge to a Portland cement rotary kiln contains 17% of a dried building clay (72 wt% SiO_2, 16% Al_2O_3, 7% Fe_2O_3, 1.7% K_2O, 3.3% Na_2O) and 83% limestone (95 wt% $CaCO_3$, 5% impurities). When the solid temperature reaches about 900°C, *calcination* of the limestone to lime (CaO)

and carbon dioxide occurs. As the temperature continues to rise to about 1450°C, the lime reacts with the minerals in the clay to form such compounds as $3CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$, and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The flow rate of CO_2 from the kiln is 1350 m^3/h at 1000°C and 1 atm. Calculate the feed rates of clay and limestone (kg/h) and the weight percent of Fe_2O_3 in the final cement.

5.62. The ultimate analysis of a No. 4 fuel oil is 86.47 wt% carbon, 11.65% hydrogen, 1.35% sulfur, and the balance noncombustible inerts. This oil is burned in a steam-generating furnace with 15% excess air. The air is preheated to 175°C and enters the furnace at a gauge pressure of 180 mm Hg. The sulfur and hydrogen in the fuel are completely oxidized to SO_2 and H_2O; 5% of the carbon is oxidized to CO, and the balance forms CO_2.

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(a) Calculate the feed ratio (m^3 air)/(kg oil).

(b) Calculate the mole fractions (dry basis) and ppm (parts per million on a wet basis, or moles contained in 10^6 moles of the wet stack gas) of the stack-gas species that might be considered environmental hazards.

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5.63. A stream of liquid *n*-pentane flows at a rate of 50.4 L/min into a heating chamber, where it evaporates into a stream of air 15% in excess of the amount needed to burn the pentane completely. The temperature and gauge pressure of the entering air are 336 K and 208.6 kPa. The pentane-laden heated gas flows into a combustion furnace in which a fraction of the pentane is burned. The product gas, which contains all of the unreacted pentane and no CO, goes to a condenser in which both the water formed in the furnace and the unreacted pentane are liquefied. The uncondensed gas leaves the condenser at 275 K and 1 atm absolute. The liquid condensate is separated into its components, and the flow rate of the pentane is measured and found to be 3.175 kg/min.

(a) Calculate the fractional conversion of pentane achieved in the furnace and the volumetric flow rates (L/min) of the feed air, the gas leaving the condenser, and the liquid condensate before its components are separated.

(b) Sketch the apparatus that could have been used to separate the pentane and water in the condensate. *Hint:* Remember that pentane is a hydrocarbon and recall what is said about oil (hydrocarbons) and water.

BIOENGINEERING

*__5.64.__ Alka-Seltzer® is an over-the-counter medicine used to treat acid indigestion and heartburn. The active pharmaceutical ingredients (API) in each Alka-Seltzer® tablet are aspirin (325 mg), citric acid (1.000×10^3 mg), and sodium bicarbonate (1.916×10^3 mg). For a single dose, two Alka-Seltzer® tablets are dissolved in 4.0 fluid ounces of water (1.0 fluid ounce = 29.57 mL), causing the following reaction:

$$\underbrace{C_6H_8O_7(aq)}_{\text{citric acid}} + \underbrace{3NaHCO_3(aq)}_{\substack{\text{sodium}\\ \text{bicarbonate}}} \rightarrow 3H_2O(l) + 3CO_2(g) + \underbrace{Na_3C_6H_5O_7(aq)}_{\text{sodium citrate}}$$

(a) What volume of CO_2 gas (mL) at 25°C and 1 atm would be produced by a normal dose of Alka-Seltzer®? Assume ideal-gas behavior and that the reaction goes to completion.

(b) You wake up feeling miserable before your material-and-energy-balances final exam, but you know you can't miss it. You grab some Alka-Seltzer® and an 11-ounce bottle of water. You drink just enough water to leave 4.0 fluid ounces in the bottle (you've had lots of practice with this). Then you drop in the two tablets, screw the cap tightly onto the bottle, and rush out the door. Calculate the pressure inside the bottle, assuming the temperature remains constant at 25°C and neglecting the volume of the tablets.

(c) How reasonable are the assumptions of ideal-gas behavior in Parts (a) and (b)?

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5.65. Hydrogen sulfide has the distinctive unpleasant odor associated with rotten eggs, and it is poisonous. It often must be removed from crude natural gas and is therefore a product of refining natural gas. In such instances, the *Claus process* provides a means of converting H_2S to elemental sulfur.

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater, (2010). "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses–Part I," http://pharmahub.org/resources/360.

Consider a feed stream to a Claus process that consists of 10.0 mole% H_2S and 90.0% CO_2. One-third of the stream is sent to a furnace where the H_2S is burned completely with a stoichiometric amount of air fed at 1 atm and 25°C. The combustion reaction is

$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O$$

The product gases from this reaction are then mixed with the remaining two-thirds of the feed stream and sent to a reactor in which the following reaction goes to completion:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The gases leave the reactor at 10.0 m^3/min, 320°C, and 205 kPa absolute. Assuming ideal-gas behavior, determine the feed rate of air in kmol/min. Provide a single balanced chemical equation reflecting the overall process stoichiometry. How much sulfur is produced in kg/min?

5.66. The quantity of sulfuric acid used globally places it among the most plentiful of all commodity chemicals. In the modern chemical industry, synthesis of most sulfuric acid utilizes elemental sulfur as a feedstock. However, an alternative and historically important source of sulfuric acid was the conversion of an ore containing iron pyrites (FeS_2) to sulfur oxides by roasting (burning) the ore with air. The following reactions occurred in an oven:

$$2FeS_2(s) + \tfrac{11}{2}O_2(g) \rightarrow Fe_2O_3(s) + 4SO_2(g) \quad \textbf{(1)}$$

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \quad \textbf{(2)}$$

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The gases leaving the oven were fed to a catalytic converter in which most of the remaining SO_2 produced was oxidized to SO_3. Finally, the gas leaving the converter was sent to an absorption column where the SO_3 was taken up by water to produce sulfuric acid (H_2SO_4).

(a) The ore fed to the oven was 90.0 wt% FeS_2, and the remaining material may be considered inert. Dry air was fed to the oven in 30.0% excess of the amount required to oxidize all of the sulfur in the ore to SO_3. Eighty-five percent of the FeS_2 was oxidized, and 60% of the SO_2 produced was oxidized to SO_3. Leaving the roaster were (i) a gas stream containing SO_2, SO_3, O_2, and N_2 and (ii) a solid stream containing unconverted pyrites, ferric oxide (Fe_2O_3), and the inert material. Calculate the required feed rate of air in standard cubic meters per 100 kg of ore fed to the process. Also determine the molar composition and volume (SCM/100 kg ore) of the gas leaving the oven.

(b) The gas leaving the oven entered the catalytic converter, which operated at 1.0 atm. Reaction (2) proceeded to equilibrium, at which point the component partial pressures are related by the expression

$$K_P(T) = \frac{p_{SO_3}}{p_{SO_2}p_{O_2}^{0.5}}$$

The gases were first heated to 600°C to accelerate the rate of reaction, and then cooled to 400°C to enhance SO_2 conversion. The equilibrium constant K_P at these two temperatures is 9.53 $atm^{0.5}$ and 397 $atm^{0.5}$, respectively. Calculate the equilibrium fractional conversions of SO_2 at these two temperatures.

(c) Estimate the production rate of sulfuric acid in kg/kg ore if all of the SO_3 leaving the converter was transformed to sulfuric acid. What would this value be if all the sulfur in the ore had been converted?

Exploratory Exercises—Research and Discover

(d) Two of the important factors affecting the utility of a chemical reaction are the maximum extent of the reaction and the rate at which the reaction occurs. Consider these two factors and explain the steps in the converter in which the gas was heated first and then cooled.

(e) Why has elemental sulfur come to be the dominant feedstock in sulfuric acid manufacturing?

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5.67. A small power plant produces 500 MW of electricity through combustion of coal that has the following composition on a dry basis: 76.2 wt% carbon, 5.6% hydrogen, 3.5% sulfur, 7.5% oxygen, and the remainder ash. The coal contains 4.0 wt% water. The feed rate of coal is 183 tons/h, and it is burned with 15% excess air at 1 atm, 80°F, and 30.0% relative humidity.

(a) Estimate the volumetric flow rate (ft^3/min) of air drawn into the furnace.
(b) Effluent gases are discharged from the furnace at 625°F and 1 atm. Estimate the molar (lb-mole/min) and volumetric (ft^3/min) flow rates of gas leaving the furnace.
(c) Injection of dry limestone ($CaCO_3$) into the furnace is being considered as a means of reducing the SO_2 emitted from the plant. The technology calls for SO_2 to react with limestone:

$$CaCO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$$

Unfortunately, the process is expected to remove only 75% of the SO_2 in the effluent gases, even though the limestone is fed at a rate 2.5 times the stoichiometric amount. What is the required feed rate of limestone? Since some of the SO_2 is removed from the furnace effluent [in contrast to Part (b)], recalculate the molar flow rate and composition of the effluent from the furnace.
(d) The gas leaving the furnace passes through an electrostatic precipitator, where particulates from ash and limestone are removed, and then enters a stack (chimney) for release to the atmosphere. What is the gas velocity at a point in the stack where the stack diameter is 25 ft and the temperature is 300°F? Does the gas discharged from the stack meet the new Environmental Protection Agency standard that emissions from such power plants contain less than 75 parts of SO_2 per billion?

5.68. You have been assigned the task of measuring the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ as a function of temperature. To do so, you evacuate a rigid 2-liter vessel equipped with a pressure gauge, fill the vessel with a mixture of NO_2 and N_2O_4, and then heat it to $T_0 = 473$ K, a temperature at which you know the gas is essentially pure NO_2. The gauge pressure at this point is noted to be 1.00 atm. You then decrease the temperature in stages, recording the equilibrium gauge pressure at each temperature. The data are as follows:

T(K)	473	350	335	315	300
P_{gauge}(atm)	1.00	0.272	0.111	−0.097	−0.224
	↑				
	Pure NO_2				

(a) How many gram-moles of NO_2 are in the vessel at 473 K?
(b) The reaction equilibrium constant is

$$K_p = p_{NO_2}^2 / p_{N_2O_4}$$

where p_{NO_2} and $p_{N_2O_4}$ are the equilibrium partial pressures of NO_2 and N_2O_4. Derive an equation or a series of equations for calculating K_p(atm) from specified values of T and P_{gauge}. (*Suggestion:* Begin by defining n_1 and n_2 as the moles of NO_2 and N_2O_4 present at equilibrium.) Then calculate K_p for $T = 350$ K, 335 K, 315 K, and 300 K. (*Suggestion:* Use a spreadsheet.)
(c) The equilibrium constant should vary with temperature according to the relation

$$K_p = ae^{-b/T}$$

Use the results of Part (b) to determine the values of a and b by curve-fitting. [*Suggestion:* Use the spreadsheet from Part (b).]

5.69. The demand for a particular hydrogenated compound, S, is 5.00 kmol/h. This chemical is synthesized in the gas-phase reaction

$$A + H_2 \rightleftharpoons S$$

The reaction equilibrium constant at the reactor operating temperature is

$$K_p = \frac{p_S}{p_A p_{H_2}} = 0.1 \text{ atm}^{-1}$$

The fresh feed to the process is a mixture of A and hydrogen that is mixed with a recycle stream consisting of the same two species. The resulting mixture, which contains 3 kmol A/kmol H_2, is fed to the reactor, which operates at an absolute pressure of 10.0 atm. The reaction products are in equilibrium. The effluent from the reactor is sent to a separation unit that recovers all of the S in

essentially pure form. The A and hydrogen leaving the separation unit form the recycle that is mixed with fresh feed to the process. Calculate the feed rates of hydrogen and A to the process in kmol/h and the recycle stream flow rate in SCMH (standard cubic meters per hour).

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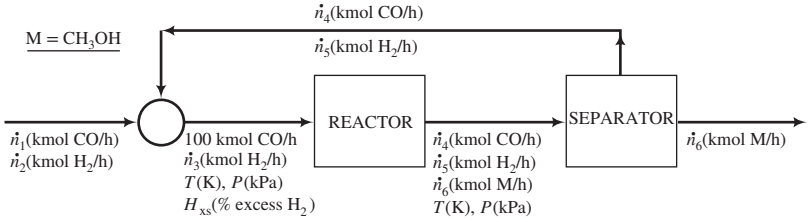
5.70. Methanol is synthesized from carbon monoxide and hydrogen in the reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

A process flowchart is shown below.



The fresh feed to the system, which contains only CO and H_2, is blended with a recycle stream containing the same species. The combined stream is heated and compressed to a temperature T(K) and a pressure P(kPa) and fed to the reactor. The percentage excess hydrogen in this stream is H_{xs}. The reactor effluent—also at T and P—goes to a separation unit where essentially all of the methanol produced in the reactor is condensed and removed as product. The unreacted CO and H_2 constitute the recycle stream blended with the fresh feed.

Provided that the reaction temperature (and hence the rate of reaction) is high enough and the ideal-gas equation of state is a reasonable approximation at the reactor outlet conditions (a questionable assumption), the ratio

$$K_{pc} = \frac{p_{CH_3OH}}{p_{CO}p_{H_2}^2}$$

approaches the equilibrium value, which is given by the expression

$$K_p(\mathrm{T}) = 1.390 \times 10^{-4} \exp\left(21.225 + \frac{9143.6}{T} - 7.492 \ln T + 4.076 \times 10^{-3} T - 7.161 \times 10^{-8} T^2\right)$$

In these equations, p_i is the partial pressure of species i in kilopascals ($i = CH_3OH, CO, H_2$) and T is in Kelvin.

(a) Suppose $P = 5000$ kPa, $T = 500$ K, and the percentage excess of hydrogen in the feed to the reactor (H_{xs}) = 5.0%. Calculate $\dot{n}_4$, $\dot{n}_5$, and $\dot{n}_6$, the component flow rates (kmol/h) in the reactor effluent. [*Suggestion:* Use the known value of H_{xs}, atomic balances around the reactor, and the equilibrium relationship, $K_{pc} = K_p(T)$, to write four equations in the four variables $\dot{n}_3$ to $\dot{n}_6$; use algebra to eliminate all but $\dot{n}_6$; and use Goal Seek or Solver in Excel to solve the remaining nonlinear equation for $\dot{n}_6$.] Then calculate component fresh feed rates ($\dot{n}_1$ and $\dot{n}_2$) and the flow rate (SCMH) of the recycle stream.

(b) Prepare a spreadsheet to perform the calculations of Part (a) for the same basis of calculation (100 kmol CO/h fed to the reactor) and different specified values of P(kPa), T(K), and H_{xs}(%). The spreadsheet should have the following columns:

A. P(kPa)
B. T(K)
C. H_{xs}(%)
D. $K_p(T) \times 10^8$. (The given function of T multiplied by 10^8. When $T = 500$ K, the value in this column should be 91.113.)
E. K_pP^2
F. $\dot{n}_3$. The rate (kmol/h) at which H_2 enters the reactor.
G. $\dot{n}_4$. The rate (kmol/h) at which CO leaves the reactor.
H. $\dot{n}_5$. The rate (kmol/h) at which H_2 leaves the reactor.
I. $\dot{n}_6$. The rate (kmol/h) at which methanol leaves the reactor.

J. $\dot{n}_{tot}$. The total molar flow rate (kmol/h) of the reactor effluent.
K. $K_{pc} \times 10^8$. The ratio $y_M/(y_{CO}y_{H_2}^2)$ multiplied by 10^8. When the correct solution has been attained, this value should equal the one in Column E.
L. $K_pP^2 - K_{pc}P^2$. Column E–Column K, which equals zero for the correct solution.
M. $\dot{n}_1$. The molar flow rate (kmol/h) of CO in the fresh feed.
N. $\dot{n}_2$. The molar flow rate (kmol/h) of H_2 in the fresh feed.
O. $\dot{V}_{rec}$(SCMH). The flow rate of the recycle stream in m^3(STP)/h.

When the correct formulas have been entered, the value in Column I should be varied until the value in Column L equals 0.

Run the program for the following nine conditions (three of which are the same):

- $T = 500$ K, $H_{xs} = 5\%$, and $P = 1000$ kPa, 5000 kPa, and 10,000 kPa.
- $P = 5000$ kPa, $H_{xs} = 5\%$, and $T = 400$ K, 500 K, and 600 K.
- $T = 500$ K, $P = 5000$ kPa, and $H_{xs} = 0\%$, 5%, and 10%.

Summarize the effects of reactor pressure, reactor temperature, and excess hydrogen on the yield of methanol (kmol M produced per 100 kmol CO fed to the reactor).

(c) You should find that the methanol yield increases with increasing pressure and decreasing temperature. What cost is associated with increasing the pressure?

(d) Why might the yield be much lower than the calculated value if the temperature is too low?

(e) If you actually ran the reaction at the given conditions and analyzed the reactor effluent, why might the spreadsheet values in Columns F–M be significantly different from the measured values of these quantities? (Give several reasons, including assumptions made in obtaining the spreadsheet values.)

Equipment Encyclopedia
batch reactor
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5.71. One gram-mole each of CO_2, O_2, and N_2 are fed to a batch reactor and heated to 3000 K and 5.0 atm. The two reactions given here proceed to equilibrium (also shown are the equilibrium constants at 3000 K).

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2$$

$$K_1 = (p_{CO}p_{O_2}^{1/2})/p_{CO_2} = 0.3272 \text{ atm}^{1/2}$$

$$\tfrac{1}{2}O_2 + \tfrac{1}{2}N_2 \rightleftharpoons NO$$

$$K_2 = p_{NO}/(p_{O_2}p_{N_2})^{1/2} = 0.1222$$

Calculate the equilibrium composition (component mole fractions) of the reactor contents. [*Suggestion:* Express K_1 and K_2 in terms of the extents of the two reactions, ξ_1 and ξ_2. (See Section 4.6d.) Then use Excel's Solver to obtain values for ξ_1 and ξ_2, and use the results to determine the equilibrium mole fractions.]

MATERIALS

5.72. Terephthalic acid (TPA), a raw material in the manufacture of polyester fiber, film, and soft drink bottles, is synthesized from *p*-xylene (PX) in the process shown below.

$$\underbrace{C_8H_{10}}_{\text{PX}} + 3O_2 \rightarrow \underbrace{C_8H_6O_4}_{\text{TPA}} + 2H_2O$$

Equipment Encyclopedia
reactor, condenser, filter
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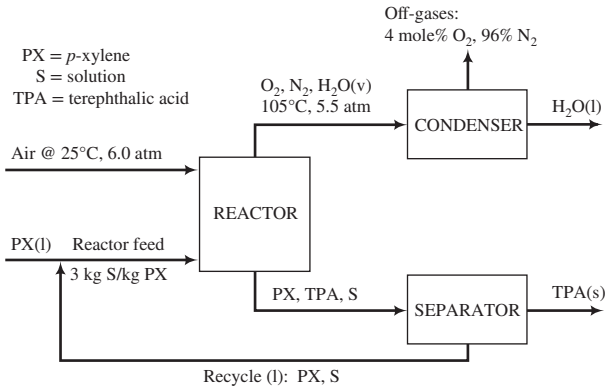


A fresh feed of pure liquid PX combines with a recycle stream containing PX and a solution (S) of a catalyst (a cobalt salt) in a solvent (methanol). The combined stream, which contains S and PX in a 3:1 mass ratio, is fed to a reactor in which 90% of the PX is converted to TPA. A stream of air at 25°C and 6.0 atm absolute is also fed to the reactor. The air bubbles through the liquid and the reaction given above takes place under the influence of the catalyst. A liquid stream containing unreacted PX, dissolved TPA, and all the S that entered the reactor goes to a separator in which solid TPA crystals are formed and filtered out of the solution. The filtrate, which contains all the S and PX leaving the reactor, is the recycle stream. A gas stream containing unreacted oxygen, nitrogen, and the water formed in the reaction leaves the reactor at 105°C and 5.5 atm absolute and goes through a condenser in which essentially all the water is condensed. The uncondensed gas contains 4.0 mole% O_2.

(a) Taking 100 kmol TPA produced/h as a basis of calculation, draw and label a flowchart for the process.
(b) What is the required fresh feed rate (kmol PX/h)?
(c) What are the volumetric flow rates (m^3/h) of the air fed to the reactor, the gas leaving the reactor, and the liquid water leaving the condenser? Assume ideal-gas behavior for the two gas streams.
(d) What is the mass flow rate (kg/h) of the recycle stream?
(e) Briefly explain in your own words the functions of the oxygen, nitrogen, catalyst, and solvent in the process.
(f) In the actual process, the liquid condensate stream contains both water and PX. Speculate on what might be done with the latter stream to improve the economics of the process. [*Hint:* Note that PX is expensive, and recall what is said about oil (hydrocarbons) and water.]

5.73. *Steam reforming* is an important technology for converting refined natural gas, which we take here to be methane, into a synthesis gas that can be used to produce a variety of other chemical compounds. For example, consider a reformer to which natural gas and steam are fed in a ratio of 3.5 moles of steam per mole of methane. The reformer operates at 18 atm, and the reaction products leave the reformer in chemical equilibrium at 875°C. The steam reforming reaction is

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \textbf{(1)}$$

and the water–gas shift reaction also occurs in the reformer.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \textbf{(2)}$$

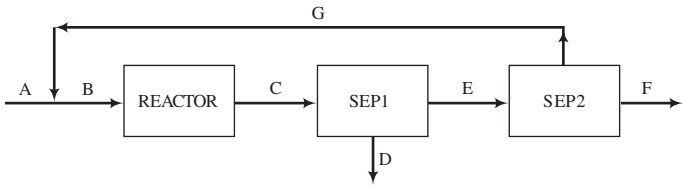
The equilibrium constants for these two reactions are given by the expressions

$$K_R = \frac{y_{CO} y_{H_2}^3}{y_{CH_4} y_{H_2O}} P^2$$

$$K_{WG} = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}}$$

At 875°C, $K_R = 872.9$ atm^2 and $K_{WG} = 0.2482$. The process is to produce 100.0 kmol/h of hydrogen. Calculate the feed rates (kmol/h) of methane and steam and the volumetric flow rate (m^3/min) of gas leaving the reformer.

5.74. A flowchart of a methanol synthesis process is shown below.



The following specifications apply to the labeled streams and process units:

A. Fresh feed—a mixture of CO, H_2, N_2, and CO_2
B. Feed to the reactor—30.0 mole% CO, 63.0% H_2, 2.0% N_2, and 5.0% CO_2.

Reactor. Two reactions occur and proceed to equilibrium at 200°C and 4925 kPa absolute:

$$CO + 2H_2 \rightleftharpoons CH_3OH(M), \qquad (K_p)_1 = \frac{p_M}{p_{CO}p_{H_2}^2} = 3.49 \times 10^{-6}\ \text{kPa}^{-2}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad (K_p)_2 = \frac{p_M p_{H_2O}}{p_{CO_2}p_{H_2}^3} = 5.19 \times 10^{-8}\ \text{kPa}^{-2}$$

C. Reactor effluent—contains all feed and product species at the reactor temperature and pressure. Species partial pressures satisfy the two given equations.
Sep1. Condenses all methanol and water in reactor effluent.
D. Liquid methanol and water. (These species will be separated by distillation in a unit not shown.)
E. Gas containing N_2 and unreacted CO, H_2, and CO_2.
Sep2. Multiple-unit separation process.
F. All of the nitrogen and some of the hydrogen in Stream E.
G. Recycle stream—CO, CO_2, and 10% of the hydrogen fed to Sep2.

(a) Taking 100 kmol/h of Stream B as a basis of calculation, calculate the molar flow rates (kmol/h) and molar compositions of the remaining six labeled streams.
(b) The process is to be used to provide 237 kmol/h of methanol. Scale up the flowchart of Part (a) to calculate the required fresh feed rate (SCMH), the flow rate of the reactor effluent (SCMH), and the actual volumetric flow rate of the reactor effluent (m^3/h), assuming ideal-gas behavior.
(c) Use the rule of thumb for a diatomic gas given in Equation 5.2-3 to test the ideal-gas assumption at the reactor outlet. If the assumption is invalid, which of the values calculated in Part (b) are in error?

5.75. The measured volumetric flow rate of ethane at 10.0 atm absolute and 35°C is 1.00×10^3 L/h. Using an estimated value of the second virial coefficient in the truncated virial equation (Equation 5.3-2), (a) calculate $\hat{V}$ (L/mol); (b) estimate the compressibility factor, z; and (c) determine the mass flow rate of ethane in kg/h.

5.76. Determining the value of newly located natural gas sites involves estimating the gas composition, quantity, and ease of access. For example, one report described a find of 2 trillion cubic feet of natural gas that is significantly offshore, in 20 feet of water, and at a drilled depth of 25,000 ft. (In North America and the OPEC countries, reported volumes are determined at 14.73 psia and 60°F.) The pressure in this find is estimated to be 750 atm, and the gas is 94 mole% methane, 3.5% ethane, and the balance CO_2.
(a) Estimate the total lb-moles of gas in the find.
(b) Use the compressibility-factor equation of state to estimate the specific volume (ft^3/lb-mole) in the well. The temperature of such wells can vary depending upon a number of factors; for the purposes of this problem, assume that it is 200°C.

5.77. Methanol is to be delivered to a process unit at a rate of 15.0 kmol/h by a stream that is 30.0 mole% methanol and 70.0 mole% propane. Estimate the volumetric flow rate of this stream at 10.0 atm and 100.0°C using the truncated virial equation and the following mixing rule:

$$B_{\text{mix}} = \sum_i \sum_j y_i y_j B_{ij}$$

where the virial coefficients for the pure species, B_{ii} and B_{jj}, are determined from Equation 5.3-6 and $B_{ij} \approx 0.5(B_{ii} + B_{jj})$.

5.78. The van der Waals equation of state (Equation 5.3-7) is to be used to estimate the specific molar volume $\hat{V}$(L/mol) of air at specified values of T(K) and P(atm). The van der Waals constants for air are $a = 1.33\ \text{atm}\cdot\text{L}^2/\text{mol}^2$ and $b = 0.0366$ L/mol.
(a) Show why the van der Waals equation is classified as a cubic equation of state by expressing it in the form

$$f(\hat{V}) = c_3\hat{V}^3 + c_2\hat{V}^2 + c_1\hat{V} + c_0 = 0$$

where the coefficients c_3, c_2, c_1, and c_0 involve P, R, T, a, and b. Calculate the values of these coefficients for air at 223 K and 50.0 atm. (Include the units when giving the values.)

(b) What would the value of $\hat{V}$ be if the ideal-gas equation of state were used for the calculation? Use this value as an initial estimate of $\hat{V}$ for air at 223 K and 50.0 atm and solve the van der Waals equation using Goal Seek or Solver in Excel. What percentage error results from the use of the ideal-gas equation of state, taking the van der Waals estimate to be correct?

(c) Set up a spreadsheet to carry out the calculations of Part (b) for air at 223 K and several pressures. The spreadsheet should appear as follows:

T(K)	P(atm)	c3	c2	c1	c0	V(ideal) (L/mol)	V(L/mol)	f(V)	% error
223	1.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
223	10.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
223	50.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
223	100.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
223	200.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

The polynomial expression for $\hat{V}(f = c_3\hat{V}^3 + c_2\hat{V}^2 + \cdots)$ should be entered in the $f(V)$ column, and the value in the V column should be determined using Goal Seek or Solver in Excel.

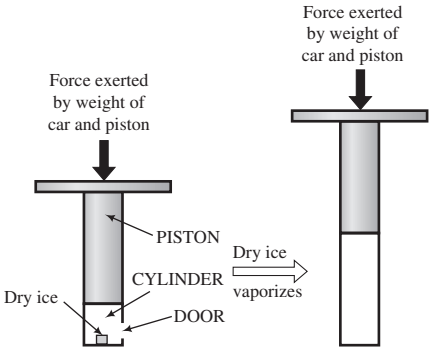
5.79. A 5.0-m^3 tank is charged with 75.0 kg of propane gas at 25°C. Use the SRK equation of state to estimate the pressure in the tank; then calculate the percentage error that would result from the use of the ideal-gas equation of state for the calculation.

5.80. The absolute pressure within a 35.0-liter gas cylinder should not exceed 51.0 atm. Suppose the cylinder contains 50.0 mol of a gas. Use the SRK equation of state to calculate the maximum permissible cylinder temperature if the gas is (a) carbon dioxide and (b) argon. Finally, calculate the values that would be predicted by the ideal-gas equation of state.

5.81. A stream of oxygen at −65°C and 8.3 atm flows at a rate of 250 kg/h. Use the SRK equation of state to estimate the volumetric flow rate of this stream. (See Example 5.3-3.)

5.82. An innovative engineer has invented a device to replace the hydraulic jacks found at many service stations. A movable piston with a diameter of 0.15 m is fitted into a cylinder. Cars are raised by opening a small door near the base of the cylinder, inserting a block of dry ice (solid CO_2), closing and sealing the door, and vaporizing the dry ice by applying just enough heat to raise the cylinder contents to ambient temperature (25°C). The car is subsequently lowered by opening a valve and venting the cylinder gas.

The device is tested by raising a car a vertical distance of 1.5 m. The combined mass of the piston and the car is 5500 kg. Before the piston rises, the cylinder contains 0.030 m^3 of CO_2 at ambient temperature and pressure (1 atm). Neglect the volume of the dry ice.



(a) Calculate the pressure in the cylinder when the piston comes to rest at the desired elevation.

(b) How much dry ice (kg) must be placed in the cylinder? Use the SRK equation of state for this calculation.

(c) Outline how you would calculate the minimum piston diameter required for any elevation of the car to occur if the calculated amount of dry ice is added. (Just give formulas and describe the procedure you would follow—no numerical calculations are required.)

SAFETY

5.83.[22] An oxygen tank with a volume of 2.5 ft^3 is kept in a room at 50°F. An engineer has used the ideal-gas equation of state to determine that if the tank is first evacuated and then charged with 35.3 lb_m of pure oxygen, its rated *maximum allowable working pressure* (MAWP) will be attained. Operation at pressures above this value is considered unsafe.

(a) What is the maximum allowable working pressure (psig) of the tank?

(b) You suspect that at the conditions of the fully charged tank, ideal-gas behavior may not be a good assumption. Use the SRK equation of state to obtain a better estimate of the maximum mass of oxygen that may be charged into the tank. Did the ideal-gas assumption lead to a conservative estimate (on the safe side) or a nonconservative estimate of the amount of oxygen that could be charged?

(c) Suppose the tank is charged and ruptures before the amount of oxygen calculated in Part (b) enters it. (It should have been able to withstand pressures up to four times the MAWP.) Think of at least five possible explanations for the failure of the tank below its rated pressure limit.

5.84. Using the SRK equation of state (or any other cubic equation of state) to determine a specific volume from a specified temperature and pressure requires a trial-and-error calculation. Three computer-based approaches to solving this problem may be used: (1) spreadsheet programs such as Excel's Solver; (2) mathematical packages such as Mathcad, Mathematica, Matlab, and Polymath; and (3) programming languages such as Fortran and C^{++}. The goal of this problem is to use the first two approaches to determine $\hat{V}$(L/mol) for CO_2 at (i) 200 K and 6.8 atm; (ii) 250 K and 12.3 atm; (iii) 300 K and 6.8 atm; (iv) 300 K and 21.5 atm; and (v) 300 K and 50.0 atm.

(a) Starting with Equation 5.3-8, derive the following equivalent expression for the SRK equation of state:

$$f(\hat{V}) = P\hat{V}^3 - RT\hat{V}^2 + (a\alpha - b^2P - bRT)\hat{V} - a\alpha b = 0$$

(b) Prepare a spreadsheet to take as inputs a species identifier (such as CO_2), the critical temperature, critical pressure, Pitzer acentric factor, and the temperatures and pressures for which $\hat{V}$ is to be calculated, and to calculate $\hat{V}$ using Equations 5.3-8 to 5.3-13 for each of the specified conditions. The spreadsheet should have the following structure:

PROBLEM 5.84—SRK EQUATION SPREADSHEET					
Species	CO2				
Tc(K)	304.2				
Pc(atm)	72.9				
w	0.225				
a	*.****				
b	*.****				
m	*.****				
T(K)	P(atm)	alpha	V(ideal)	V(SRK)	f(V)
200	6.8	1.3370	2.4135	2.1125	*.**E–**
250	12.3	*.****	*.****	*.****	*.**E–**
300	6.8	*.****	*.****	*.****	*.**E–**
300	21.5	*.****	*.****	*.****	*.**E–**
300	50.0	*.****	*.****	*.****	*.**E–**

[22] From D. A. Crowl, D. W. Hubbard, and R. M. Felder, *Problem Set: Stoichiometry*, Center for Chemical Process Safety, New York, 1993.

Single digits should appear in place of each asterisk shown on the table. Formulas should be entered into the row for 200 K and 6.8 atm and copied into the next four rows. The Goal Seek tool should be used to determine each $\hat{V}$(SRK), starting with the ideal-gas value and varying the cell value to make $f(\hat{V})$ as close as possible to zero.

(c) Use a root-finding procedure in a mathematical software package to determine $\hat{V}$ for each of the five conditions.

5.85. Use the generalized compressibility chart to estimate z for (a) nitrogen at 40°C and 40 MPa and (b) helium at −200°C and 350 atm. (Don't forget Newton's corrections.)

Exploratory Exercise—Research and Discover

As you examine Figures 5.4-1 through 5.4-4, you will notice curvature of plots of z vs. P_r at constant T_r. For example, consider the curve for $T_r = 1.1$: As P_r approaches 0, z approaches 1.0, but as P_r increases, z decreases to a minimum around $P_r = 2$, and then begins to increase, surpassing 1.0 at around $P_r = 9$. After you have thought through your observations, establish criteria for ideal-gas behavior involving T_r and P_r. Translate these criteria for nitrogen and helium by recommending limitations on temperature and pressure for use of the ideal-gas equation of state. Speculate about the molecular interactions leading to transitions from $z < 1.0$ to $z > 1.0$.

5.86. A certain gas has a molecular weight of 30.0, a critical temperature of 310 K, and a critical pressure of 4.5 MPa. Calculate the density in kg/m^3 of this gas at 465 K and 9.0 MPa (a) if the gas is ideal and (b) if the gas obeys the law of corresponding states.

5.87. One hundred pounds of CO_2 is contained in a 10.0-ft^3 tank. The safety limit of the tank is 1600 psig. Use the compressibility chart to estimate the maximum permissible gas temperature.

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5.88. A stream of oxygen enters a compressor at 298 K and 1.00 atm at a rate of 127 m^3/h and is compressed to 358 K and 1000 atm. Estimate the volumetric flow rate of compressed O_2, using the compressibility-factor equation of state.

BIOENGINEERING

5.89. *Oxygen therapy* uses various devices to provide oxygen to patients having difficulty getting sufficient amounts from air through normal breathing. Among the devices is a *nasal cannula*, which transports oxygen through small plastic tubes from a supply tank to prongs placed in the nostril. Consider a specific configuration in which the supply tank, whose volume is 6.0 ft^3, is filled to a pressure of 2100 psig at a temperature of 85°F. The patient is in an environment where the ambient temperature is 40°F. When the cannula is put into use, the pressure in the tank begins to decrease as oxygen flows at 10–15 L/min through a tube and the cannula into the nostrils.

(a) Estimate the original mass of oxygen in the tank using the compressibility-factor equation of state.

(b) What is the initial pressure when the temperature is 40°F? How much oxygen remains in the tank when application of the ideal-gas equation of state produces a result that is within 3% of that predicted by the compressibility-factor equation of state (i.e., when $0.97 \le z \le 1.03$)?

(c) How long will it take for the gauge on the tank to read 50 psig, assuming an average flow rate of 12.5 L/min?

ALTERNATIVE ENERGY

5.90.* A **fuel cell is an electrochemical device that reacts hydrogen with oxygen from the air to produce water and DC electricity. A proposed application is replacement of the gasoline-fueled internal combustion engine in an automobile with a 100 kW fuel cell.

You are on a summer internship with a gas supplier planning to transport hydrogen to service stations for use in cars powered by fuel cells. The hydrogen is to be transported in *tube trailers*, each of which has 10 tubes of length 10.5 m and diameter 0.56 m. Hydrogen in the tubes at 2600 psig and an average temperature of 298 K is discharged at service stations to a final pressure of 55 psig. Refueling each fuel-cell-powered automobile is estimated to require 4.0 kg of hydrogen.

(a) You and your office-mate—an intern from a different university—have been asked to estimate the number of automobiles that can be refueled by one tube-trailer load of hydrogen. He does a very quick calculation and comes up with a value of 95 cars. Speculate how he did it and provide support for your speculation. What was his mistake?

* Adapted from a problem contributed by Jason M. Keith of Mississippi State University.

(b) Do the calculation using the SRK equation of state. Instead of using Eqs. 5.3-11 and 5.3-13 for the parameter α, use the following correlation developed specifically for hydrogen:[23] $\alpha = 1.202 \exp(-0.3228 T_r)$.
(c) Do the calculation using the law of corresponding states.
(d) In which of the three estimates would you have the greatest confidence, and why?

BIOENGINEERING

ENVIRONMENTAL

*__5.91.__ In a **metered-dose inhaler** (MDI), such as those used for asthma medication, medicine is delivered by a compressed-gas propellant. (The device is similar in concept to a can of spray paint.) When the inhaler is activated, a fixed amount of the medicine suspended in the propellant is expelled from the mouthpiece and inhaled. In the past, chlorofluorocarbons (CFCs) were used as propellants; however, because of their reactivity with the Earth's ozone layer, they have been replaced by hydrofluorocarbons (HFCs), which do not react with ozone.

In one brand of inhalers, the original CFC propellant has been replaced by HFC 227ea (C_3HF_7, heptafluoropropane). The volume of the inhaler propellant reservoir is 1.00×10^2 mL, and the propellant is charged into the reservoir to a gauge pressure of 4.443 atm at 23°C. An online search for properties of HFC 227ea yields the information that the critical temperature and pressure of the substance are 374.83K and 28.74 atm, and the acentric factor is $\omega = 0.180$.

(a) Assuming ideal-gas behavior, estimate the mass(g) of propellant in the fully charged inhaler.
(b) Someone in the manufacturer's Quality Control Division has raised a concern that assuming ideal-gas behavior might be inaccurate at the charging pressure. Use the SRK equation of state to recalculate the moles of propellant at the specified conditions. What percentage error resulted from using the ideal-gas assumption?

__5.92.__ The concentration of oxygen in a 5000-liter tank containing air at 1 atm is to be reduced by pressure purging prior to charging a fuel into the tank. The tank is charged with nitrogen up to a high pressure and then vented back down to atmospheric pressure. The process is repeated as many times as required to bring the oxygen concentration below 10 ppm (i.e., to bring the mole fraction of O_2 below 10.0×10^{-6}). Assume that the temperature is 25°C at the beginning and end of each charging cycle.

When doing *PVT* calculations in Parts (b) and (c), use the generalized compressibility chart if possible for the fully charged tank and assume that the tank contains pure nitrogen.

(a) Speculate on why the tank is being purged.
(b) Estimate the gauge pressure (atm) to which the tank must be charged if the purge is to be done in one charge–vent cycle. Then estimate the mass of nitrogen (kg) used in the process. (For this part, if you can't find the tank condition on the compressibility chart, assume ideal-gas behavior and state whether the resulting estimate of the pressure is too high or too low.)
(c) Suppose nitrogen at 700 kPa gauge is used for the charging. Calculate the number of charge–vent cycles required and the total mass of nitrogen used.
(d) Use your results to explain why multiple cycles at a lower gas pressure are preferable to a single cycle. What is a probable disadvantage of multiple cycles?

__5.93.__ A stream of propane at an average temperature $T = 566$°R and absolute pressure $P = 6.8$ atm flows from a hydrocarbon processing plant to a nearby customer's production facility. A technician at the processing plant periodically measures the volumetric flow rate of the stream, $\dot{V}(\text{ft}^3/\text{h})$, and reports the value to the billing office. The customer is charged for the propane at a rate

$$C(\$/\text{h}) = 60.4 \frac{SP\dot{V}}{T}$$

where $S(\$/\text{lb}_\text{m})$ is the unit cost of propane.

(a) Derive the given formula, assuming ideal-gas behavior.
(b) One day a recent chemical engineering graduate working at the processing plant comes across the formula used to calculate the charge for the propane stream. She figures out the basis of the

[23] M. S. Graboski and T. E. Daubert, *Industrial and Engineering Chemistry Process Design and Development*, **18**, 300 (1979).

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater (2010). "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses–Part I," http://pharmahub.org/resources/360.

formula and uses the generalized compressibility chart to derive an improved formula. What is her result? Calculate the percentage by which the plant was overcharging or undercharging the customer (state which) when it used the old formula.

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5.94. Approximately 150 SCFM (standard cubic feet per minute) of nitrogen is required by a process facility. As shown in the diagram below, plans call for supplying the facility from a tank of liquid nitrogen (SG = 0.81) at its normal boiling point (−350°F) and 1 atm. Nitrogen vapor leaves the tank and is compressed and heated to obtain the desired conditions, 150°F and 600 psia.

(a) Using the generalized compressibility charts, determine the volumetric flow rate of nitrogen delivered from the heater.

(b) What would the required minimum tank size be if deliveries are made to the site no more frequently than every two weeks?

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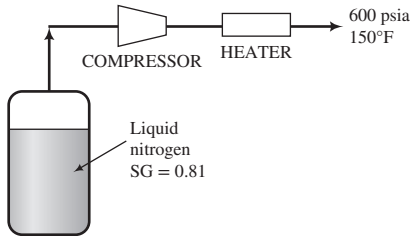

SAFETY

5.95. A 150-liter cylinder of carbon monoxide is stored in a 30.7-m^3 room. The pressure gauge on the tank reads 2500 psi when the tank is delivered. Sixty hours later the gauge reads 2245 psi. The *Threshold Limit Value Ceiling* (TLV-C) molar concentration of CO—that is, the concentration considered unsafe for even instantaneous human exposure—is 200 ppm (200×10^{-6} mol CO/mol room air).[24] The temperature of the room is constant at 27°C.

(a) The decrease in pressure is a source of concern, but it may have resulted from a reduction in the temperature of the tank as it was transported from the loading dock to the air-conditioned laboratory. Without assuming that the gas behaves ideally, show that this is unlikely to be the case.

(b) Having determined that the pressure decrease must be due to a leak, estimate the average leak rate (mol CO/h), again without assuming that the gas behaves ideally.

(c) Calculate t_{min}(h), the minimum time from delivery at which the average concentration of CO in the room could have reached the TLV-C concentration. Explain why the actual time to reach this concentration would be greater.

(d) Why could it be disastrous to enter the room at any time without wearing proper personal protective equipment, even at a time $t < t_{min}$? (Think of at least three possible reasons.)

5.96. A gas consists of 20.0 mole% CH_4, 30.0% C_2H_6, and 50.0% C_2H_4. Ten kilograms of this gas is to be compressed to a pressure of 200 bar at 90°C. Using Kay's rule, estimate the final volume of the gas.

5.97. A 30-liter cylinder is evacuated and filled with 5.00 kg of a gas containing 10.0 mole% N_2O and the balance N_2. The gas temperature is 24°C. Use the compressibility chart to solve the following problems.

(a) What is the gauge pressure (atm) of the cylinder gas after the tank is filled?

(b) A fire breaks out in the plant where the cylinder is kept, and the cylinder valve ruptures when the gas gauge pressure reaches 273 atm. What was the gas temperature (°C) at the moment before the rupture occurred?

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boiler, turbine

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5.98. The product gas from a coal gasification plant consists of 60.0 mole% CO and the balance H_2; it leaves the plant at 150°C and 135 bar absolute. The gas expands through a turbine, and the outlet gas from the turbine is fed to a boiler furnace at 100°C and 1 atm at a rate of 425 m^3/min. Estimate the inlet flow rate to the turbine in ft^3/min, using Kay's rule. What percentage error would result from the use of the ideal-gas equation of state at the turbine inlet?

5.99. Methanol is produced by reacting carbon monoxide and hydrogen at 644 K over a $ZnO–Cr_2O_3$ catalyst. A mixture of CO and H_2 in a ratio 2 mol H_2/mol CO is compressed and fed to the catalyst bed at 644 K and 34.5 MPa absolute. A single-pass conversion of 25% is obtained. The **space velocity**, or ratio of the

[24] R. J. Lewis, *Hazardous Chemicals Desk Reference*, 6th Edition, John Wiley & Sons, New York, 2008, p. 287.

volumetric flow rate of the feed gas to the volume of the catalyst bed, is (25,000 m^3/h)/(1 m^3 catalyst bed). The product gases are passed through a condenser, in which the methanol is liquefied.

(a) You are designing a reactor to produce 54.5 kmol CH_3OH/h. Estimate (i) the volumetric flow rate that the compressor must be capable of delivering if no gases are recycled, and (ii) the required volume of the catalyst bed. (Use Kay's rule for pressure–volume calculations.)

(b) If (as is done in practice) the gases from the condenser are recycled to the reactor, the compressor is then required to deliver only the fresh feed. What volumetric flow rate must it deliver assuming that the methanol produced is completely recovered in the condenser? (In practice it is not; moreover, a purge stream must be taken off to prevent the buildup of impurities in the system.)

5.100. A process stream flowing at 35 kmol/h contains 15 mole% hydrogen and the remainder 1-butene. The stream pressure is 10.0 atm absolute, the temperature is 50°C, and the velocity is 150 m/min. Determine the diameter (in cm) of the pipe transporting this stream, using Kay's rule in your calculations.

5.101. A gas mixture consisting of 15.0 mole% methane, 60.0% ethylene, and 25.0% ethane is compressed to a pressure of 175 bar at 90°C. It flows through a process line in which the velocity should be no greater than 10 m/s. What flow rate (kmol/min) of the mixture can be handled by a 2-cm internal diameter pipe?

*__5.102.__ A system has been devised to store acetonitrile safely at high pressures and temperatures. The acetonitrile is contained in a 0.2-ft^3 tank maintained at 4500 psia and 550°F. This tank is placed inside a second tank whose volume, excluding the volume of the first tank, is 2 ft^3. Nitrogen at 10.0 atm and 550°F is contained in the second tank. Use the compressibility chart to estimate the final system pressure (atm) if the first tank ruptures and the final system temperature is 550°F. The critical temperature and pressure of acetonitrile are 548 K and 47.7 atm, respectively.

5.103. A solid carbohydrate ($C_aH_bO_c$) with a specific gravity of 1.59 is placed in a 1.000-liter combustion chamber. The chamber is evacuated and then charged with pure oxygen. Complete combustion of the carbohydrate takes place. A sample of the product gas is cooled to condense all the water formed in the combustion, and the remaining gas is analyzed by gas chromatography. The following data are obtained:

Mass of Carbohydrate Charged:	3.42 g
Chamber Conditions Prior to Combustion:	$T = 26.8°C, P = 499.9$ kPa
Chamber Conditions Following Combustion:	$T = 483.4°C, P = 1950.0$ kPa
Product Gas Analysis:	38.7 mole% CO_2, 25.8% O_2, 35.5% H_2O

Assume (i) none of the carbohydrate is lost when the chamber is evacuated and (ii) the vapor pressure of the carbohydrate at 27°C is negligible. Do *not* neglect the volume of the carbohydrate and do not assume ideal-gas behavior.

(a) Determine at least two possible molecular formulas for the carbohydrate (i.e., sets of integer values of a, b, and c) consistent with the given data.

(b) If the molecular weight of the carbohydrate is independently determined to be in the range 300 to 350, what is its molecular formula?

5.104. The **adiabatic flame temperature** of a fuel is the temperature achieved if the fuel is burned completely in a perfectly insulated container.

You are performing an experiment to measure the adiabatic flame temperature of cyclopentane. You put 10.0 mL of liquid cyclopentane into a well-insulated steel vessel with a volume of 11.2 L and pressurize the vessel with air to achieve a stoichiometric ratio of oxygen to cyclopentane. You then ignite the fuel, planning to record the final temperature. The vessel is equipped with a thermocouple and a pressure gauge.

(a) If room temperature is 27°C and barometric pressure is 1.00 bar, what should the pressure gauge read prior to ignition?

(b) Suppose you discover after the combustion has been carried out that the thermocouple is not functioning properly. Use the final pressure gauge reading of 75.3 bar to estimate the adiabatic flame temperature of cyclopentane. Do not assume ideal-gas behavior.

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* This problem is adapted from *Professional Engineering Examinations*, Volume 1, National Council of Engineering Examiners, 1972, p. 347.

CHAPTER 6

Multiphase Systems

Virtually all commercial chemical processes involve operations in which material is transferred from one phase (gas, liquid, or solid) into another. These multiphase operations include all **phase-change operations** on a single species, such as freezing, melting, evaporation, and condensation, and most **separation** and **purification** processes, which are designed to separate components of mixtures from one another. Most separations are accomplished by feeding a mixture of species A and B into a two-phase system under conditions such that most of the A remains in its original phase and most of the B transfers into a second phase. The two phases then either separate themselves under the influence of gravity—as when gases and liquids or two immiscible liquids separate—or are separated with the aid of a device such as a filter or a skimmer.

Here are some examples of multiphase separation processes.

- ***Brewing a cup of coffee.*** Hot liquid water and solid ground coffee beans are contacted. Soluble constituents of the beans are transferred from the solid phase to a liquid solution (coffee), and then the residual solids (grounds) are filtered from the solution. The operation of dissolving a component of a solid phase in a liquid solvent is referred to as **leaching**.

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Equipment Encyclopedia
absorption column, scrubber
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- ***Removal of sulfur dioxide from a gas stream.*** If a fuel that contains sulfur is burned, the product gas contains sulfur dioxide. If the gas is released directly into the atmosphere, the SO_2 combines with atmospheric oxygen to form sulfur trioxide. The SO_3 in turn combines with water vapor in the atmosphere to form sulfuric acid (H_2SO_4), which eventually precipitates as *acid rain*. To prevent this occurrence, the combustion product gas is contacted with a liquid solution in an **absorption** or **scrubbing** process. The SO_2 dissolves in the solvent and the clean gas that remains is released to the atmosphere.

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distillation column
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- ***Recovery of methanol from an aqueous solution.*** After being used as a reactant or solvent, methanol (methyl alcohol) often leaves a process in an aqueous mixture (combined with water). Methanol has a higher *vapor pressure* than water, meaning that it has a greater tendency to vaporize when a mixture of the two species is heated. The separation process **distillation** exploits this difference by partially vaporizing a liquid mixture, yielding a vapor relatively rich in methanol and a residual liquid relatively rich in water. Subsequent partial condensations and vaporizations can be used to recover almost pure methanol. The recovered methanol can be recycled and reused, resulting in considerable savings in raw material costs.

- ***Separation of paraffinic and aromatic hydrocarbons.*** Liquid paraffinic hydrocarbons (such as pentane, hexane, and heptane) and liquid aromatic hydrocarbons (such as benzene, toluene, and xylene) have different chemical characteristics; for example, the paraffinic compounds are almost completely immiscible with liquid ethylene glycol, while aromatic compounds and ethylene glycol readily form homogeneous liquid mixtures. Paraffinics and aromatics may therefore be separated from each other by blending a mixture of the two with ethylene glycol. When allowed to settle, the aromatic compounds distribute between a paraffin-rich phase and a glycol phase. This process is known as **liquid extraction**. Subsequent processing separates the aromatics from the glycol, recovering the glycol for recycle and reuse in the extraction process.

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extractors
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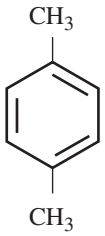
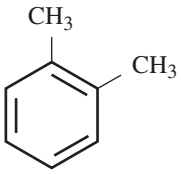
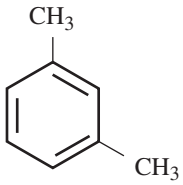
- ***Separation of an isomeric mixture.*** A mixture containing three isomers of xylene (C_8H_{10}) is one of the product streams recovered from crude oil.



para-xylene



ortho-xylene



meta-xylene

Para-xylene (*p*-xylene) is separated from its two isomers and used as a raw material in the synthesis of *p*-teraphthalic acid, which in turn is used in the production of several important polymers. Since the three isomers have similar volatilities, their separation by distillation is difficult and uneconomical.

Two alternative commercial operations have been developed to perform the separation. In one, a mixture of the isomers is contacted with a *molecular sieve* that has pores large enough to accommodate *para*-xylene but not the *meta* or *ortho* isomers. This operation is referred to as **adsorption**. In another process, the difference in freezing points of the three isomers (*para*-xylene freezes at 13.3°C, *ortho* at −25.2°C, and *meta* at −47.9°C) forms the basis of a **crystallization** operation. The mixture is cooled to a temperature at which *para* crystallizes and can then be separated physically from the remaining *ortho* and *meta* liquid.

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adsorption column, crystallizer
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When a species transfers from one phase to another, the transfer rate generally decreases with time until the second phase is **saturated** with the species, holding as much as it can at the prevailing process conditions. When the concentrations of all species in each phase no longer change with time, the phases are said to be in **phase equilibrium**. The effectiveness of any of the separation processes described above depends both on how species are distributed between the phases at equilibrium and on the rate at which the system approaches equilibrium from its initial state.

Test Yourself

(Answers, p. 657)

Suggest a method that might be suitable to achieve each of the following separations.

1. Separate crude oil into volatile low molecular weight compounds (naphthas used to make gasoline and light chemicals), intermediate molecular weight compounds (used for heating oils), and nonvolatile high molecular weight compounds (used for lubricating oils).
2. Remove water from an aqueous slurry of bleached wood pulp.
3. Obtain fresh water from seawater.
4. Separate NH_3 from a mixture of N_2, H_2, and NH_3. Ammonia is highly soluble in water; also, it condenses at −33.4°C.
5. Concentrate O_2 for breathing-impaired patients.

CREATIVITY EXERCISE

A gas contains two species, A and B. Suggest as many methods as you can think of, both conventional and unconventional, for separating the two species. Briefly indicate the conditions required for each method to work. (For example, find a third substance, C, that reacts with A to form a solid, and introduce C into the mixture. A will react and the product will deposit as a solid, leaving B in the gas phase.)

6.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

Equipment Encyclopedia
distillation column, scrubber, liquid extractor, crystallizer, adsorption column

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- Explain in your own words the terms *separation process, distillation, absorption, scrubbing, liquid extraction, crystallization, adsorption,* and *leaching*. (What are they and how do they work?)
- Sketch a phase diagram (P versus T) for a single species and label the regions (solid, liquid, vapor, gas). Explain the difference between a vapor and a gas. Use the phase diagram to define (a) the vapor pressure at a specified temperature, (b) the boiling point at a specified pressure, (c) the normal boiling point, (d) the melting point at a specified pressure, (e) the sublimation point at a specified pressure, (f) the triple point, and (g) the critical temperature and pressure. Explain how the melting and boiling point temperatures of water vary with pressure and how P and T vary (increase, decrease, or remain constant) as a specified path on the diagram is followed.
- Estimate the vapor pressure of a pure substance at a specified temperature or the boiling point at a specified pressure using (a) the Antoine equation, (b) the Clausius–Clapeyron equation and known vapor pressures at two specified temperatures, or (c) Table B.3 for water.
- Distinguish between intensive and extensive variables, giving examples of each. Use the Gibbs phase rule to determine the number of degrees of freedom for a multicomponent multiphase system at equilibrium, and state the meaning of the value you calculate in terms of the system's intensive variables. Specify a feasible set of intensive variables that will enable the remaining intensive variables to be calculated.
- In the context of a system containing a single condensable species and noncondensable gases, explain in your own words the terms *saturated vapor, superheated vapor, dew point, degrees of superheat,* and *relative saturation*. Explain the following statement from a weather report in terms a first-year engineering student could understand: *The temperature is 75°F, barometric pressure is 29.87 inches of mercury and falling, the relative humidity is 50%, and the dew point is 54°F*.
- Given an equilibrated gas–liquid system containing only a single condensable component A, a correlation for $p_A^*(T)$, and any two of the variables y_A (mole fraction of A in the gas phase), temperature, and total pressure, calculate the third variable using Raoult's law.
- Given a mixture of a single condensable vapor, A, and one or more noncondensable gases, a correlation for $p_A^*(T)$, and any two of the variables y_A (mole fraction of A), temperature, total pressure, dew point, degrees of superheat, and relative, molal, absolute, and percentage saturation (or humidity if A is water and the noncondensable gas is air), use Raoult's law for a single condensable species to calculate the remaining variables.
- For a process system that involves a single condensable component, a vapor-liquid phase change, and specified or requested values of feed or product stream properties (temperature, pressure, dew point, relative saturation or humidity, degrees of superheat, etc.), draw and label the flowchart, carry out the degree-of-freedom analysis, and perform the required calculations.
- Explain the meaning of the term *ideal solution behavior* applied to a liquid mixture of volatile species. Write and clearly explain the equations for Raoult's law and Henry's law, state the conditions for which each relationship is most likely to be accurate, and apply the appropriate one to determine any of the variables T, P, x_A, or y_A (temperature, pressure, and mole fractions of A in the liquid and gas phases) from given values of the other three.
- Explain in your own words the terms *bubble point, boiling point*, and *dew point* of a mixture of condensable species, and the difference between *vaporization* and *boiling*. Use Raoult's law to determine (a) the bubble-point temperature (or pressure) of a liquid mixture of known

composition at a specified pressure (or temperature) and the composition of the first bubble that forms; (b) the dew-point temperature (or pressure) of a vapor mixture of known composition at a specified pressure (or temperature) and the composition of the first liquid drop that forms; (c) whether a mixture of known amount (moles) and composition (component mole fractions) at a given temperature and pressure is a liquid, a gas, or a gas–liquid mixture and, if the latter, the amounts and compositions of each phase; and (d) the boiling point temperature of a liquid mixture of known composition at a specified total pressure.

- Use a *Txy* or *Pxy* diagram to determine bubble- and dew-point temperatures and pressures, compositions and relative amounts of each phase in a two-phase mixture, and the effects of varying temperature and pressure on bubble points, dew points, and phase amounts and compositions. Outline how the diagrams are constructed for mixtures of components that obey Raoult's law.
- For a process system that involves liquid and gas streams in equilibrium and vapor–liquid equilibrium relations for all distributed components, draw and label the flowchart, carry out the degree-of-freedom analysis, and perform the required calculations.
- Explain in your own words the terms *solubility* of a solid in a liquid, *saturated solution*, and *hydrated salt*. Given solubility data, determine the saturation temperature of a feed solution of given composition and the quantity of solid crystals that form if the solution is cooled to a specified temperature below the saturation point.
- Given a liquid solution of a nonvolatile solute, estimate the solvent vapor-pressure lowering, the boiling-point elevation, and the freezing-point depression, and list the assumptions required for your estimate to be accurate.
- Explain the term *distribution coefficient* (or *partition ratio*) for a solute distributed between two nearly immiscible liquids. Given feed-stream flow rates and compositions for a liquid extraction process and either solute distribution coefficient data or a triangular phase diagram, calculate the product stream flow rates and compositions.
- Explain the term *adsorption isotherm*. Given adsorption equilibrium data or an expression for an adsorption isotherm, calculate the maximum quantity of adsorbate that can be removed from a gas by a specified quantity of adsorbent or, conversely, the minimum quantity of adsorbent needed to remove a specified quantity of adsorbate.

6.1 SINGLE-COMPONENT PHASE EQUILIBRIUM

6.1a Phase Diagrams

At most temperatures and pressures, a single pure substance at equilibrium exists entirely as a solid, liquid, or gas; but at certain temperatures and pressures, two and even all three phases may coexist. Pure water is a gas at 130°C and 100 mm Hg, for example, and a solid at −40°C and 10 atm, but at 100°C and 1 atm it may be a gas, a liquid, or a mixture of both, and at approximately 0.0098°C and 4.58 mm Hg it may be a solid, a liquid, a gas, or any combination of the three.

A **phase diagram** of a pure substance is a plot of one system variable against another that shows the conditions at which the substance exists as a solid, a liquid, and a gas. The most common of these diagrams plots pressure on the vertical axis versus temperature on the horizontal axis. The boundaries between the single-phase regions represent the pressures and temperatures at which two phases may coexist. The phase diagrams of water and carbon dioxide are shown in Figure 6.1-1.

What the phase diagram means and what can be done with it are illustrated by a hypothetical experiment in which pure water is placed in a leakproof evacuated cylinder fitted with a movable piston, as shown in the diagram on the next page. Heat can be added to or withdrawn from the cylinder, so that the temperature in the chamber can be adjusted to any desired value, and the

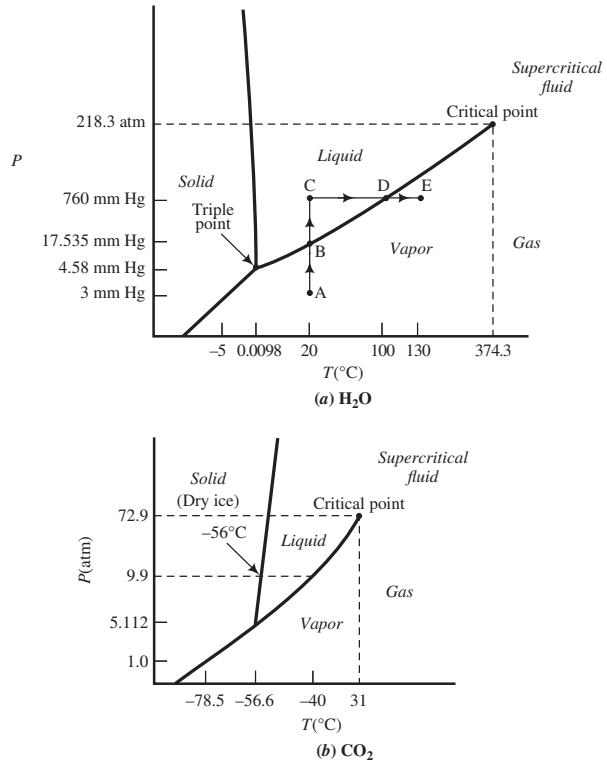
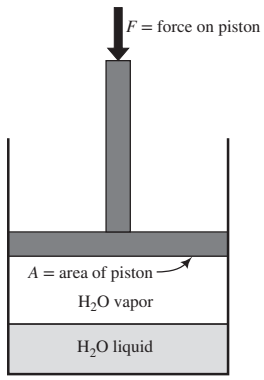


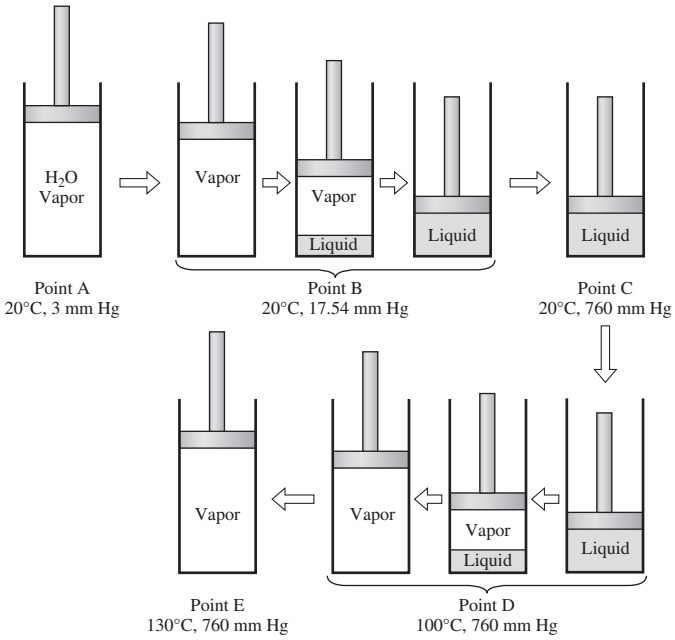
FIGURE 6.1-1 Phase diagrams of (a) H_2O and (b) CO_2 (not drawn to scale).

absolute pressure of the cylinder contents [which equals $(F + W)/A$, where W is the weight of the piston] can similarly be adjusted by varying the force F on the piston.



Suppose the system is initially at 20°C, and the force is set at a value such that the system pressure is 3 mm Hg. As the phase diagram shows, water can only exist as a vapor at these conditions, so any liquid that may initially have been in the chamber evaporates, until finally the chamber contains only water vapor at 20°C and 3 mm Hg (point A on Figure 6.1-1*a*).

Now suppose the force on the piston is slowly increased with the system temperature held constant at 20°C until the pressure in the cylinder reaches 760 mm Hg, and thereafter heat is added to the system with the pressure remaining constant until the temperature reaches 130°C. The state of the water throughout this process can be determined by following path A → B → C → D → E on Figure 6.1-1*a*. The conditions of the system at various stages of the process are shown schematically on the next page.



Notice that the phase transitions—condensation at point B and evaporation at point D—take place at boundaries on the phase diagram; the system cannot move off these boundaries until the transitions are complete.

Several familiar terms may be defined with reference to the phase diagram.

1. If T and P correspond to a point on the vapor–liquid equilibrium curve for a substance, P is the **vapor pressure** (denoted by p^* in the book) of the substance at temperature T, and T is the **boiling point**—more precisely, the **boiling point temperature** (T_b)—of the substance at pressure P.
2. The boiling point of a substance at $P = 1$ atm is the **normal boiling point** of that substance.
3. If (T, P) falls on the solid–liquid equilibrium curve, then T is the **melting point** or **freezing point** (T_m) at pressure P.
4. If (T, P) falls on the solid–vapor equilibrium curve, then P is the vapor pressure of the solid at temperature T, and T is the **sublimation point** (T_s) at pressure P.
5. The point (T, P) at which solid, liquid, and vapor phases can all coexist is called the **triple point** of the substance.
6. The vapor–liquid equilibrium curve terminates at the **critical temperature** and **critical pressure** (T_c and P_c). Above and to the right of the critical point, two separate phases never coexist.

As you can see from Figure 6.1-1*a*, the freezing point of water decreases with increasing pressure. (*Verify*.) This behavior is extremely unusual; most substances, including carbon dioxide, exhibit the opposite behavior. Note also, however, that the changes are very slight; the solid–liquid equilibrium curves are in fact nearly vertical. Their slopes have been exaggerated in Figure 6.1-1 for illustrative purposes.

Normal boiling and melting points for many substances are given in Table B.1 of Appendix B and by functions Tb and Tm of APEx, and values for many more substances are tabulated on

pp. 2-7 through 2-47 of *Perry's Chemical Engineers' Handbook.*[1] Boiling points of many species at specified pressures may be calculated from the Antoine equation using coefficients in Table B.4 and from the APEx function AntoineT. Vapor pressures of water at temperatures from 0°C to 100°C are tabulated in Table B.3 and can be obtained using function VPWater of APEx, and vapor pressures of many other species at specified temperatures may be calculated using the Antoine equation and coefficients in Table B.4 or the APEx function AntoineP, and from data tabulated on pp. 2-48 through 2-79 of *Perry's Handbook* and on the website of the National Institute of Standards and Technology (http://webbook.nist.gov/). Techniques for estimating vapor pressures of species for which neither tabulated data nor Antoine equation coefficients are available are given in Section 6.1b.

Test Yourself

(Answers, p. 657)

(Referring to Figure 6.1-1)

1. What is the sublimation point of H_2O at 3 mm Hg? What is the vapor pressure of ice at −5°C?
2. What is the triple point of CO_2?
3. Describe what happens when the pressure of pure CO_2 is raised from 1 atm to 9.9 atm at −78.5°C, and then the temperature is raised from −78.5°C to 0°C at 9.9 atm.
4. What is the vapor pressure of CO_2 at −78.5°C? At −40°C?
5. What is the sublimation point of CO_2 at 1 atm? The melting point at 9.9 atm? The boiling point at the latter pressure?
6. Does the state of water at point E in Figure 6.1-1*a* depend on the path followed in changing the temperature and pressure at point A to the values at point E?

6.1b Estimation of Vapor Pressures

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The **volatility** of a species is the tendency of the species to transfer from the liquid (or solid) state to the vapor state. At a given temperature and pressure, a highly volatile substance is much more likely to be found as a vapor than is a substance with low volatility, which is more likely to be found in a condensed phase (liquid or solid).

Separation processes including partial vaporization, partial condensation, and distillation are used to separate mixtures according to the relative volatilities of their components. For example, if a liquid mixture is partially vaporized, the products are a vapor rich in more volatile species and a liquid rich in less volatile species. The vapor pressure of a species reflects its volatility: generally, the higher the vapor pressure at a given temperature, the greater the volatility of the species at that temperature.

It often happens that tabulated vapor pressures are not available at temperatures of interest, or they may not be available at all for a given species. One solution to this problem is to measure p^* at the desired temperatures. Doing so is not always convenient, however, especially if a highly precise value is not required. An alternative is to *estimate* the vapor pressure using an empirical correlation for $p^*(T)$. Poling, Prausnitz, and O'Connell[2] summarize and compare methods for estimating vapor pressure, several of which are given in the paragraphs that follow.

A relationship between p^*, the vapor pressure of a pure substance, and T, the *absolute* temperature, is the **Clapeyron equation**

$$\frac{dp^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_g - \hat{V}_l)} \tag{6.1-1}$$

[1] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008.

[2] B. E. Poling, J. H. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th Edition, McGraw-Hill, New York, 2001.

where $\hat{V}_g$ and $\hat{V}_l$ are the specific molar volumes (volume/mole) of gas (vapor) and liquid, respectively, and $\Delta\hat{H}_v$ is the **latent heat of vaporization**, or the energy required to vaporize one mole of the liquid (to be defined more precisely in Chapter 8).

Unless the pressure is extremely high, the specific volume of the liquid is negligible relative to that of the vapor (i.e., $\hat{V}_g - \hat{V}_l \approx \hat{V}_g$). If we assume this is the case, apply the ideal-gas equation of state to the vapor (so that $\hat{V}_g$ is replaced with RT/p^* in Equation 6.1-1), and rearrange the resulting equation with the aid of elementary calculus, we obtain

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R} \tag{6.1-2}$$

(Convince yourself that Equation 6.1-2 is correct by working backward to derive Equation 6.1-1.)

If the vapor pressure of a substance is measured at several temperatures and $\ln p^*$ is plotted versus $1/T$ (or p^* is plotted versus $1/T$ on semilog axes), then from Equation 6.1-2, the slope of the resulting curve at a given temperature equals $-\Delta\hat{H}_v/R$. This is the method most commonly used to determine heats of vaporization experimentally.

Suppose now that the heat of vaporization of a substance is independent of temperature (or nearly so) in the temperature range over which vapor pressures are available. Equation 6.1-2 may then be integrated to yield the **Clausius–Clapeyron equation**

$$\ln p^* = -\frac{\Delta\hat{H}_v}{RT} + B \tag{6.1-3}$$

where B is a constant that varies from one substance to another. According to this equation, a plot of $\ln p^*$ versus $1/T$ (or a semilog plot of p^* versus $1/T$) should be a straight line with slope $-\Delta\hat{H}_v/R$ and intercept B.

If you know $\Delta\hat{H}_v$ and p^* at a single temperature T_0, you can solve the Clausius–Clapeyron equation for B and thereafter use this equation to estimate p^* at any temperature close to T_0. If you have p^* versus T data, you can plot $\ln p^*$ versus $1/T$ and determine $\Delta\hat{H}_v/R$ and B graphically or by the method of least squares (see Appendix A.1).

Example 6.1-1 Vapor Pressure Estimation Using the Clausius–Clapeyron Equation

The vapor pressure of benzene is measured at two temperatures, with the following results:

$$T_1 = 7.6°C, \qquad p_1^* = 40 \text{ mm Hg}$$
$$T_2 = 15.4°C, \qquad p_2^* = 60 \text{ mm Hg}$$

Calculate the latent heat of vaporization and the parameter B in the Clausius–Clapeyron equation and then estimate p^* at 42.2°C using this equation.

Solution

p^*(mm Hg)	T(°C)	T(K)
40	7.6	280.8
60	15.4	288.6

The slope of the line through the two data points on a plot of $\ln p^*$ versus $1/T$ is

$$-\frac{\Delta\hat{H}_v}{R} = \frac{\ln(p_2^*/p_1^*)}{[(1/T_2) - (1/T_1)]} = \frac{T_1 T_2 \ln(p_2^*/p_1^*)}{(T_1 - T_2)}$$
$$= \frac{(280.8 \text{ K})(288.6 \text{ K}) \ln(60 \text{ mm Hg}/40 \text{ mm Hg})}{(280.8 - 288.6) \text{ K}} = -4213 \text{ K}$$

The intercept B is obtained from Equation 6.1-3 as

$$B = \ln p_1^* + \frac{\Delta\hat{H}_v}{RT_1}$$
$$= \ln 40 + (4213/280.8) = 18.69$$

The Clausius–Clapeyron equation is therefore

$$\boxed{\ln p^* = -\frac{4213\text{ K}}{T(\text{K})} + 18.69} \quad p^* \text{ in mm Hg}$$

Check: $T = 15.4°\text{C} \Longrightarrow 288.6\text{ K}$

$$\ln p^* = -\frac{4213}{288.6} + 18.69 = 4.093$$
$$\Downarrow$$
$$p^* = \exp(4.093) = 60\text{ mm Hg} \quad \checkmark$$

Finally, at $T = 42.2°\text{C} = 315.4\text{ K}$

$$\ln p^* = -\frac{4213}{315.4} + 18.69 = 5.334$$
$$\Downarrow$$
$$p^* = \exp(5.334) = \boxed{207\text{ mm Hg}}$$

Perry's Chemical Engineers' Handbook, p. 2-65, lists the vapor pressure of benzene at 42.2°C as 200 mm Hg, so that the use of the Clausius–Clapeyron equation results in an estimation error of approximately 3.5%.

The heat of vaporization of benzene $\Delta\hat{H}_v$ may be estimated from the slope of the Clausius–Clapeyron plot $(-\Delta\hat{H}_v/R)$ as

$$\Delta\hat{H}_v = (\Delta\hat{H}_v/R)(R)$$
$$= \frac{4213\text{ K}}{}\left|\frac{8.314\text{ J}}{\text{mol}\cdot\text{K}}\right. = \boxed{35{,}030\text{ J/mol}}$$

(The true value is approximately 31,000 J/mol.)

Suppose you need to know the vapor pressure of a species at a specified temperature. Tables of p^* at different temperatures exist for many species, but it is difficult to interpolate between tabulated values since p^* varies sharply with T. Plots of p^* versus T for different species would not be particularly useful since many closely spaced data points would be required to generate each plot, and the curvature of the plots would make it awkward to show data for many different species on a single graph.

A relatively simple empirical equation that correlates vapor pressure–temperature data extremely well is the **Antoine equation**

$$\log_{10} p^* = A - \frac{B}{T + C} \tag{6.1-4}$$

Equation 6.1-4 can be easily rearranged to derive a formula for the boiling point temperature T_b at a specified pressure, P. (Try it.)

Values of A, B, and C for several compounds are listed in Table B.4. If you use the tabulated coefficients, be sure to substitute the value of temperature in Celsius degrees. Once you have calculated the right-hand side (RHS) of the equation, you can determine p^*(mm Hg) as 10^{RHS}. *Cautions:* (1) Don't rely on the Antoine equation to estimate vapor pressures at temperatures well outside the range used to determine the coefficients in Table B.4; such extrapolation may lead to

significant errors. (2) Other references may express the Antoine equation in different units and using base *e* logarithms.

In APEx, you can use the Antoine equation to determine a vapor pressure at a specified temperature using the function AntoineP and the value of a boiling point temperature at a specified pressure using AntoineT.

Test Yourself

(Answers, p. 657)

1. Determine the vapor pressure of *n*-hexane at 87°C using (a) Table B.4, (b) APEx.
2. Name three ways you could determine the normal boiling point of benzene from data in this book—one that involves looking it up, one that requires a hand calculation, and one that uses APEx.
3. Suppose you are given the vapor pressure p^* of a substance at three closely spaced temperatures T_1, T_2, and T_3, and you wish to determine p^* at a fourth temperature T_4 far removed from the other three. If you use the Clausius–Clapeyron equation to correlate p^* and T, how would you plot the data and extrapolate it to T_4?

CREATIVITY EXERCISE

Give as many reasons as you can think of, however farfetched, for wanting to know the vapor pressure of a substance at a given temperature. (*Example:* You want to know whether you can leave it overnight in an unstoppered flask without most of it evaporating.)

6.2 THE GIBBS PHASE RULE

When two phases are brought into contact with each other, a redistribution of the components of each phase normally takes place—species evaporate, condense, dissolve, or solidify until a state of phase equilibrium is reached in which the temperatures and pressures of both phases are the same and the composition of each phase no longer changes with time.

Suppose you have a closed vessel containing three components A, B, and C distributed between gas and liquid phases, and you wish to describe this system to someone else in sufficient detail for that person to duplicate it exactly. Specifying the system temperature and pressure, the masses of each phase, and two mass or mole fractions for each phase would certainly be sufficient; however, these variables are not all independent—once some of them are specified, others are fixed by nature and, in some cases, may be calculated from physical properties of the system components.

The variables that describe the condition of a process system fall into two categories: **extensive variables**, which depend on the size of the system, and **intensive variables**, which do not. Mass and volume are examples of extensive variables; intensive variables include temperature, pressure, density and specific volume, and mass and mole fractions of individual system components in each phase.

The number of intensive variables that can be specified independently for a system at equilibrium is called the **degrees of freedom** of the system. Let

Π = number of phases in a system at equilibrium
c = number of independent chemical species
r = number of independent equilibrated chemical reactions among the species
DF = degrees of freedom

The relationship among DF, Π, c and r is given by the **Gibbs phase rule**:

$$DF = 2 + c - \Pi - r \tag{6.2-1}$$

[*Note: Perry's Chemical Engineers' Handbook* (see Footnote 1), p. 4-27, presents a proof of the phase rule and outlines a method for determining how many independent reactions may occur among the components of a system.]

The meaning of the term *degrees of freedom* in the Gibbs phase rule is similar to its meaning in the degree-of-freedom analyses you have been performing since Chapter 4. In those analyses, the degrees of freedom represents the number of process variables that must be specified for a process system before the remaining variables can be calculated. In the Gibbs phase rule, the degrees of freedom equals the number of *intensive* variables that must be specified for a system *at equilibrium* before the remaining intensive variables can be calculated.

The example that follows illustrates the application of the Gibbs phase rule to several simple systems. The remainder of the chapter presents the equilibrium relationships that are used to determine the remaining intensive system variables once the allowed number of these variables has been specified.

Example 6.2-1 The Gibbs Phase Rule

Determine the degrees of freedom for each of the following systems at equilibrium. Specify a feasible set of independent variables for each system.

1. ***Pure liquid water***

$$\text{One phase } (\Pi = 1),\ \text{one component } (c = 1),\ \text{no reactions } (r = 0)$$
$$\Downarrow$$
$$DF = 2 + 1 - 1 = 2$$

Two intensive variables must be specified to fix the state of the system, for example, T and P. Once these variables have been specified, other intensive variables such as density and viscosity may be determined.

2. ***A mixture of liquid, solid, and vapor water***

$$\text{Three phases } (\Pi = 3),\ \text{one component } (c = 1),\ \text{no reactions } (r = 0)$$
$$\Downarrow$$
$$DF = 2 + 1 - 3 = 0$$

No further information about the system may be specified and all intensive variables are fixed. Note from Figure 6.1-1*a* that three phases coexist at equilibrium at only one temperature and pressure.

3. ***A vapor–liquid mixture of acetone and methyl ethyl ketone***

$$\text{Two phases } (\Pi = 2),\ \text{two components } (c = 2),\ \text{no reactions } (r = 0)$$
$$\Downarrow$$
$$DF = 2 + 2 - 2 = 2$$

Two variables must be specified to fix the state of the system. For example, setting T and P fixes the acetone and MEK mole fractions in both the vapor and liquid phases. Alternatively, T and the acetone mole fraction in the vapor may be specified, and P and the acetone mole fraction in the liquid are then fixed.

Test Yourself

(Answers, p. 657)

1. Define and give examples of extensive and intensive variables. Define "degrees of freedom of a system." What is the Gibbs phase rule?

2. Use the phase rule to determine the degrees of freedom of each of the following equilibrium systems and give a possible set of variables that may be specified.

(a) NaCl crystals suspended in an aqueous NaCl solution.

(b) Humid air in equilibrium with condensed water (dry air may be considered a single species).

(c) A vapor–liquid mixture of four hydrocarbons.

(d) A gaseous mixture of H_2, Br_2, and HBr, given that the single reaction

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

has proceeded to equilibrium.

6.3 GAS–LIQUID SYSTEMS: ONE CONDENSABLE COMPONENT

Systems containing several components, of which only one is capable of existing as a liquid at the process conditions, are common in industrial processes. Operations such as **evaporation, drying**, and **humidification**—all of which involve transfer of liquid into the gas phase—and **condensation** and **dehumidification**, which involve transfer of the condensable species from the gas to the liquid phase, are examples of such processes.

Suppose liquid water is introduced into a chamber that initially contains dry air and that the temperature and pressure in the system are kept constant at 75°C and 760 mm Hg. Initially the gas phase contains no water ($p_{H_2O} = 0$), and water molecules consequently begin to evaporate. The mole fraction of water in the gas phase, y_{H_2O}, increases, and hence so does the partial pressure of water, $p_{H_2O} = y_{H_2O}P$. Eventually, however, the amount of water in the gas phase is such that the rate at which water molecules enter the gas phase approaches zero, and thereafter no change occurs in the amount or composition of either phase. The gas phase is then said to be **saturated** with water—it contains all the water it can hold at the system temperature and pressure—and the water in the gas phase is referred to as a **saturated vapor**.

Let us apply the Gibbs phase rule to this equilibrium system. Since there are two phases and two components,

$$DF = 2 + c - \Pi = 2$$

It follows that only two out of the three intensive variables T, P, and y_{H_2O} can be specified, and that some relationship must exist that uniquely determines the value of the third variable once the first two have been specified.[3]

A law that describes the behavior of gas–liquid systems over a wide range of conditions provides the desired relationship. *If a gas at temperature T and pressure P contains a saturated vapor whose mole fraction is y_i (mol vapor/mol total gas), and if this vapor is the only species that would condense if the temperature were slightly lowered, then the partial pressure of the vapor in the gas equals the pure-component vapor pressure $p_i^*(T)$ at the system temperature.*

Raoult's Law*, *Single Condensable Species: $$p_i = \boxed{y_i P = p_i^*(T)} \qquad \textbf{(6.3-1)}$$

Equation 6.3-1 is a limiting case of **Raoult's law**, which will be introduced in a more general context in Section 6.4. It is the fundamental relation used in the analysis of equilibrated gas–liquid systems containing one condensable component. A wide variety of problems occur in connection with such systems, but they all eventually involve knowing two of the variables y_i, P, and T and having to determine the third using Equation 6.3-1.

Example 6.3-1 Composition of a Saturated Gas–Vapor System

Air and liquid water are contained at equilibrium in a closed chamber at 75°C and 760 mm Hg. Calculate the molar composition of the gas phase.

[3] It could be argued that setting the mole fraction of air in the liquid water to zero uses up a degree of freedom. In fact, however, we are not fixing a precise value of this variable; all we are saying is that the mole fraction of air in the liquid water approaches zero and the value is so small that it does not affect liquid-phase behavior and mass balances on the system.

Solution Since the gas and liquid are in equilibrium, the air must be saturated with water vapor (if it were not, more water would evaporate), so that Raoult's law may be applied:

$$y_{H_2O} = p^*_{H_2O}(75°C)/P$$

From Table B.3 in Appendix B, $p^*_{H_2O}(75°C) = 289$ mm Hg. Consequently,

$$y_{H_2O} = \frac{289 \text{ mm Hg}}{760 \text{ mm Hg}} = \boxed{0.380 \frac{\text{mol } H_2O}{\text{mol}}}$$

$$y_{\text{dry air}} = 1 - y_{H_2O} = \boxed{0.620 \frac{\text{mol dry air}}{\text{mol}}}$$

Several important points concerning the behavior of gas–liquid systems and several terms used to describe the state of such systems are summarized here.

1. A gas in equilibrium with a liquid must be saturated with the volatile components of that liquid.
2. The partial pressure of a vapor at equilibrium in a gas mixture containing a single condensable component cannot exceed the vapor pressure of the pure component at the system temperature. If $p_i = p_i^*$, the vapor is saturated; any attempt to increase p_i—either by adding more vapor to the gas phase or by increasing the total pressure at constant temperature—must instead lead to condensation.
3. A vapor present in a gas in less than its saturation amount is referred to as a **superheated vapor**. For such a vapor,

$$p_i = \boxed{y_i P < p_i^*(T)} \qquad \textbf{(6.3-2)}$$

   Since only a saturated vapor can condense (why?), condensation in a system containing a superheated vapor requires changing one or more of the variables of Equation 6.3-2 so that the inequality becomes the equality of Raoult's law. This can be done in several ways, such as by increasing the pressure at constant temperature (the left side increases, while the right side stays constant) or by decreasing the temperature at constant pressure (the left side remains constant, and the right side decreases).
4. If a gas containing a single superheated vapor is cooled at constant pressure, the temperature at which the vapor becomes saturated is referred to as the **dew point** of the gas. From Raoult's law (Equation 6.3-1),

$$p_i = \boxed{y_i P = p_i^*(T_{dp})} \qquad \textbf{(6.3-3)}$$

   The difference between the temperature and the dew point of a gas is called the **degrees of superheat** of the gas. If any two of the quantities y_i, P, and T_{dp} (or, equivalently, the temperature of the gas and the degrees of superheat) are known, the third quantity may be determined from Equation 6.3-3 and a table, graph, or equation relating p_i^* and T.

Example 6.3-2 Material Balances Around a Condenser

A stream of air at 100°C and 5260 mm Hg contains 10.0% water by volume.

1. Calculate the dew point and degrees of superheat of the air.
2. Calculate the percentage of the vapor that condenses and the final composition of the gas phase if the air is cooled to 80°C at constant pressure.
3. Calculate the percentage condensation and the final gas-phase composition if, instead of being cooled, the air is compressed isothermally to 8500 mm Hg.

4. Suppose the process of Part 2 is run, the product gas is analyzed, and the mole fraction of water differs considerably from the calculated value. What could be responsible for the disparity between calculated and measured values? (List several possibilities.)

Solution **1.** $p_{H_2O} = y_{H_2O}P = (0.100)(5260 \text{ mm Hg}) = 526 \text{ mm Hg}$

$p^*_{H_2O}(100°\text{C}) = 760 \text{ mm Hg} > p_{H_2O} \Longrightarrow$ the vapor is superheated (see Inequality 6.3-2)

From Equation 6.3-3

$$p_{H_2O} = p^*_{H_2O}(T_{dp}) = 526 \text{ mm Hg}$$

$$\Downarrow \text{Table B.3}$$

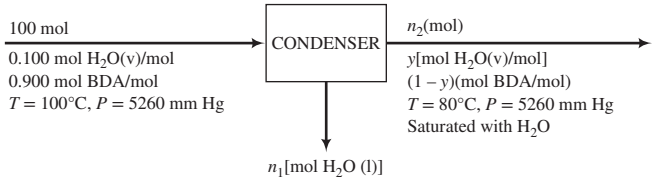
$$\boxed{T_{dp} = 90°\text{C}}$$

and the air has $100°\text{C} - 90°\text{C} = \boxed{10°\text{C of superheat}}$

2. Since the air becomes saturated at 90°C, further cooling must lead to condensation. Since the products are liquid water in equilibrium with a gas phase, the water vapor in the gas must remain saturated.

On the following flowchart, the symbol BDA stands for **bone-dry air**, a term used to signify the water-free component of an air–water vapor mixture.

Basis: 100 mol Feed Gas



Let us first do the degree-of-freedom analysis. Three unknown variables appear on the chart—n_1, n_2, and y. Since only two species are involved in the process, we can only write two independent material balances, leaving us one equation short. If we fail to observe that the gas at the condenser outlet is saturated with water, solution of the problem would be impossible; however, the saturation condition supplies the needed third equation, Raoult's law.

The solution outline is as follows: apply Raoult's law at the outlet to determine y, the mole fraction of water in the outlet gas; then use a dry air balance to determine n_2 and a total mole balance or a water balance to determine the final unknown, n_1.

Raoult's Law at Outlet: $yP = p^*_{H_2O}(T)$

$$\Downarrow$$

$$y = \frac{p^*_{H_2O}(80°\text{C})}{P} = \frac{355 \text{ mm Hg}}{5260 \text{ mm Hg}} = \boxed{0.0675 \frac{\text{mol H}_2\text{O}}{\text{mol}}}$$

Balance on Dry Air: $\dfrac{100 \text{ mol}}{} \left| \dfrac{0.900 \text{ mol BDA}}{\text{mol}} \right. = n_2(1 - y)$

$$\Downarrow y = 0.0675$$

$$n_2 = 96.5 \text{ mol}$$

Total Mole Balance: $100 \text{ mol} = n_1 + n_2$

$$\Downarrow n_2 = 96.5 \text{ mol}$$

$$n_1 = 3.5 \text{ mol H}_2\text{O condensed}$$

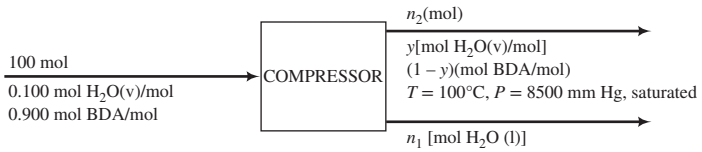
Percentage Condensation: $\dfrac{3.5 \text{ mol H}_2\text{O condensed}}{(0.100 \times 100) \text{ mol H}_2\text{O fed}} \times 100\% = \boxed{35\%}$

3. Initially $y_{H_2O}P < p^*_{H_2O}(100°C)$. Saturation occurs when P is high enough for the inequality to become an equality, or

$$P_{\text{saturation}} = \frac{p^*_{H_2O}(100°C)}{y_{H_2O}} = \frac{760\text{ mm}}{0.100} = 7600\text{ mm Hg}$$

Any increase in P above 7600 mm Hg must cause condensation, so that the products from the compression to 8500 mm Hg must include a liquid stream.

Basis: 100 mol Feed Gas



Before going through the solution, try to outline it as was done following the flowchart of Part 2.

Raoult's Law: $y = \dfrac{p^*_{H_2O}(100°C)}{P} = \dfrac{760\text{ mm Hg}}{8500\text{ mm Hg}} = \boxed{0.0894\ \dfrac{\text{mol H}_2\text{O}}{\text{mol}}}$

Balance on Dry Air:

$$(100\text{ mol})(0.900) = n_2(1-y)$$
$$\Downarrow\ y = 0.0894$$
$$n_2 = 98.8\text{ mol}$$

Total Mole Balance:

$$100\text{ mol} = n_1 + n_2$$
$$\Downarrow\ n_2 = 98.8\text{ mol}$$
$$n_1 = 1.2\text{ mol H}_2\text{O condensed}$$

Percentage Condensation: $\dfrac{1.2\text{ mol H}_2\text{O condensed}}{(0.100\times 100)\text{ mol H}_2\text{O fed}} \times 100\% = \boxed{12\%}$

4. (a) Experimental error (you should be able to list many possibilities). (b) The condenser was not at steady state when the measurements were made, possibly because the system had not yet leveled out following startup or because water vapor was adsorbing on the walls of the condenser. (c) The emerging gas and liquid streams were not at equilibrium (e.g., condensation actually occurred at a temperature below 100°C and the product streams were separated and reheated before emerging). (d) Raoult's law does not apply (this is not a likely explanation for the air–water system at the given conditions).

The mechanism of evaporation of a liquid depends on the relative values of the vapor pressure of the liquid and the total system pressure. If evaporation takes place at a temperature such that $p^* < P$, the process involves transfer of molecules from the surface of the liquid to the gas above the surface, while if $p^* = P$, vapor bubbles form throughout the entire liquid, but predominantly at the heated container walls: that is, the liquid *boils*. The temperature at which $p^* = P$ is the boiling point of the liquid at the given pressure.

Test Yourself

(Answers, p. 657)

1. If water vapor is in equilibrium with liquid water, must the vapor be saturated? Can a vapor be saturated if there is no liquid present in the system?
2. The vapor pressure of acetone is 200 mm Hg at 22.7°C. Liquid acetone is kept in a sealed flask at 22.7°C, and the gas above the liquid contains air and acetone vapor at a pressure of 960 mm Hg. What is (a) the partial pressure of acetone in the gas, (b) the partial pressure of

N_2, and (c) the mole fraction of acetone in the gas? What assumption have you made in answering the preceding question? How would you determine the boiling point of the acetone, assuming a constant total pressure of 960 mm Hg?

3. Suppose you have a curve of $p^*_{H_2O}$ versus T, and you are given the temperature and pressure (T_0 and P_0) of a mixture of water and noncondensable gases.
   (a) Define the dew point of the gas. Would the vapor be saturated or superheated if $T_0 > T_{dp}$? If $T_0 = T_{dp}$?
   (b) If you are told that the gas is saturated, how would you calculate the mole fraction of water in it? What would happen to the vapor if you (i) heated the gas isobarically (at constant pressure), (ii) cooled the gas isobarically, (iii) compressed the gas isothermally (at constant temperature), and (iv) expanded the gas isothermally?
   (c) If you are given the mole fraction of water in the gas, how would you calculate the dew point of the gas?
   (d) If you are given the degrees of superheat of the gas, how would you calculate the mole fraction of water in the gas?

Several quantities besides those introduced in the previous section are commonly used to describe the state and composition of a gas containing a single condensable vapor. *In the definitions to be given, the term "saturation" refers to any gas–vapor combination, while "humidity" refers specifically to an air–water system.*

Suppose a gas at temperature T and pressure P contains a vapor whose partial pressure is p_i and whose vapor pressure is $p_i^*(T)$.

Relative Saturation (Relative Humidity):

$$s_r(h_r) = \frac{p_i}{p_i^*(T)} \times 100\% \tag{6.3-4}$$

A relative humidity of 40%, for example, signifies that the partial pressure of water vapor equals $\frac{4}{10}$ of the vapor pressure of water at the system temperature.

Molal Saturation (Molal Humidity):

$$s_m(h_m) = \frac{p_i}{P - p_i} = \frac{\text{moles of vapor}}{\text{moles of vapor-free (dry) gas}} \tag{6.3-5}$$

(Can you prove the second equality?)

Absolute Saturation (Absolute Humidity):

$$s_a(h_a) = \frac{p_i M_i}{(P - p_i) M_{dry}} = \frac{\text{mass of vapor}}{\text{mass of dry gas}} \tag{6.3-6}$$

where M_i is the molecular weight of the vapor and M_{dry} is the average molecular weight of the dry (vapor-free) gas.

Percentage Saturation (Percentage Humidity):

$$s_p(h_p) = \frac{s_m}{s_m^*} \times 100\% = \frac{p_i/(P - p_i)}{p_i^*/(P - p_i^*)} \times 100\% \tag{6.3-7}$$

If you are given any of these quantities for a gas at a given temperature and pressure, you can solve the defining equation to calculate the partial pressure or mole fraction of the vapor in the gas; thereafter, you can use the formulas given previously to calculate the dew point and degrees of superheat.

Test Yourself

(Answers, p. 657)

The vapor pressure of styrene is 100 mm Hg at 82°C and 200 mm Hg at 100°C. A gas that consists of 10 mole% styrene and 90 mole% noncondensables is contained in a tank at 100°C and 1000 mm Hg. Calculate:

1. The dew point of the gas.
2. The relative saturation.
3. The molal saturation and percentage saturation.

CREATIVITY EXERCISES

1. Suppose you know the temperature and barometric pressure on a given day. List as many ways as you can think of to determine—exactly or approximately—the mole fraction of water vapor in the air.
2. Repeat question 1, only this time limit yourself to methods in which a stuffed bear plays a part in the determination. (*Example:* Saturate the bear with water, and measure the rate at which it loses weight due to evaporation.)

Example 6.3-3

Humid air at 75°C, 1.1 bar, and 30% relative humidity is fed into a process unit at a rate of 1000 m^3/h. Determine (1) the molar flow rates of water, dry air, and oxygen entering the process unit, (2) the molal humidity, absolute humidity, and percentage humidity of the air, and (3) the dew point.

Solution

1.

$$h_r(\%) = 100 p_{H_2O}/p^*_{H_2O}(75°C)$$

$$\Downarrow \quad h_r = 30\%, \quad p^*_{H_2O}(75°C) = 289 \text{ mm Hg (from Table B.3)}$$

$$p_{H_2O} = (0.3)(289 \text{ mm Hg}) = 86.7 \text{ mm Hg}$$

$$\Downarrow \quad y_{H_2O} = p_{H_2O}/P, \quad P = 1.1 \text{ bar} \Longrightarrow 825 \text{ mm Hg}$$

$$y_{H_2O} = (86.7 \text{ mm Hg})/(825 \text{ mm Hg}) = 0.105 \text{ mol } H_2O/\text{mol}$$

The molar flow rate of wet air is given by the ideal-gas equation of state as

$$\dot{n} = P\dot{V}/RT = \frac{1000 \text{ m}^3}{\text{h}} \left| \frac{1.1 \text{ bar}}{348 \text{ K}} \right| \frac{\text{kmol}\cdot\text{K}}{0.0831 \text{ m}^3\cdot\text{bar}} = 38.0 \frac{\text{kmol}}{\text{h}}$$

Consequently,

$$\dot{n}_{H_2O} = \frac{38.0 \text{ kmol}}{\text{h}} \left| \frac{0.105 \text{ kmol } H_2O}{\text{kmol}} \right| = \boxed{3.99 \frac{\text{kmol } H_2O}{\text{h}}}$$

$$\dot{n}_{BDA} = \frac{38.0 \text{ kmol}}{\text{h}} \left| \frac{(1 - 0.105) \text{ kmol BDA}}{\text{kmol}} \right| = \boxed{34.0 \frac{\text{kmol BDA}}{\text{h}}}$$

$$\dot{n}_{O_2} = \frac{34.0 \text{ kmol BDA}}{\text{h}} \left| \frac{0.21 \text{ kmol } O_2}{\text{kmol BDA}} \right| = \boxed{7.14 \frac{\text{kmol } O_2}{\text{h}}}$$

2.

$$h_m = \frac{p_{H_2O}}{P - p_{H_2O}} = \frac{86.7 \text{ mm Hg}}{(825 - 86.7) \text{ mm Hg}} = \boxed{0.117 \frac{\text{mol } H_2O}{\text{mol BDA}}}$$

The same result could have been obtained from the results of Part 1 as (3.99 kmol H_2O/h)/(34.0 kmol BDA/h).

$$h_a = \frac{0.117\ \text{kmol } H_2O}{\text{kmol BDA}} \left| \frac{18.0\ \text{kg } H_2O}{\text{kmol } H_2O} \right| \frac{1\ \text{kmol BDA}}{29.0\ \text{kg BDA}} = \boxed{0.0726\ \frac{\text{kg } H_2O}{\text{kg BDA}}}$$

$$h_m^* = \frac{p_{H_2O}^*}{P - p_{H_2O}^*} = \frac{289\ \text{mm Hg}}{(825 - 289)\ \text{mm Hg}} = 0.539\ \frac{\text{kmol } H_2O}{\text{kmol BDA}}$$

$$h_p = 100 h_m / h_m^* = (100)(0.117)/(0.539) = \boxed{21.7\%}$$

3. $p_{H_2O} = 86.7\ \text{mm Hg} = p_{H_2O}^*(T_{dp})$

$\Downarrow$ Table B.3

$$\boxed{T_{dp} = 48.7°\text{C}}$$

6.4 MULTICOMPONENT GAS–LIQUID SYSTEMS

Gas–liquid processes that involve several components in each phase include many chemical reactions, distillation, and transfer of one or more species from a gas to a liquid (**absorption** or **scrubbing**) or vice versa (**stripping**).

When multicomponent gas and liquid phases are in equilibrium, a limited number of intensive system variables may be specified arbitrarily (the number is given by the Gibbs phase rule), and the remaining variables can then be determined using equilibrium relationships for the distribution of components between the two phases. In this section we define several such relationships and illustrate how they are used in the solution of material balance problems.

6.4a Vapor–Liquid Equilibrium Data

The best way to evaluate equilibrium compositions is from tabulated data. *Perry's Chemical Engineers' Handbook* (see Footnote 1), pp. 2-80 through 2-94, gives partial pressures of vapors over various liquid solutions. Example 6.4-1 illustrates the use of such data.

Example 6.4-1 Absorption of SO_2

ENVIRONMENTAL

Equipment Encyclopedia
absorber

@

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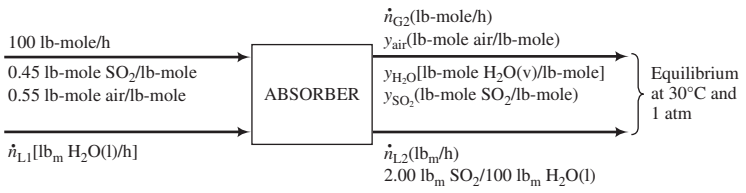
Sulfur dioxide (SO_2) is produced when coal is burned in power plants. Prior to implementation of clean-air standards, SO_2 emissions were responsible for acid rain, but utilization of absorbers (sometimes referred to as *scrubbers*) to remove SO_2 from combustion products has significantly reduced the problem.

In a simple implementation of that emission-control strategy, a gas mixture containing 45 mole% SO_2 and the balance air (an SO_2 concentration much higher than values normally encountered in power-plant emissions) flowing at a rate of 100 lb-mole/h is contacted with liquid water in a continuous absorber. The liquid leaving the absorber is analyzed and found to contain 2.00 g of SO_2 per 100 g of H_2O. Assuming that the gas and liquid streams leaving the absorber are in equilibrium at 30°C and 1 atm, calculate the fraction of the entering SO_2 absorbed in the water and the required water feed rate.

Solution **Basis: Given Feed Rate of Gas**



From Table 3-12 on p. 3-65 of the 6th Edition of *Perry's Chemical Engineers' Handbook*,[4] the equilibrium partial pressures of H_2O and SO_2 over a solution of the indicated composition are

$$p_{H_2O} = 31.6 \text{ mm Hg}$$
$$p_{SO_2} = 176 \text{ mm Hg}$$

so that the composition of the exit gas stream is

$$y_{H_2O} = \frac{31.6 \text{ mm Hg}}{760 \text{ mm Hg}} = 0.0416 \frac{\text{lb-mole } H_2O}{\text{lb-mole}}$$
$$y_{SO_2} = \frac{176 \text{ mm Hg}}{760 \text{ mm Hg}} = 0.232 \frac{\text{lb-mole } SO_2}{\text{lb-mole}}$$
$$y_{air} = 1 - y_{H_2O} - y_{SO_2} = 0.727 \frac{\text{lb-mole air}}{\text{lb-mole}}$$

Three unknown process variables remain—$\dot{n}_{L1}$, $\dot{n}_{G2}$, and $\dot{n}_{L2}$—and since a total of three independent balances can be written, the system is determinate.

Air Balance:

$$(0.55 \times 100)\frac{\text{lb-mole air}}{\text{h}} = y_{air}\dot{n}_{G2}$$
$$\Downarrow \; y_{air} = 0.727 \text{ lb-mole air/lb-mole}$$
$$\dot{n}_{G2} = 75.7 \text{ lb-mole/h}$$

To write the remaining two balances, it is necessary to determine the mass fractions of SO_2 and H_2O in the liquid effluent.

$$\frac{2.00 \text{ lb}_m \text{ SO}_2}{100 \text{ lb}_m \text{ H}_2O} \Longrightarrow \frac{2.00 \text{ lb}_m \text{ SO}_2}{102 \text{ lb}_m \text{ total}} \Longrightarrow x_{SO_2} = 0.0196 \text{ lb}_m \text{ SO}_2/\text{lb}_m$$
$$\Downarrow \; x_{SO_2} + x_{H_2O} = 1$$
$$x_{H_2O} = 0.9804 \text{ lb}_m \text{ H}_2O/\text{lb}_m$$

SO_2 Balance:

$$\frac{100 \text{ lb-mole}}{\text{h}} \left| \frac{0.45 \text{ lb-mole } SO_2}{\text{lb-mole}} \right. = \dot{n}_{G2}\, y_{SO_2} + \frac{\dot{n}_{L2}\,(\text{lb}_m)}{(\text{h})} \left| \frac{x_{SO_2}\,(\text{lb}_m \text{ SO}_2)}{(\text{lb}_m)} \right| \frac{\text{lb-mole}}{64 \text{ lb}_m \text{ SO}_2}$$
$$\Downarrow \; \dot{n}_{G2} = 75.7 \text{ lb-mole/h}, \; y_{SO_2} = 0.232, \; x_{SO_2} = 0.0196$$
$$\dot{n}_{L2} = 89{,}600 \text{ lb}_m/\text{h}$$

H_2O Balance:

$$\dot{n}_{L1}(\text{lb}_m \text{ H}_2O/\text{h}) = \frac{\dot{n}_{G2}\,(\text{lb-mole})}{(\text{h})} \left| \frac{y_{H_2O}(\text{lb-mole } H_2O)}{(\text{lb-mole})} \right| \frac{18 \text{ lb}_m \text{ H}_2O}{\text{lb-mole}} + \dot{n}_{L2}x_{H_2O}$$
$$\Downarrow \; \dot{n}_{G2} = 75.7 \text{ lb-mole/h}, \; y_{H_2O} = 0.0416 \text{ lb-mole } H_2O/\text{lb-mole}, \; \dot{n}_{L2} = 89{,}600 \text{ lb}_m/\text{h}, \; x_{H_2O} = 0.9804 \text{ lb}_m \text{ H}_2O/\text{lb}_m$$
$$\boxed{\dot{n}_{L1} = 87{,}900 \text{ lb}_m \text{ H}_2O/\text{h}} \quad \text{(feed to absorber)}$$

[4] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 6th Edition, McGraw-Hill, New York, 1984. (*Note:* These data do not appear in the later editions.)

Fraction SO_2 Absorbed:

$$\text{SO}_2 \text{ absorbed} = \frac{89{,}600 \text{ lb}_\text{m} \text{ liquid effluent}}{\text{h}} \left| \frac{0.0196 \text{ lb}_\text{m} \text{ SO}_2}{\text{lb}_\text{m}} \right.$$

$$= 1756 \frac{\text{lb}_\text{m} \text{ SO}_2 \text{ absorbed}}{\text{h}}$$

$$\text{SO}_2 \text{ fed} = \frac{100 \text{ lb-mole}}{\text{h}} \left| \frac{0.45 \text{ lb-mole SO}_2}{\text{lb-mole}} \right| \frac{64 \text{ lb}_\text{m} \text{ SO}_2}{\text{lb-mole SO}_2} = 2880 \frac{\text{lb}_\text{m} \text{SO}_2 \text{ fed}}{\text{h}}$$

$$\Downarrow$$

$$\frac{1756 \text{ lb}_\text{m} \text{ SO}_2 \text{ absorbed/h}}{2880 \text{ lb}_\text{m} \text{ SO}_2 \text{ fed/h}} = \boxed{0.610 \frac{\text{lb}_\text{m} \text{ SO}_2 \text{ absorbed}}{\text{lb}_\text{m} \text{ SO}_2 \text{ fed}}}$$

6.4b Raoult's Law and Henry's Law

If you apply the Gibbs phase rule to a multicomponent gas–liquid system at equilibrium, you will discover that the compositions of the two phases at a given temperature and pressure are not independent. Once the composition of one of the phases is specified (in terms of mole fractions, mass fractions, concentrations, or, for the vapor phase, partial pressures), the composition of the other phase is fixed and, in principle, can be determined from physical properties of the system components.

Relationships governing the distribution of a substance between equilibrated gas and liquid phases are the subject matter of **phase-equilibrium thermodynamics** and, for the most part, fall beyond the scope of this text. However, we will cover several simple approximate relationships that often provide reasonably accurate results. Such relationships form the bases of more precise methods that must be used when system conditions require them.

Suppose A is a substance contained in a gas–liquid system in equilibrium at temperature T and pressure P. Two simple expressions—**Raoult's law** and **Henry's law**—provide relationships between p_A, the partial pressure of A in the gas phase, and x_A, the mole fraction of A in the liquid phase.

Raoult's Law:
$$p_\text{A} \equiv \boxed{y_\text{A} P = x_\text{A} p_\text{A}^*(T)} \tag{6.4-1}$$

where p_A^* is the vapor pressure of pure liquid A at temperature T and y_A is the mole fraction of A in the gas phase.

Raoult's law is an approximation that is generally valid when x_A is close to 1—that is, when the liquid is almost pure A. It is also sometimes valid over the entire range of compositions for mixtures of similar substances, such as paraffinic hydrocarbons of similar molecular weights.

Note: When $x_\text{A} = 1$—that is, when the liquid is pure A—Raoult's law reduces to the expression $p_\text{A} = p_\text{A}^*(T)$ given previously for systems with only one condensable component.

Henry's Law:
$$p_\text{A} \equiv \boxed{y_\text{A} P = x_\text{A} H_\text{A}(T)} \tag{6.4-2}$$

where $H_\text{A}(T)$ is the **Henry's law constant** for A in a specific solvent.

Henry's law is generally valid for solutions in which x_A is close to 0 (dilute solutions of A*) provided that* A *does not dissociate, ionize, or react in the liquid phase*. The law is often applied to

solutions of noncondensable gases. Values of Henry's law constants (or closely related quantities) are given for several gases in water on pp. 2-130 through 2-133 of *Perry's Chemical Engineers' Handbook* (see Footnote 1).

A gas–liquid system in which the vapor–liquid equilibrium relationship for every volatile species is either Raoult's law or Henry's law is said to exhibit **ideal-solution** behavior. In such systems the ideal-gas equation of state describes the gas phase.

Test Yourself

(Answers, p. 657)

1. What is Raoult's law, and when is it most likely to be valid?
2. What is Henry's law, and when is it most likely to be valid?
3. What is an ideal solution?
4. A gas containing CO_2 is in equilibrium with liquid water containing a small amount of dissolved CO_2 at 30°C and 3 atm. Would you use Raoult's law or Henry's law to estimate the relationship between (a) x_{CO_2} and p_{CO_2}, and (b) x_{H_2O} and p_{H_2O}, where x denotes mole fraction in the liquid and p denotes partial pressure in the gas? In each case, what would you look up and where would you look for it? Would you expect to observe ideal-solution behavior for this system?
5. After a cold bottle of soda (CO_2 dissolved in water and nonvolatile additives) is opened, bubbles slowly form and emerge. Explain why, using Henry's law in your explanation.

Example 6.4-2 Raoult's Law and Henry's Law

Use either Raoult's law or Henry's law (whichever is most appropriate) to solve the following problems.

1. A gas containing 1.00 mole% ethane is in contact with water at 25.0°C and 20.0 atm. Estimate the mole fraction of dissolved ethane.
2. An equimolar liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapor at 30.0°C. What is the system pressure and the composition of the vapor?

Solution

1. Hydrocarbons normally are relatively insoluble in water, so that the solution of ethane is probably extremely dilute. Let us therefore apply Henry's law. Page 2-130 of *Perry's Chemical Engineers' Handbook* (see Footnote 1) gives the Henry's law constant for ethane in water at 25°C as 2.67×10^4 atm/mole fraction.[5] From Equation 6.4-2

$$x_{C_2H_6} = \frac{y_{C_2H_6}P}{H_{C_2H_6}} = \frac{(0.0100)(20.0\text{ atm})}{2.67 \times 10^4\text{ atm/mole fraction}} = \boxed{7.49 \times 10^{-6}\ \frac{\text{mol } C_2H_6}{\text{mol}}}$$

2. Since benzene and toluene are structurally similar compounds, we may apply Raoult's law. From Table B.4,

$$\log_{10} p_B^* = 6.906 - \frac{1211}{T + 220.8} \xrightarrow{T = 30°C} p_B^* = 119\text{ mm Hg}$$

$$\log_{10} p_T^* = 6.9533 - \frac{1343.9}{T + 219.38} \xrightarrow{T = 30°C} p_T^* = 36.7\text{ mm Hg}$$

(The values of p_B^* and p_T^* could have been obtained using the AntoineP function of APEx.)

[5] The uncertainty associated with Henry's law constants is illustrated by the fact that on page 2-130 of *Perry's Chemical Engineers' Handbook* (see Footnote 1), two different values for ethane in water at 25°C are given: Table 2-123 gives $H = 2.94 \times 10^4$ atm/mole fraction while Table 2-124 gives $H = 2.67 \times 10^4$ atm/mole fraction, a 9% difference.

Using Equation 6.4-1,

$$p_B = x_B p_B^* = (0.500)(119 \text{ mm Hg}) = 59.5 \text{ mm Hg}$$
$$p_T = x_T p_T^* = (0.500)(36.7 \text{ mm Hg}) = 18.35 \text{ mm Hg}$$
$$P = p_B + p_T = \boxed{77.9 \text{ mm Hg}}$$
$$y_B = p_B/P = \boxed{0.764 \text{ mole benzene/mole}}$$
$$y_T = p_T/P = \boxed{0.236 \text{ mole toluene/mole}}$$

CREATIVITY EXERCISE

Give as many cases as you can think of where it would be useful or necessary to know the Henry's law constant for a gas in a liquid. (*Example:* You wish to calculate the pressure needed to achieve a specified level of carbonation in bottled soda.) In your list, include several examples with environmental relevance.

6.4c Vapor–Liquid Equilibrium Calculations for Solutions That Obey Raoult's Law

Suppose heat is added slowly to a closed vessel that contains a liquid and that the pressure in the vessel is held constant. We have already examined what happens in a situation of this sort if the liquid is a single species: the temperature increases until the boiling point of the liquid is reached, and thereafter the liquid vaporizes at a constant temperature. Once the vaporization is complete, further addition of heat raises the temperature of the vapor.

Consider now what happens if the liquid is a mixture of several components. As heat is added, the liquid temperature rises until a temperature is reached at which the first bubble of vapor forms. Up to this point, the process looks like that for a single component. However, if the liquid is a mixture, the vapor generated generally will have a composition different from that of the liquid. *As vaporization proceeds, the composition of the remaining liquid continuously changes, and hence so does its vaporization temperature*. A similar phenomenon occurs if a mixture of vapors is subjected to a condensation process at constant pressure: at some temperature the first droplet of liquid forms, and thereafter the composition of the vapor and the condensation temperature both change.

To design or control an evaporation or condensation process, you must know the conditions at which the transition from liquid to vapor or vapor to liquid takes place. Design or control of other separation processes such as distillation, absorption, and stripping also requires information on the conditions at which phase transitions occur and on the compositions of the resulting phases. This section outlines the required calculations for a relatively simple class of mixtures.

When a liquid is heated slowly at constant pressure, the temperature at which the first vapor bubble forms is the **bubble-point temperature** of the liquid at the given pressure. When a gas (vapor) is cooled slowly at constant pressure, the temperature at which the first liquid droplet forms is the **dew-point temperature** at the given pressure. Calculating bubble-point and dew-point temperatures can be a complex task for an arbitrary mixture of components. However, if the liquid behaves as an **ideal solution** (one for which Raoult's or Henry's law is obeyed for all components) and the gas phase can also be considered ideal, the calculations are relatively straightforward.

Suppose a liquid solution follows Raoult's law for all components and contains species A, B, C, . . . with known mole fractions $x_A, x_B, x_C, \ldots$. If the mixture is heated at a constant pressure P to its bubble-point temperature T_{bp}, the further addition of a slight amount of heat will lead to the

formation of a vapor phase. If we assume the vapor is in equilibrium with the liquid, and that the vapor is ideal (follows the ideal-gas equation of state), the partial pressures of the components are given by Raoult's law, Equation 6.4-1.

$$p_i = x_i p_i^*(T_{\text{bp}}), \quad i = \text{A, B, } \ldots \tag{6.4-3}$$

where p_i^* is the vapor pressure of component i at the bubble-point temperature. Moreover, since we have assumed that only A, B, C, . . . are present in the system, the sum of the partial pressures must be the total system pressure, P; hence,

$$P = x_{\text{A}} p_{\text{A}}^*(T_{\text{bp}}) + x_{\text{B}} p_{\text{B}}^*(T_{\text{bp}}) + \cdots \tag{6.4-4}$$

Since the bubble-point temperature is the only unknown, it may be calculated using Excel's Goal Seek or Solver as the value of T_{bp} that satisfies this equation; all that is needed is a set of relationships for $p_i^*(T)$, such as the Antoine equation for each species. Once T_{bp} is known, the composition of the vapor phase can easily be determined by evaluating the partial pressures of each component from Equation 6.4-3 and determining each vapor–phase mole fraction as $y_i = p_i/P$.

The pressure at which the first vapor forms when a liquid is decompressed at a constant temperature is the **bubble-point pressure** of the liquid at the given temperature. Equation 6.4-4 can be used to determine such a pressure for a liquid mixture for which Raoult's law applies to all species at a specific temperature, and the mole fractions in the vapor in equilibrium with the liquid can then be determined as

$$y_i = \frac{p_i}{P_{\text{bp}}} = \frac{x_i p_i^*(T)}{P_{\text{bp}}} \tag{6.4-5}$$

The dew-point temperature of a gas (vapor) may be found using a method similar to that for bubble-point temperature estimation. Again, suppose a gas phase contains the condensable components A, B, C, . . . and a noncondensable component G at a fixed pressure P. Let y_i be the mole fraction of component i in the gas. If the gas mixture is cooled slowly to its dew point, T_{dp}, it will be in equilibrium with the first liquid that forms. Assuming that Raoult's law applies, the liquid-phase mole fractions may be calculated as

$$x_i = \frac{y_i P}{p_i^*(T_{\text{dp}})}, \qquad i = \text{A, B, C, } \ldots \quad \text{excluding } G \tag{6.4-6}$$

At the dew point of the gas mixture, the mole fractions of the liquid components (those that are condensable) must sum to 1:

$$x_{\text{A}} + x_{\text{B}} + x_{\text{C}} + \cdots = 1$$

$$\Downarrow \text{ Equation 6.4-6}$$

$$\frac{y_{\text{A}} P}{p_{\text{A}}^*(T_{\text{dp}})} + \frac{y_{\text{B}} P}{p_{\text{B}}^*(T_{\text{dp}})} + \cdots = 1 \tag{6.4-7}$$

The value of T_{dp} can be found once expressions for $p_i^*(T)$ have been substituted. The composition of the liquid phase may then be determined from Equation 6.4-6.

The **dew-point pressure**, which relates to condensation brought about by increasing system pressure at constant temperature, can be determined by solving Equation 6.4-7 for P:

$$P_{\text{dp}} = \frac{1}{\dfrac{y_{\text{A}}}{p_{\text{A}}^*(T)} + \dfrac{y_{\text{B}}}{p_{\text{B}}^*(T)} + \dfrac{y_{\text{C}}}{p_{\text{C}}^*(T)} + \cdots} \tag{6.4-8}$$

Liquid mole fractions may then be calculated from Equation 6.4-6 with T_{dp} replaced by the system temperature, T.

Example 6.4-3 Bubble- and Dew-Point Calculations

1. Calculate the temperature and composition of a vapor in equilibrium with a liquid that is 40.0 mole% benzene–60.0 mole% toluene at 1 atm. Is the calculated temperature a bubble-point or dew-point temperature?
2. Calculate the temperature and composition of a liquid in equilibrium with a gas mixture containing 10.0 mole% benzene, 10.0% toluene, and the balance nitrogen (which may be considered non-condensable) at 1 atm. Is the calculated temperature a bubble-point or dew-point temperature?
3. A gas mixture consisting of 15.0 mole% benzene, 10.0% toluene, and 75.0% nitrogen is compressed isothermally at 80°C until condensation occurs. At what pressure will condensation begin? What will be the composition of the initial condensate?

Solution Let A = benzene and B = toluene.

1. Equation 6.4-4 may be written in the form

$$f(T_{bp}) = 0.400p_A^*(T_{bp}) + 0.600p_B^*(T_{bp}) - 760 \text{ mm Hg} = 0$$

The solution procedure is to substitute for p_A^* and p_B^* either the Antoine equation (Table B.4) or the APEx function AntoineP, and then use any equation-solving program or (on a spreadsheet) Excel's Solver or the Goal Seek tool to determine the boiling point. The solution is $\boxed{T_{bp} = 95.1°C}$. At this temperature, Equation 6.4-1 yields

$$p_A = 0.400\,(1181 \text{ mm Hg}) = 472.5 \text{ mm Hg}$$
$$p_B = 0.600\,(479 \text{ mm Hg}) = 287.5 \text{ mm Hg}$$
$$\Downarrow$$
$$P = (472.5 + 287.5) \text{ mm Hg} = 760 \text{ mm Hg}$$

Furthermore, from Equation 6.4-5,

$$y_A = \frac{472.5}{760.0} = \boxed{0.622 \text{ mol benzene/mol}}$$
$$y_B = 1 - y_A = \boxed{0.378 \text{ mol toluene/mol}}$$

Since the composition of the liquid was given, this was a $\boxed{\text{bubble-point}}$ calculation.

2. Equation 6.4-7 may be written as

$$f(T_{dp}) = \frac{(0.100)(760 \text{ mm Hg})}{p_A^*(T_{dp})} + \frac{(0.100)(760 \text{ mm Hg})}{p_B^*(T_{dp})} - 1.00 = 0$$

A solution procedure similar to that in Part (1) leads to the result $\boxed{T_{dp} = 52.4°C}$, at which temperature $p_A^* = 297.4$ mm Hg and $p_B^* = 102.1$ mm Hg. Then, from Equation 6.4-6,

$$x_A = \frac{0.100(760 \text{ mm Hg})}{p_A^*(52.4°C)} = \boxed{0.256 \text{ mol benzene/mol}}$$
$$x_B = 1 - x_A = \boxed{0.744 \text{ mol toluene/mol}}$$

The composition of the vapor was given and that of the liquid was calculated; therefore, this was a $\boxed{\text{dew-point}}$ calculation.

3. The vapor pressures of benzene and toluene at 80°C are determined from the Antoine equation to be 757.7 mm Hg and 291.2 mm Hg, respectively. Assuming that nitrogen is insoluble in the condensate, Equation 6.4-8 gives

$$P = \frac{1}{(0.150/757.7\text{ mm Hg}) + (0.100/291.2\text{ mm Hg})} = \boxed{1847\text{ mm Hg}}$$

$$x_A = \frac{y_A P}{p_A^*} = \frac{0.150(1847\text{ mm Hg})}{757.7\text{ mm Hg}} = \boxed{0.366\text{ mol benzene/mol}}$$

$$x_B = 1 - x_A = \boxed{0.634\text{ mol toluene/mol}}$$

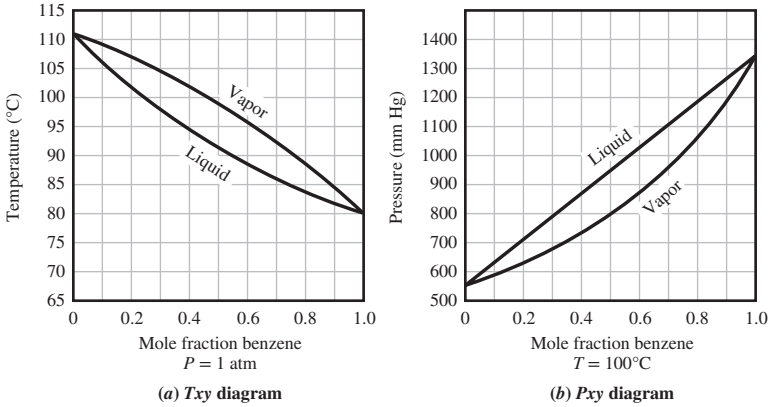
6.4d Graphical Representations of Vapor–Liquid Equilibrium

Suppose the bubble-point temperature T of a solution of two components—A (the more volatile component) and B—is determined at a fixed pressure P, and several values of liquid-phase mole fraction, x_A and the equilibrium vapor mole fraction, y_A are determined for each liquid composition. This information can be graphed in a ***Txy* diagram**, a plot of the equilibrium temperature versus the mole fraction of A, with curves being drawn for both the liquid phase (T versus x_A) and the vapor phase (T versus y_A). A plot of this type is shown in Figure 6.4-1*a* for the benzene-toluene system at $P = 1$ atm. A similar procedure that plots equilibrium pressure vs. mole fractions results in a ***Pxy* diagram** (Figure 6.4-1*b*).

Once you have a *Txy* diagram like that of Figure 6.4-1*a*, bubble- and dew-point calculations become trivial. To determine a bubble-point temperature for a given liquid composition, go to the liquid curve on the *Txy* diagram for the system pressure and read the desired temperature from the ordinate scale. (If you are not sure why this works, go back and consider again how the curve was generated.) You can then move horizontally to the vapor curve to determine the composition of the vapor in equilibrium with the given liquid at that temperature.

The dew point of a vapor mixture of A and B at P can be determined from the *Txy* diagram if there are no species other than A and B in the gas phase. Look up the specified mole fraction of A in the vapor phase, read the dew-point temperature from the corresponding ordinate value of the vapor curve, and move horizontally to the liquid curve and down to read the composition of the liquid in equilibrium with the vapor. If a noncondensable species is present in the gas phase, however, you must use Equation 6.4-6 to find the dew point, as in the previous example.

What happens as a liquid mixture is continuously vaporized is easily seen from the *Txy* diagram. Consider the benzene–toluene system again, and suppose heat is added to a 55 mole% benzene and 45 mole% toluene liquid mixture at a fixed pressure of 1 atm. As Figure 6.4-1*a* shows, the mixture will begin to boil at 90°C, and the vapor generated will contain 77% benzene. However, once a small amount of liquid has been vaporized, the remainder no longer contains



(*a*) ***Txy* diagram** (*b*) ***Pxy* diagram**

FIGURE 6.4-1 *Txy* and *Pxy* diagrams for benzene–toluene system.

55% benzene; it contains less, since the vapor produced is relatively rich in this component. Consequently, the temperature of the system steadily rises as more and more liquid is vaporized, and the compositions of both phases change continuously during the process.

Example 6.4-4 Bubble- and Dew-Point Calculations Using *Txy* Diagrams

1. Using the *Txy* diagram, estimate the bubble-point temperature and the equilibrium vapor composition associated with a 40 mole% benzene–60 mole% toluene liquid mixture at 1 atm. If the mixture is steadily vaporized until the remaining liquid contains 25% benzene, what is the final temperature?
2. Using the *Txy* diagram, estimate the dew-point temperature and the equilibrium liquid composition associated with a vapor mixture of benzene and toluene containing 40 mole% benzene at 1 atm. If condensation proceeds until the remaining vapor contains 60% benzene, what is the final temperature?

Solution

1. From Figure 6.4-1*a*, for $x_B = 0.40$, $\boxed{T_{bp} \approx 95°C}$ and $\boxed{y_B \approx 0.62}$. (This matches the result of the much lengthier solution of the previous example.) When $x_B = 0.25$, $\boxed{T_{bp} \approx 100°C}$. The temperature thus rises by 5°C as the vaporization proceeds.
2. From Figure 6.4-1*a*, for $y_B = 0.40$, $\boxed{T_{dp} \approx 102°C}$ and $\boxed{x_B \approx 0.20}$. When $y_B = 0.60$, $\boxed{T_{bp} \approx 96°C}$.

Note: The precision associated with *Txy* and *Pxy* diagrams is less than that of numerical calculations, as reflected in this example by the use of the ≈. However, the ease of following the process path makes the diagrams quite useful.

The term "boiling" is sometimes incorrectly used to describe any process involving the transition from liquid to vapor. In fact, boiling refers to a specific type of vaporization process in which vapor bubbles form at a heated surface and escape from the liquid; it does *not* refer to molecular evaporation of liquid from a gas–liquid interface, which may occur at temperatures below the boiling point. (Recall your experience with leaving a container of liquid open to the atmosphere and finding the liquid partially or completely evaporated on your return.)

In our discussion of single-component systems, we considered the case of a liquid being heated in a container exposed to the atmosphere and observed that the liquid boils at a temperature at which the vapor pressure of the liquid equals the total pressure of the atmosphere above it. A similar phenomenon occurs for liquid mixtures. If a mixture is heated slowly in an open container, vapor bubbles will form at the heated surface and emerge into the gas phase when the vapor pressure of the liquid equals the pressure above the liquid.[6] Some reflection should convince you that the temperature at which this occurs is the bubble point of the liquid at that pressure. For a liquid mixture that follows Raoult's law, the boiling point may therefore be determined *approximately* from Equation 6.4-9.

$$x_A p_A^*(T_{bp}) + x_B p_B^*(T_{bp}) + \cdots = P \tag{6.4-9}$$

Example 6.4-5 Boiling Point of a Mixture

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distillation column
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A mixture that is 70 mole% benzene and 30 mole% toluene is to be distilled in a batch distillation column. The column startup procedure calls for charging the reboiler at the base of the column and slowly adding heat until boiling begins. Estimate the temperature at which boiling begins and the initial composition of the vapor generated, assuming the system pressure is 760 mm Hg.

Solution

From the *Txy* diagram, the mixture will boil at approximately $\boxed{87°C}$. The initial vapor composition is approximately $\boxed{88 \text{ mole\% benzene and } 12 \text{ mole\% toluene}}$.

[6] This is only an approximation, albeit generally a good one. In fact, the vapor pressure must be slightly greater than the gas-phase pressure to overcome the effects of liquid surface tension and the hydrostatic head of liquid at the heated surface.

We conclude this discussion with one final reminder. The vapor–liquid equilibrium calculations we have shown in Section 6.4c are based on the ideal-solution assumption and the corresponding use of Raoult's law. Many commercially important systems involve nonideal solutions, or systems of immiscible or partially miscible liquids, for which Raoult's law is inapplicable and the *Txy* diagram looks nothing like the one shown for benzene and toluene. Calculations for systems of this sort are considered in texts on phase-equilibrium thermodynamics.

Test Yourself

(Answers, p. 657)

1. What is the bubble point of a liquid mixture at a given pressure? What is the dew point of a vapor mixture at a given pressure?
2. At what temperature will an equimolar liquid mixture of benzene and toluene begin to boil at 1 atm? What is the mole fraction of benzene in the first bubble?
3. At what temperature will an equimolar vapor mixture of benzene and toluene at 1 atm begin to condense? What is the mole fraction of benzene in the first drop? What happens to the system temperature as the condensation proceeds?
4. Would you expect the bubble-point temperature of a liquid mixture to increase, decrease, or remain the same as the pressure increases? What about the dew-point temperature of a vapor mixture?
5. When you raise a liquid to its boiling point, the pressure beneath the liquid surface where the bubbles form is different from the gas-phase pressure (why?), so that the boiling does not take place at precisely the calculated temperature. Explain. If the bottom of a vat of water is heated on a day when atmospheric pressure is 1 atm and the height of the water is 5 ft, how would you estimate the boiling temperature?
6. Why does determination of T_{bp} from Equation 6.4-4 or T_{dp} from Equation 6.4-8 involve a trial-and-error calculation?

6.5 SOLUTIONS OF SOLIDS IN LIQUIDS

6.5a Solubility and Saturation

The **solubility** of a solid in a liquid is the maximum amount of that substance that can be dissolved in a specified amount of the liquid at equilibrium. This physical property varies considerably from one solute–solvent pair to another: for example, 100 g of water at 20°C can dissolve 222 g of $AgNO_3$, 0.003 g of $AgCO_3$, and 0.00002 g of AgBr. The limit may also depend strongly on temperature: the solubility of $AgNO_3$ in 100 g of water increases from 222 g at 20°C to 952 g at 100°C. *Perry's Chemical Engineers' Handbook* (see Footnote 1) on pp. 2-7 through 2-47 and 2-126 through 2-129 gives the solubilities of many substances in water, ethyl alcohol, and diethyl ether at specified temperatures.

A solution that contains as much of a dissolved species as it can *at equilibrium* is said to be **saturated** with that species. *A solution in equilibrium with solid solute must be saturated with that solute; if it were not, more solute would dissolve*.

If a saturated solution is cooled, the solubility of the solute generally (but not always) decreases; in order for the cooled solution to return to equilibrium, some solute must come out of solution as solid. The rate at which solid comes out of solution may be slow, however, so that a metastable condition can exist in which the concentration of the solute is higher than the equilibrium value at the solution temperature. Under such conditions, the solution is said to be **supersaturated**, and the difference between actual and equilibrium concentrations is referred to as **supersaturation**. All problems involving solid–liquid separations in this text assume that equilibrium exists between the solid and liquid phases, so that supersaturation need not be considered.

Example 6.5-1 Crystallization and Filtration

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crystallizer, filter, dryer
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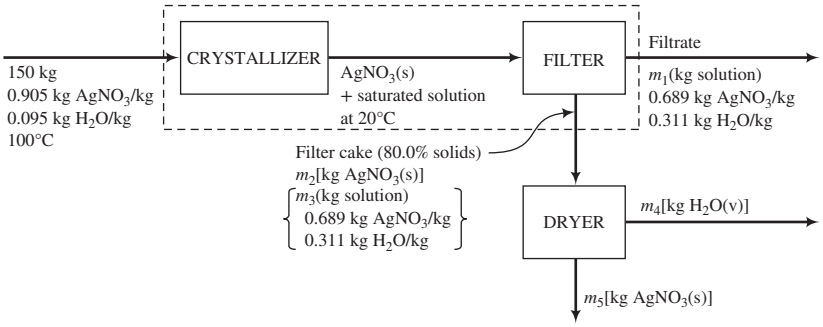
One hundred fifty kilograms of a saturated aqueous solution of $AgNO_3$ at 100°C is cooled to 20°C, thereby forming $AgNO_3$ crystals, which are filtered from the remaining solution. The wet filter cake, which contains 80.0% solid crystals and 20.0% saturated solution by mass, is sent to a dryer in which the remaining water is vaporized. Calculate the fraction of the $AgNO_3$ in the feed stream eventually recovered as dry crystals and the amount of water that must be removed in the drying stage.

Solution

Basis: 150 kg Feed

Both the filtrate and the liquid retained in the filter cake are in equilibrium with solid $AgNO_3$ crystals and must therefore be saturated with $AgNO_3$ at 20°C. The compositions of saturated solutions of silver nitrate at 100°C and 20°C are given at the beginning of this section and are used in the flowchart.



Solubilities:

$$100°C: \quad \frac{952 \text{ g } AgNO_3}{100 \text{ g } H_2O} \Longrightarrow \frac{952 \text{ g } AgNO_3}{(100+952) \text{ g}} = 0.905 \text{ g } AgNO_3/\text{g}$$

$$\Downarrow$$

$$0.095 \text{ g } H_2O/\text{g}$$

$$20°C: \quad \frac{222 \text{ g } AgNO_3}{100 \text{ g } H_2O} \Longrightarrow \frac{222 \text{ g } AgNO_3}{(100+222) \text{ g}} = 0.689 \text{ g } AgNO_3/\text{g}$$

$$\Downarrow$$

$$0.311 \text{ g } H_2O/\text{g}$$

Degree-of-Freedom Analysis:

Since we know a great deal about the feed to the crystallizer and the two streams leaving the filter, we first determine the degrees of freedom of the process subsystem that includes both units (shown as a dashed rectangle in the flowchart).

$$\begin{aligned} &3 \text{ unknown variables } (m_1, m_2, \text{ and } m_3) \\ &-2 \text{ material balances } (AgNO_3 \text{ and } H_2O) \\ &-1 \text{ percentage by mass of solids in the filter cake } (80.0\% \text{ solids}) \\ &= 0 \text{ degrees of freedom} \end{aligned}$$

We may therefore solve for the three unknowns associated with this subsystem. Overall system balances or balances around the dryer may then be used to solve for the remaining two system unknowns (m_4 and m_5), following which the fractional recovery of silver nitrate and the quantity of water evaporated in the dryer may be calculated.

Composition of the Filter Cake: $\quad m_2 = 0.800(m_2 + m_3) \Longrightarrow m_2 = 4m_3$

H_2O Balance about the Crystallizer and Filter: $\quad (0.095 \times 150) \text{ kg } H_2O = 0.311m_1 + 0.311m_3$

Mass Balance about the Crystallizer and Filter: $\quad 150 \text{ kg} = m_1 + m_2 + m_3$

The simultaneous solution of these three equations yields

$$m_1 = 20\text{ kg}$$
$$m_2 = 104\text{ kg}$$
$$m_3 = 26\text{ kg}$$

Overall $AgNO_3$ Balance: $(0.905 \times 150)\text{ kg } AgNO_3 = 0.689m_1 + m_5$

$$\Downarrow\ m_1 = 20\text{ kg}$$

$$m_5 = 122\text{ kg } AgNO_3 \text{ crystals recovered}$$

Percentage Recovery: $$\frac{122\text{ kg } AgNO_3 \text{ recovered}}{(0.905 \times 150)\text{ kg } AgNO_3 \text{ fed}} \times 100\% = \boxed{89.9\%}$$

Overall Mass Balance: $150\text{ kg} = m_1 + m_4 + m_5$

$$\Downarrow\ m_1 = 20\text{ kg}$$
$$\Downarrow\ m_5 = 122\text{ kg}$$

$$m_4 = \boxed{8\text{ kg } H_2O \text{ removed in the dryer}}$$

6.5b Solid Solubilities and Hydrated Salts

The Gibbs phase rule shows that specifying temperature and pressure for a two-component system at equilibrium containing a solid solute and a liquid solution determines the values of all other intensive variables. (Verify this statement.) Furthermore, because the properties of liquids and solids are only slightly affected by pressure, a single plot of solubility (an intensive variable) versus temperature may be applicable over a wide pressure range.

The solubility plots shown in Figure 6.5-1 illustrate how the effect of temperature on solubility can vary from system to system. Increasing the temperature from 0°C to 100°C barely changes NaCl solubility but increases the solubility of KNO_3 by more than a factor of 10. For Na_2SO_4, solubility increases up to about 40°C and decreases thereafter.

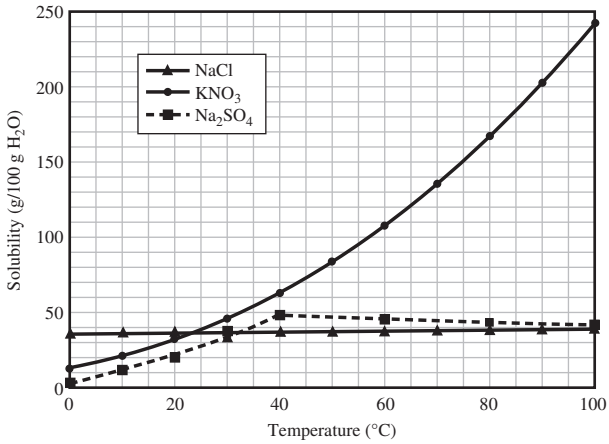


FIGURE 6.5-1 Solubilities of inorganic solutes.

Example 6.5-2 Material Balances on a Crystallizer

Equipment Encyclopedia
crystallizer
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An aqueous potassium nitrate solution containing 60.0 wt% KNO_3 at 80°C is fed to a cooling crystallizer in which the temperature is reduced to 40°C. Determine the temperature at which the solution reaches saturation and the percentage of the potassium nitrate in the feed that forms crystals.

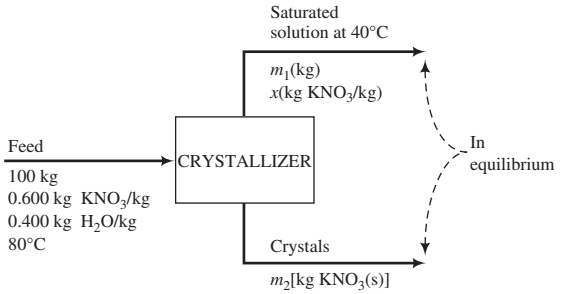
Solution

The feed concentration must be converted to a solute/solvent ratio to use Figure 6.5-1. Since 100.0 g of the solution contains 60.0 g KNO_3 and 40.0 g H_2O, the desired ratio is

$$\frac{60.0\text{ g KNO}_3}{40.0\text{ g H}_2\text{O}} = 1.50\,\frac{\text{g KNO}_3}{\text{g H}_2\text{O}} = \frac{150\text{ g KNO}_3}{100\text{ g H}_2\text{O}}$$

From Figure 6.5-1, the saturation temperature of this solution is $\boxed{74°\text{C}}$.

Here is a flowchart of the process for an assumed basis of 100 kg feed.



There are three unknowns on the chart (m_1, x, m_2). We will assume that the solution leaving the crystallizer is saturated at 40°C. Accordingly, the value of x may be determined from the known solubility of KNO_3 at that temperature, and the remaining two variables may be determined from material balances. From Figure 6.5-1, the solubility at 40°C is roughly 63 kg KNO_3/100 kg H_2O. The calculations follow.

$$x = \frac{63\text{ kg KNO}_3}{(63+100)\text{kg solution}} = 0.386\text{ kg KNO}_3/\text{kg}$$

H_2O Balance:

$$\frac{100\text{ kg}}{}\left|\frac{0.400\text{ kg H}_2\text{O}}{\text{kg}}\right. = \frac{m_1\text{(kg)}}{}\left|\frac{(1-0.386)\text{ kg H}_2\text{O}}{\text{kg}}\right. \Longrightarrow m_1 = 65.1\text{ kg}$$

Mass Balance:

$$100\text{ kg} = m_1 + m_2 \xrightarrow{m_1\,=\,65.1\text{ kg}} m_2 = 34.9\text{ kg KNO}_3\text{(s)}$$

The percentage of the potassium nitrate in the feed that crystallizes is therefore

$$\frac{34.9\text{ kg KNO}_3\text{ crystallized}}{60.0\text{ kg KNO}_3\text{ fed}} \times 100\% = \boxed{58.2\%}$$

The solid crystals that formed in the preceding example consisted of *anhydrous* (water-free) potassium nitrate. When certain solutes crystallize from aqueous solutions, the crystals are **hydrated salts**, containing water molecules bonded to solute molecules (**water of hydration**). The number of water molecules associated with each solute molecule may vary with the crystallization temperature.

For example, when sodium sulfate crystallizes from aqueous solution above 40°C the equilibrated crystals that form are anhydrous Na_2SO_4, while below 40°C each molecule of Na_2SO_4 that crystallizes has 10 molecules of water associated with it. The hydrated salt, $Na_2SO_4 \cdot 10\,H_2O(s)$, is called *sodium sulfate decahydrate*. The change from the anhydrous to the hydrated form

TABLE 6.5-1 Hydrated $MgSO_4$ Salts

Form	Name	Wt% $MgSO_4$	Conditions
$MgSO_4$	Anhydrous magnesium sulfate	100.0	> 100°C
$MgSO_4 \cdot H_2O$	Magnesium sulfate monohydrate	87.0	67 to 100°C
$MgSO_4 \cdot 6H_2O$	Magnesium sulfate hexahydrate	52.7	48 to 67°C
$MgSO_4 \cdot 7H_2O$	Magnesium sulfate heptahydrate	48.8	2 to 48°C
$MgSO_4 \cdot 12H_2O$	Magnesium sulfate dodecahydrate	35.8	−4 to 2°C

of the solid at 40°C is responsible for the discontinuity in the plot of Figure 6.5-1. Another solute that forms hydrated salts is magnesium sulfate, which can exist in five different forms in different temperature ranges. (See Table 6.5-1.)

Example 6.5-3 Production of a Hydrated Salt

Equipment Encyclopedia
crystallizer
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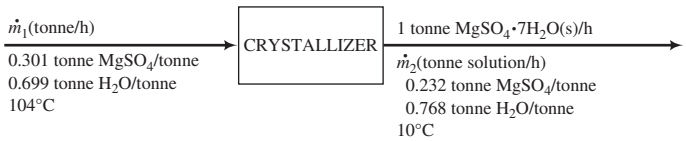
An aqueous solution of magnesium sulfate at 104°C containing 30.1 wt% $MgSO_4$ is fed to a cooling crystallizer that operates at 10°C. The stream leaving the crystallizer is a slurry of solid magnesium sulfate heptahydrate particles [$MgSO_4 \cdot 7H_2O$(s)] suspended in a liquid solution. Solubility data for magnesium sulfate [*Perry's Chemical Engineers' Handbook* (see Footnote 1), p. 18-40] show that a saturated solution at 10°C contains 23.2 wt% $MgSO_4$. Determine the rate at which solution must be fed to the crystallizer to produce 1 metric ton (1 tonne, 1000 kg) of magnesium sulfate heptahydrate per hour.

Solution

Basis: 1 tonne $MgSO_4 \cdot 7H_2O$(s) Produced/h

We assume that the solution leaving the crystallizer is in equilibrium with the solid crystals and is therefore saturated with $MgSO_4$. A flowchart of the crystallizer follows:



There are two unknowns on the chart ($\dot{m}_1$ and $\dot{m}_2$) and two independent molecular species on which balances may be written ($MgSO_4$ and H_2O), so that the problem can be solved. The atomic weights on the inside back cover may be used to show that the molecular weight of anhydrous magnesium sulfate is 120.4 and that of the heptahydrate salt is 246.4. The balances follow.

Total Mass Balance:

$$\dot{m}_1 = 1 \text{ tonne/h} + \dot{m}_2$$

$MgSO_4$ Balance:

$$0.301\dot{m}_1 \left(\frac{\text{tonne } MgSO_4}{\text{h}}\right) = \frac{1 \text{ tonne } MgSO_4 \cdot 7H_2O}{\text{h}} \left|\frac{120.4 \text{ tonne } MgSO_4}{246.4 \text{ tonne } MgSO_4 \cdot 7H_2O}\right. + \frac{\dot{m}_2(\text{tonne solution/h})}{} \left|\frac{0.232 \text{ tonne } MgSO_4}{\text{tonne solution}}\right.$$

Solving these two equations simultaneously yields $\boxed{\dot{m}_1 = 3.71 \text{ tonne/h}}$ and $\dot{m}_2 = 2.71$ tonne/h.

Test Yourself

(Answers, p. 657)

1. Solid crystals of sodium chloride are slowly added to 1000 kg of water at 60°C. After each small addition, the mixture is stirred until the salt dissolves, and then more salt is added. How much salt can be dissolved if the temperature is maintained at 60°C? What will happen if more than this quantity of salt is added? (Refer to Figure 6.5-1.)

2. An aqueous solution contains 50.0 wt% KNO_3 at 80°C. To what temperature would this solution have to be cooled before solid crystals begin to form? What happens as the solution is cooled to progressively lower temperatures?
3. What do the terms *hydrated salt, water of hydration*, and *anhydrous salt* mean? What would $MgSO_4 \cdot 4H_2O(s)$ probably be called if this species were found in nature? (*Hint:* Think about CCl_4.)
4. Given that the molecular weight of $MgSO_4$ is 120.4, what is the mass fraction of $MgSO_4$ in magnesium sulfate monohydrate?
5. Why is there a slope discontinuity at 40°C in the Na_2SO_4 solubility curve of Figure 6.5-1?

6.5c Colligative Solution Properties

Physical properties of a solution generally differ from the same properties of the pure solvent. Under certain conditions, the changes in the values of several properties—such as vapor pressure, boiling point, and freezing point—depend only on the concentration of solute in the solution, and not on what the solute and solvent are. Such properties are referred to as **colligative solution properties**. (A fourth colligative property—osmotic pressure—will not concern us in this text.)

An understanding of colligative properties is important in the determination of the operating conditions of certain processes. For example, a process can be designed to recover pure water by evaporation or freezing of seawater. In the first instance, pure water is recovered by condensation of vapor from the evaporator, while in the second it is recovered by separating and melting ice from the freezer. An engineer who intends to design or operate an evaporator or an ice crystallizer clearly must know the temperature at which the phase transition takes place—the boiling point in the first case, the freezing point in the second. In addition, measured values of colligative solution properties are often used to deduce properties of either the solvent or the solute, such as molecular weight, which cannot easily be determined by more direct means.

This section presents an introductory view of colligative properties, considering only the simple case of a solution in which the solute is nonvolatile (i.e., has a negligible vapor pressure at the solution temperature) and the dissolved solute neither dissociates (which rules out ionizing acids, bases, and salts) nor reacts with the solvent. Discussions of more complex systems can be found in most physical chemistry texts.

Consider a solution in which the solute mole fraction is x and the vapor pressure of the pure solvent at the solution temperature is p_s^*. Applying Raoult's law (Equation 6.4-1) to the solution, we obtain for the partial pressure of the solvent

$$p_s(T) = (1 - x)p_s^*(T) \tag{6.5-1}$$

If the liquid is pure solvent ($x = 0$), this equation predicts that the partial pressure of the solvent vapor equals the vapor pressure of the solvent, as we would expect. Since the solute is nonvolatile, the solvent is the only component of the liquid solution that is also in the vapor. The pressure exerted by this vapor is commonly referred to as the *effective* solvent vapor pressure:

$$(p_s^*)_e = p_s = (1 - x)p_s^* \tag{6.5-2}$$

Since x—and hence $(1 - x)$—is less than one, the effect of the solute is to lower the effective solvent vapor pressure. The **vapor pressure lowering**, defined as the difference between the vapor pressure of the pure component and the effective vapor pressure of the solvent, is

$$\Delta p_s^* = p_s^* - (p_s^*)_e = xp_s^* \tag{6.5-3}$$

The simplicity and generality of Equation 6.5-3 are surprising. According to the equation, if a solution contains 20 mole% solute, then the solvent partial pressure is 80% of the vapor pressure of pure solvent at the system temperature, regardless of the temperature, the pressure, *and what the solute and solvent are*. (Hence, vapor pressure lowering is a colligative property, by definition.) The only stipulations are that Raoult's law holds and the solute is nonvolatile, nonreactive, and nondissociative.

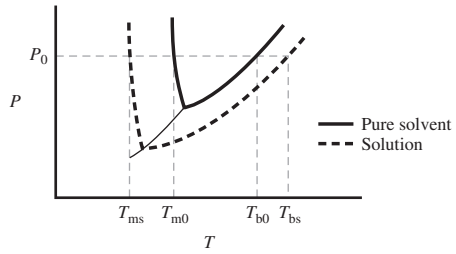


FIGURE 6.5-2 Phase-equilibrium curves for pure solvent and solution.

The lowering of solvent vapor pressure has two important consequences. *The solvent in a solution at a given pressure boils at a higher temperature and freezes at a lower temperature than does the pure solvent at the same pressure*. The validity of these statements can be seen by referring to Figure 6.5-2, a phase diagram for an arbitrary solute–solvent system. Shown on this figure are the vapor–liquid and solid–liquid equilibrium curves for a pure solvent (solid curves) and for a solution of a fixed solute concentration (dashed curves). The solution vapor–liquid and solid–liquid equilibrium curves lie below the solvent curves, reflecting the fact that the effective vapor pressure at a given temperature and freezing point at a given pressure for the solution are lower than those of the pure solvent. The higher the solute concentration, the greater is the separation between the pure solvent and the solution curves.

The effect of the solute on the solution boiling point is easy to see from the diagram. Recall that the boiling point of a liquid at a given pressure is the intersection of a horizontal line at that pressure with the vapor–liquid equilibrium curve. At pressure P_0, the pure solvent boils at temperature T_{b0}, while the solution boils at a higher temperature, T_{bs}.

The change in the solvent freezing point is a little less obvious. First, consider the triple point—the intersection of the solid–vapor and the liquid–vapor equilibrium curves. It is clear from Figure 6.5-2 that the effect of the vapor pressure lowering is to lower the triple point of the solution relative to pure solvent. If in addition the solid–liquid equilibrium curve for the solution is (like that for the pure solvent) almost vertical, then the freezing point at an arbitrary pressure P_0 also drops—on the diagram, from T_{m0} for the pure solvent to T_{ms} for the solution.

Since we know how the solution vapor pressure varies with concentration (the relationship being given by Equation 6.5-2) and temperature (through the Clausius–Clapeyron equation, Equation 6.1-3), we can determine the relationships between concentration and both boiling point elevation and freezing point depression. The relationships are particularly simple for dilute solutions ($x \to 0$, where x is solute mole fraction).

$$\Delta T_b = T_{bs} - T_{b0} = \frac{RT_{b0}^2}{\Delta \hat{H}_v} x \tag{6.5-4}$$

$$\Delta T_m = T_{m0} - T_{ms} = \frac{RT_{m0}^2}{\Delta \hat{H}_m} x \tag{6.5-5}$$

In these equations, $\Delta \hat{H}_v$ refers to the heat of vaporization of the pure solvent at its boiling point T_{b0}, and $\Delta \hat{H}_m$ denotes the heat of fusion of the pure solvent at its melting point T_{m0}. These properties of the solvent can be looked up in data tables, such as Table B.1 of this text. Their physical significance is discussed in Chapter 8. The derivation of Equation 6.5-4 is dealt with in Problem 6.95 at the end of this chapter.

Since the coefficients of x in these two equations are constant, it follows that for dilute solutions of nonvolatile, nonreactive, nondissociative solutes, both boiling point elevation and freezing point depression vary linearly with solute mole fraction.

The next example shows applications of Equations 6.5-2 through 6.5-5 to the determination of a vapor pressure and phase-transition temperatures for a known solution concentration, and to the calculation of a solution composition and solute molecular weight from a measured colligative property.

Test Yourself

(Answers, p. 657)

1. What is a colligative solution property? Name three of them.
2. The vapor pressure of a solvent at 120°C is 1000 mm Hg. A solution contains 15 mole% of a solute in this solvent at 120°C. If the behavior described in this section is followed, what is the effective vapor pressure of the solvent? What conditions must be met for your answer to be valid?
3. The solution described in question 2 is heated to a temperature at which boiling occurs at a total pressure of 1000 mm Hg. Is the boiling temperature greater than, less than, or equal to 120°C? What is the vapor pressure of the pure solvent at the solution boiling point?
4. Explain why salt is scattered on roads and sidewalks on a snowy day.
5. Explain why antifreeze (which you may think of as a nonvolatile solute) is a useful addition to an automobile radiator in both the cold of winter and the heat of summer.

Example 6.5-4 Colligative Property Calculations

A solution of 5.000 g of a solute in 100.0 g of water is heated slowly at a constant pressure of 1.00 atm and is observed to boil at 100.421°C. Estimate the molecular weight of the solute, the effective solvent vapor pressure at 25°C, and the solution freezing point at 1 atm. The necessary properties of water can be found in Table B.1.

Solution If the values of the normal boiling point and heat of vaporization of pure water (from Table B.1) and the gas constant are substituted into Equation 6.5-4, the result is

$$\Delta T_b(\mathrm{K}) = \frac{[8.314\ \mathrm{J/(mol\cdot K)}](373.16\ \mathrm{K})^2 x}{40{,}656\ \mathrm{J/mol}} = 28.5x$$

From the measured boiling point elevation, $\Delta T_b = 0.421$ K, we may deduce that the mole fraction of the solute in the solution is $x = 0.421/28.5 = 0.0148$. But since the solution is known to contain $(5.000/M_s)$ mol of solute, where M_s is the solute molecular weight, and 100.0 g/18.016 g/mol = 5.551 mol of water, we may write

$$0.0148 = (5.000\ \mathrm{g}/M_s)/(5.000\ \mathrm{g}/M_s + 5.551\ \mathrm{mol})$$

$$\Downarrow$$

$$\boxed{M_s = 60.1\ \mathrm{g/mol}}$$

From Equation 6.5-2 the effective solvent vapor pressure at 25°C is determined from the vapor pressure of pure water at this temperature (found in Table B.3) as

$$(p_s^*)_e = (1.000 - 0.0148)(23.756\ \mathrm{mm\ Hg}) = \boxed{23.40\ \mathrm{mm\ Hg}}$$

Finally, substituting values of the melting point and heat of fusion of water (from Table B.1) and the gas constant into Equation 6.5-5, we obtain

$$\Delta T_m = \frac{[8.314\ \mathrm{J/(mol\cdot K)}](273.16\ \mathrm{K})^2(0.0148)}{(6009.5\ \mathrm{J/mol})} = 1.53\ \mathrm{K} = 1.53°\mathrm{C}$$

$$\Downarrow$$

$$T_{ms} = (0.000 - 1.53)°\mathrm{C} = \boxed{-1.53°\mathrm{C}}$$

CREATIVITY EXERCISE

A solution contains an unknown amount of table salt dissolved in water. List as many ways as you can think of to measure or estimate the concentration of salt in the solution without leaving the kitchen of your home. The only instruments you are allowed to bring home from work are a thermometer that covers the range −10°C to 120°C and a small laboratory balance. (*Example:*

Make up several solutions with known salt concentrations, and compare their tastes with that of the unknown solution.)

6.6 EQUILIBRIUM BETWEEN TWO LIQUID PHASES

6.6a Miscibility and Distribution Coefficients

Equipment Encyclopedia
extractor, settler

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If water and methyl isobutyl ketone (MIBK) are mixed at 25°C, a single phase results if the mixture contains more than either 98% water or 97.7% MIBK by mass; otherwise, the mixture separates into two liquid phases, one of which contains 98% H_2O and 2% MIBK and the other 97.7% MIBK and 2.3% H_2O. Water and MIBK are examples of **partially miscible** liquids; they would be termed **immiscible** if one phase contained a negligible amount of water and the other a negligible amount of MIBK.

If a third substance is added to a two-phase liquid mixture, it distributes itself according to its relative solubility in each phase. For example, acetone is soluble in both water and chloroform—two nearly immiscible liquids—but much more so in chloroform. If a mixture of acetone and water is contacted with chloroform, a substantial portion of the acetone enters the chloroform-rich phase. Therefore, a partial separation of the acetone from water may be accomplished by allowing the mixture to settle and separating the two phases. This example illustrates the separation process of **liquid extraction**.

Suppose A and S are two nearly immiscible liquids and B is a solute distributed between the phases of an A–S mixture. The **distribution coefficient** (also known as **partition ratio**) of component B is the ratio of the mass fraction of B in the S phase to that in the A phase. *Perry's Chemical Engineers' Handbook* (see Footnote 1) on pp. 15-29 through 15-31 lists distribution coefficients for a number of ternary (three-component) liquid systems. Example 6.6-1 illustrates the use of this physical property in a material balance calculation.

Example 6.6-1 Extraction of Acetone from Water

Equipment Encyclopedia
extractor

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Two hundred cubic centimeters of an acetone–water mixture that contains 10.0 wt% acetone is mixed with 400.0 cm^3 of chloroform at 25°C, and the phases are then allowed to settle. What percentage of the acetone is transferred from the water to the chloroform?

Solution **Basis: Given Quantities**

The densities of the pure substances are given in Table B.1:

Acetone (A)	0.792 g/cm^3
Chloroform (C)	1.489 g/cm^3
Water (W)	1.000 g/cm^3

Since density data for the acetone–water system are not readily available, let us use Equation 5.1-1 to estimate the density of the feed solution:

$$\frac{1}{\overline{\rho}} = \frac{x_A}{\rho_A} + \frac{x_W}{\rho_W} = \left(\frac{0.100}{0.792} + \frac{0.900}{1.000}\right)\frac{\text{cm}^3}{\text{g}} = 1.026\,\frac{\text{cm}^3}{\text{g}}$$

$$\Downarrow$$

$$\overline{\rho} = 0.974\ \text{g/cm}^3$$

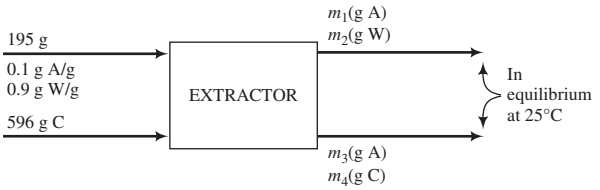
The mass of the solution fed is therefore

$$200.0\ \text{cm}^3 \left|\frac{0.974\ \text{g}}{\text{cm}^3}\right. = 195\ \text{g}$$

and that of the chloroform is

$$400.0\ \text{cm}^3 \left|\frac{1.489\ \text{g}}{\text{cm}^3}\right. = 596\ \text{g}$$

Let us next assume that chloroform and water are immiscible. (How to deal with partial miscibility is discussed in Section 6.6b.) In drawing the flowchart for this problem, it is advisable to label the quantities of each component in each of the two output streams, rather than the total stream masses and component mass fractions. (Labeling in the latter manner results in having to solve four simultaneous equations in four unknowns.)



The distribution coefficient for the A-C-W system is given on p. 15-12 of *Perry's Chemical Engineers' Handbook* (see Footnote 1) as 1.72. If x denotes mass fraction of acetone,

$$K = \frac{(x)_{\text{C phase}}}{(x)_{\text{W phase}}} = \frac{m_3/(m_3 + m_4)}{m_1/(m_1 + m_2)} = 1.72 \qquad \textbf{(6.6-1)}$$

This provides one equation in the four unknowns m_1, m_2, m_3, and m_4. The others are provided by material balances.

C Balance: $596\text{ g} = m_4$

W Balance: $(0.900)(195\text{ g}) = m_2 \Longrightarrow m_2 = 175.5\text{ g}$

A Balance: $(0.100)(195\text{ g}) = m_1 + m_3$

Substituting the known values of m_2 and m_4 into the first equation yields (with the acetone balance) two equations in two unknowns, which may be solved to obtain

$m_1 = 2.7$ g A in water phase

$m_3 = 16.8$ g A in chloroform phase

The percentage of acetone transferred is therefore

$$\frac{16.8\text{ g acetone in chloroform phase}}{(0.100 \times 195)\text{ g acetone fed}} \times 100\% = \boxed{86.1\%}$$

In practice, extraction is often carried out in several consecutive stages, with the solution leaving each stage being contacted with additional solvent in the next stage. If enough stages are used, almost complete transfer of the solute can be achieved. Problem 6.99 at the end of this chapter illustrates this method of operation.

Test Yourself

(Answers, p. 657)

1. What is liquid extraction? What is a distribution coefficient?

2. The distribution coefficient for the system water–acetic acid–vinyl acetate is

$$\frac{\text{mass fraction of acetic acid in vinyl acetate}}{\text{mass fraction of acetic acid in water}} = 0.294$$

Is acetic acid more or less soluble in vinyl acetate than in water? If you use vinyl acetate to extract a large portion of the acetic acid in an aqueous solution, how would the relative masses of the two phases compare ($m_{VA} \ll m_W$, $m_{VA} \approx m_W$, or $m_{VA} \gg m_A$)?

6.6b Phase Diagrams for Partially Miscible Ternary Systems

The behavior of partially miscible ternary (three-component) systems may be represented on a **triangular phase diagram**, which may take the form of an equilateral triangle (as shown in Figure 6.6-1*a* for H_2O–MIBK–acetone at 25°C) or a right triangle (as shown in Figure 6.6-1*b*).

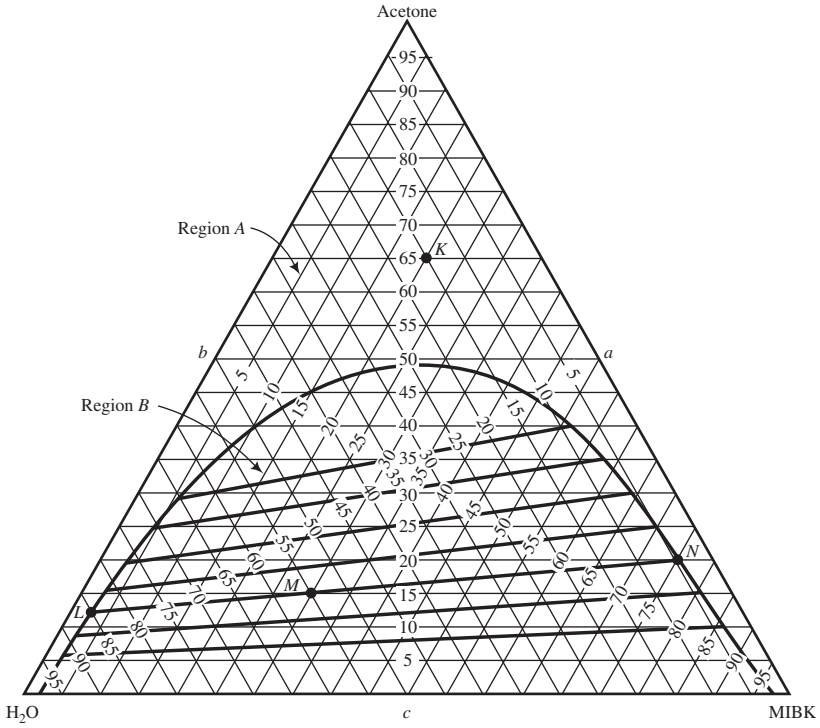


FIGURE 6.6-1
Triangular phase diagrams for water–acetone–methyl isobutyl ketone (composition in wt%) at 25°C. (a) equilateral triangle, (b) right triangle. (Based on D. F. Othmer, R. E. White, and E. Trueger, *Ind. Eng. Chem.* 33: 1240, 1941.)

The latter is easier to construct on rectangular axes, but the two forms are equally easy to use. In both cases, each apex of the triangle represents a single component and edges represent binary solutions. For example, edge *b* on Figure 6.6-1 represents solutions of H_2O and acetone. Point *K* represents a mixture that is 20.0 wt% MIBK, 65.0% acetone, and 15.0% water. Any mixture whose composition falls in region *A*, such as at point *K*, is a single-phase liquid, whereas any mixture whose *overall* composition falls in region *B* separates into two phases.

The lines shown within region *B*—called **tie lines**—connect compositions of the two liquid phases in equilibrium with each other. For example, if MIBK, water, and acetone are blended so that a mixture with overall composition at point *M* (55.0 wt% water, 15.0% acetone, 30.0% MIBK) results, the mixture separates into phases having compositions given by points *L* (85 wt% water, 12% acetone, 3% MIBK) and *N* (4 wt% water, 20% acetone, 76% MIBK). When a mixture does not fall on a tie line, interpolation between the lines is necessary to determine the composition of each phase.

The Gibbs phase rule demonstrates that a mixture of three components that forms two liquid phases at equilibrium has three degrees of freedom. (*Verify*.) If pressure (which generally has little effect on liquid properties) and temperature are fixed, one degree of freedom remains. Specifying the mole fraction of one of the components in one of the phases is therefore sufficient to determine the compositions of both phases. For example (referring to Figure 6.6-1), specifying that the weight fraction of acetone is 0.25 in the MIBK-rich phase fixes both the composition of that phase and the composition of the water-rich phase. (Verify this statement by determining both compositions.)

Test Yourself

(Answers, p. 657)

1. What is a tie line on a triangular phase diagram?
2. Show that a mixture with a composition of 4% acetone, 51% MIBK, and 45% H_2O separates into two phases. What is the composition of each phase? Calculate the ratio of the mass of the MIBK-rich phase to the mass of the H_2O-rich phase.

Example 6.6-2 Extraction of Acetone from Water: Use of the Phase Diagram

Equipment Encyclopedia
mixer-settler
@
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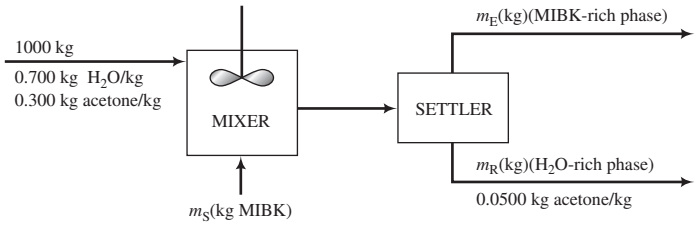
One thousand kilograms of a 30.0 wt% solution of acetone in water and a second stream of pure methyl isobutyl ketone (MIBK) is fed to a mixer. The mixture is then fed to a settler where two phases form and are withdrawn separately at 25°C. How much MIBK must be fed to the process to reduce the acetone concentration in the water-rich phase to 5.00 wt%, assuming that the fluids remain in the settler long enough for equilibrium to be achieved?



Solution Since the two product streams are in equilibrium, their compositions must lie on the phase envelope and must be connected by a tie line. Accordingly, the composition of m_R is 5% acetone, 93% H_2O, and 2% MIBK and that of m_E is 10% acetone, 87% MIBK, and 3% H_2O. Overall balances can now be used to determine m_E, m_R, and m_S.

Mass Balance: $m_S + 1000\,\text{kg} = m_E + m_R$

Acetone Balance: $(0.30)(1000\,\text{kg}) = 0.10m_E + 0.05m_R$

H_2O Balance: $(0.70)(1000\,\text{kg}) = 0.03m_E + 0.93m_R$

Solving these three equations yields (before rounding for significant figures)

$$m_E = 2667\,\text{kg}$$
$$m_R = 667\,\text{kg}$$

and

$$\boxed{m_S = 2334\,\text{kg MIBK}}$$

6.7 ADSORPTION ON SOLID SURFACES

Equipment Encyclopedia
adsorption column

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The attraction of chemical species in gases and liquids to the surfaces of solids is the basis of a number of separation processes. For example, baking soda or charcoal may be placed in a refrigerator to remove unacceptable odors, and compressed air may be dried and purified by passing it through a bed of calcium chloride to remove water vapor and then through a bed of activated carbon to separate hydrocarbons taken up by the air during compression. Each of these operations utilizes a solid with an extremely high surface area (e.g., about 800 m^2/g of activated carbon)[7] and takes advantage of the affinity of specific components in a fluid for the surface of a solid. The solid is known as an **adsorbent** and the component attracted to the solid surface is an **adsorbate**.

Adsorbate equilibrium data on a specific adsorbent are often taken at a specific temperature and are referred to as **adsorption isotherms**. These functions or plots relate X_i^*, the maximum mass of adsorbate i that can be held by a unit mass of the adsorbent, to c_i or p_i, the concentration or partial pressure of adsorbate i in the fluid contacting the solid.

Consider how an isotherm might be determined for the system carbon tetrachloride and activated carbon.

- Place a known mass of activated carbon in a chamber whose temperature is controlled at a specified value.
- Draw a vacuum in the chamber and then admit carbon tetrachloride vapor until a desired pressure is reached.
- Allow the system to come to equilibrium, read the equilibrium pressure, and determine the mass of carbon tetrachloride adsorbed by weighing the solid.
- Admit more carbon tetrachloride into the system and repeat the procedure.

Data resulting from a series of such experiments might appear as shown in Table 6.7-1.

TABLE 6.7-1 Equilibrium Data for CCl_4 Adsorbed on Activated Carbon at 34°C

p(mm Hg)	0	1.69	3.38	6.76	8.45	11.8	20.7	32.1	40.0	84.5	104	123	133
X^*(g CCl_4/g carbon)	0	0.07	0.14	0.27	0.34	0.48	0.57	0.63	0.68	0.70	0.71	0.71	0.71

[7] By way of comparison, the area of a baseball diamond is about 750 m^2 and a football field is 4180 m^2.

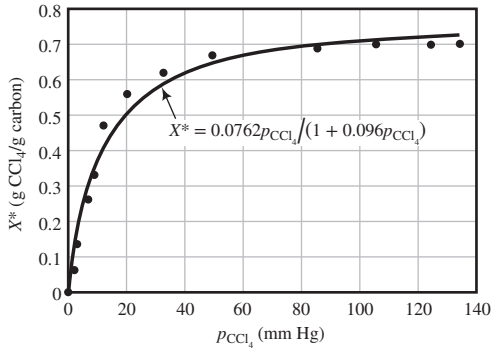


FIGURE 6.7-1 Langmuir adsorption isotherm for carbon tetrachloride on activated carbon at 34°C.

Chapter 16 of *Perry's Chemical Engineers' Handbook* (see Footnote 1) gives physical properties of several important adsorbents and several different expressions for adsorption isotherms. Equilibrium data for specific adsorbent–adsorbate systems may be found in published articles, adsorbent manufacturers' specification sheets, or company records. If no data can be found, isotherms must be obtained experimentally.

At low adsorbate partial pressures, isotherms may be linear:

$$X_i^* = Kc_i \qquad \text{or} \qquad X_i^* = K'p_i \tag{6.7-1}$$

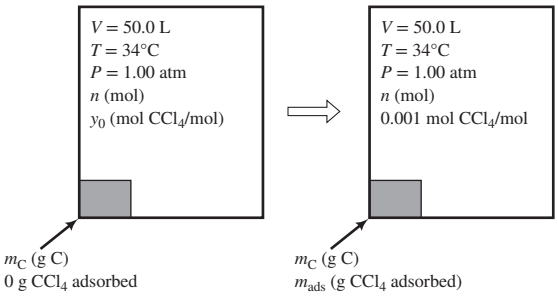
The **Langmuir isotherm** is a more complex expression that is valid for some systems over a wider range of adsorbate partial pressures or concentrations.

$$X_i^* = \frac{aK_L p_i}{1 + K_L p_i} \qquad \text{or} \qquad X_i^* = \frac{aK'_L c_i}{1 + K'_L c_i} \tag{6.7-2}$$

In these equations, a, K_L, and K'_L are parameters determined by fitting the equations to equilibrium data. Figure 6.7-1 shows the fit of the Langmuir isotherm (Equation 6.7-2) to the adsorption data in Table 6.7-1. The fitted parameter values are $a = 0.794$ g CCl_4/g carbon and $K_L = 0.096\,(\text{mm Hg})^{-1}$.

Example 6.7-1 Balances on an Adsorption Process

A 50.0-liter tank contains an air–carbon tetrachloride mixture at 1 atm absolute, 34°C, and 30.0% relative saturation. Activated carbon is placed in the tank to adsorb CCl_4. The temperature of the tank contents is maintained at 34°C, and clean air is continuously supplied to the tank throughout the process to maintain the total pressure at 1.00 atm. The process may be shown schematically as follows:



Calculate the minimum amount of activated carbon needed to reduce the CCl_4 mole fraction in the gas to 0.001. Neglect the volume of the activated carbon and the adsorbed CCl_4. Why would the actual amount placed in the tank be larger than the calculated value?

Solution The minimum amount of activated carbon is required if adsorption equilibrium is achieved in the final state, so that the adsorbent holds as much CCl_4 as it can. The strategy will be to determine

1. n from the ideal-gas equation of state.
2. y_0 from the specified initial relative saturation.
3. p_{CCl_4} (the final partial pressure of CCl_4) = $0.001P$.
4. $X^*_{CCl_4}$ (the mass ratio of adsorbed CCl_4 to carbon at equilibrium) from the Langmuir isotherm (Equation 6.7-2).
5. The mass of CCl_4 adsorbed (m_{ads}) as the difference between the mass initially present in the gas ($= y_0 n M_{CCl_4}$) and the mass present at the end ($= 0.001 n M_{CCl_4}$).
6. The mass of carbon from $X^*_{CCl_4}$ and m_{ads} ($m_C = m_{ads} X^*_{CCl_4}$).

Ideal-Gas Equation of State:

$$n = \frac{PV}{RT} = \frac{(1.00\text{ atm})(50.0\text{ L})}{\left(0.08206\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(307\text{ K})} = 1.98\text{ mol}$$

***Initial Relative Saturation* = 0.300**:

From the Antoine equation (Table B.4), the vapor pressure of carbon tetrachloride at 34°C is $p^*_{CCl_4} = 169$ mm Hg. Consequently,

$$\frac{p_{CCl_4}}{p^*_{CCl_4}(34°\text{C})} = \frac{y_0 P}{169\text{ mm Hg}} = 0.300 \xrightarrow{P\ =\ 760\text{ mm Hg}} y_0 = 0.0667\text{ mol } CCl_4/\text{mol}$$

Langmuir Isotherm:

The final partial pressure of carbon tetrachloride is

$$p_{CCl_4} = y_0 P = 0.001(760\text{ mm Hg}) = 0.760\text{ mm Hg}$$

From Equation 6.7-2,

$$X^*_{CCl_4} = \frac{aK_L p_{CCl_4}}{1 + K_L p_{CCl_4}}$$

$$\Big\Downarrow \quad a = 0.794\text{ g } CCl_4/\text{g C}$$
$$\quad K_L = 0.096\text{ (mm Hg)}^{-1}$$
$$\quad p_{CCl_4} = 0.760\text{ mm Hg}$$

$$X^*_{CCl_4} = 0.0540\ \frac{\text{g } CCl_4\text{ ads}}{\text{g C}}$$

Mass of CCl_4 Adsorbed:

$$m_{ads} = \left(\frac{0.0667\text{ mol } CCl_4}{\text{mol}}\middle|\frac{1.98\text{ mol}}{}\right. - \left.\frac{0.001\text{ mol } CCl_4}{\text{mol}}\middle|\frac{1.98\text{ mol}}{}\right)\left(\frac{154\text{ g } CCl_4}{\text{mol } CCl_4}\right)$$
$$= 20.0\text{ g } CCl_4\text{ adsorbed}$$

Mass of Carbon Required:

$$m_C = \frac{20.0\text{ g } CCl_4\text{ ads}}{0.0540\text{ g } CCl_4\text{ ads/g C}} = \boxed{370\text{ g carbon}}$$

More activated carbon than this would be put into the container, for several reasons. First, since the rate of adsorption approaches zero as the adsorbent approaches saturation, it would take an infinite amount of time for the mole fraction of CCl_4 in the gas phase to reach 0.001. If more carbon is present, the target mole fraction would be reached in a finite amount of time (before the carbon becomes saturated). Second, the Langmuir isotherm is an approximate correlation with parameters obtained by fitting scattered experimental data, and so the estimated adsorption capacity of the adsorbent (X^*) could be too high. Third, we have assumed that nothing but CCl_4 is adsorbed on the carbon. If any oxygen, nitrogen, or other species that may be present in the gas is adsorbed, it could lower the amount of carbon tetrachloride adsorbed.

In this section we have assumed that the adsorption isotherm of an adsorbate is unaffected by the presence of constituents other than the adsorbate in the fluid mixture. If such ideality is assumed for the Langmuir isotherm developed in the previous example, you could use the derived expression for any gaseous system containing carbon tetrachloride and the same activated carbon. In reality, however, the presence of other solutes that have an affinity for the carbon surface alters the CCl_4 equilibrium behavior. An accurate system representation would require data or models for the complete multicomponent mixture.

Test Yourself

(Answers, p. 658)

SAFETY

1. What is the difference between adsorption and absorption?
2. What is the difference between an adsorbate and an adsorbent?
3. Why is it possible to use either molar concentration or partial pressure as the independent variable in the Langmuir isotherm without changing the form of the expression?
4. An **air-purifying respirator**—often called a gas mask—is a device that allows its wearer to breathe in an environment that contains low levels of a toxic substance. The inspired air passes through a filter containing an adsorbent such as activated carbon. Give a brief explanation of how the device works. How would using a nonactivated carbon affect the performance of the respirator?

6.8 SUMMARY

Two phases in contact with each other are said to be in *equilibrium* when the temperature, pressure, composition, and all other variables that characterize each phase do not change with time. Many chemical process operations—particularly separation processes such as distillation, absorption, crystallization, liquid extraction, and adsorption—work by distributing mixture components between two phases and then separating the phases. An essential step in analyzing such processes is determining how the feed mixture components distribute themselves between the two phases at equilibrium. This chapter summarizes common procedures for making this determination.

- The **phase diagram** of a pure species is a plot of pressure versus temperature that shows regions where the species exists as a solid, a liquid, or a gas; curves that bound these regions where pairs of phases can coexist in equilibrium; and a point (the *triple point*) where all three phases can coexist.
- The temperature coordinate of a point on the vapor–liquid equilibrium curve (the curve separating the liquid and vapor regions on a phase diagram) is the **boiling point** of the species at the corresponding pressure, and the pressure coordinate is the **vapor pressure** of the species at the corresponding temperature. The **normal boiling point** is the boiling point at $P = 1$ atm. Normal boiling points (and normal melting points) of selected species can be found in Table B.1 or calculated using the AntoineT function of APEx. Vapor pressures at specified temperatures can be estimated using the Antoine equation (Table B.4), the AntoineP function of APEx, or Table B.3 for water.
- The vapor pressure of a species is a measure of its **volatility**, or tendency to vaporize. Heating a liquid mixture tends to form a vapor enriched in more volatile components (those with higher vapor pressures) and to leave the residual liquid enriched in components with lower volatility. The separation process **distillation** is based on this principle. Similarly, if a gas mixture contains one or more components with relatively low volatilities, cooling the mixture in a **condensation** operation can be used to recover a liquid enriched in these components.
- The **Gibbs phase rule** gives the *degrees of freedom* of a multiphase system in equilibrium, or the number of intensive (size-independent) system variables that must be specified before the others can be determined.
- For a gas at temperature T and pressure P containing a single condensable vapor A with mole fraction y_A and vapor pressure $p_A^*(T)$, **Raoult's law** $[y_A P = p_A^*(T)]$ provides the basis for a number of definitions. If Raoult's law is satisfied, the vapor is **saturated** (or equivalently, the gas is saturated with A); if $y_A P < p_A^*(T)$, the vapor is **superheated**. If A is saturated and either the temperature is decreased or the pressure is increased, A will begin to condense. If liquid A is in contact with a gas phase and the system is at equilibrium, the A vapor in the gas must be saturated.
- If a gas containing a single superheated vapor A is cooled at constant pressure, the temperature at which the vapor becomes saturated is the **dew point** of the gas. The dew point may be determined from Raoult's law, $y_A P = p_A^*(T_{dp})$. The **degrees of superheat** is the difference between the actual temperature and the dew point of the gas. The **relative saturation** of the gas (or **relative humidity** for an air–water system) is the ratio of the

partial pressure of the vapor to the vapor pressure at the system temperature, expressed as a percentage: $[y_A P/p_A^*(T)] \times 100\%$. If you are given the temperature, pressure, and either the dew point, the degrees of superheat, the relative saturation, or a related quantity (molal or absolute or percentage saturation), you can use Raoult's law to calculate the mole fraction of A in the gas.

- If pure liquid A is placed in an open container at pressure P and a temperature for which $p_A^*(T) < P$ and $p_A^*(T) > p_A$, the liquid **evaporates**: molecules of A transfer from the liquid surface to the surrounding gas. If the container is heated to a temperature such that $p_A^*(T) = P$, the liquid **boils**: vapor bubbles form at the heated surface and rise through the liquid into the surrounding gas. The liquid temperature remains constant as boiling continues.
- If the volatile components of a liquid mixture are all structurally similar compounds (e.g., all paraffins), the general form of **Raoult's law** may be a good approximation for all species: $y_i P = x_i p_i^*(T)$, where x_i and y_i are the mole fractions of species i in the liquid and gas phases, respectively. If the liquid is nearly pure A ($x_A \approx 1$), Raoult's law might apply only to species A.
- In the separation process **absorption**, a gas mixture contacts a liquid solvent and one or more mixture components dissolve in the solvent. If a liquid solution contains only small amounts of a dissolved solute, A ($x_A \approx 0$), **Henry's law** may apply to A: $y_A P = x_A H_A(T)$, where H_A is the **Henry's law constant**.
- An **ideal liquid solution** is one for which all volatile components are distributed between liquid and gas phases at equilibrium according to either Raoult's law or Henry's law.
- The **bubble-point temperature** of a liquid mixture is the temperature at which the first vapor bubble forms if the mixture is heated at constant pressure. Contrary to what many students mistakenly assume, the bubble point is *not* the boiling temperature of the most volatile species in the liquid; it is always higher than this temperature for an ideal liquid solution. The **dew-point temperature** of a vapor mixture is the temperature at which the first liquid droplet forms if the mixture is cooled at constant pressure. If Raoult's law applies to all species, either of these temperatures can be determined by trial and error using Equation 6.4-4 (for the bubble point) or Equation 6.4-7 (for the dew point).
- If a liquid mixture is heated above its bubble point, the vapor generated is rich in the more volatile mixture components. As vaporization continues, the system temperature steadily increases (unlike the case for a single-component system, in which T remains constant). Similarly, if a vapor mixture is cooled below its dew point, the liquid that condenses is rich in the less volatile components and the temperature progressively decreases.
- The **solubility** of a solid (the *solute*) in a liquid (the *solvent*) is the maximum amount of that solute that can dissolve in a specified amount of the liquid at equilibrium. A solution that contains all the dissolved solute it can hold is **saturated** with that solute. If additional solute is added, it will not dissolve unless the temperature is changed in a way that increases the solubility.
- In the separation process **crystallization**, a solution of a solute is cooled below its saturation temperature, causing solid crystals of solute to form; alternatively, solvent may be evaporated to cause solute crystallization. For aqueous solutions of some solutes in certain temperature ranges, the crystals that form are **hydrated salts**, containing **water of hydration** molecules bonded to solute molecules in specific ratios. For example, if magnesium sulfate crystallizes at a temperature above 100°C, the crystals contain **anhydrous** (water-free) $MgSO_4$, while if the crystallization takes place between 48°C and 67°C, the crystals consist of $MgSO_4 \cdot 6H_2O$ (magnesium sulfate hexahydrate).
- Provided that the solute in a solution is nonvolatile and does not react with the solvent, the vapor pressure of the solution at a given temperature is lower than that of the pure solvent, the boiling point at a given pressure is higher, and the freezing point at a given pressure is lower. Vapor pressure lowering, boiling point elevation, and freezing point depression are examples of **colligative solution properties**; formulas for them are given in Section 6.5c.
- **Liquid extraction** is a separation process in which a liquid feed solution is combined with a second solvent that is immiscible or nearly immiscible with the feed solvent, causing some (and ideally most) of the solute to transfer to the phase containing the second solvent. The **distribution coefficient** is the ratio of the solute mass fractions in the two phases at equilibrium. Its value determines how much solvent must be added to the feed solution to achieve a specified solute transfer. When the two solvents are partially miscible, a **triangular phase diagram** like that in Figure 6.6-1 simplifies balance calculations on extraction processes.
- **Adsorption** is a process in which a species in a fluid (liquid or gas) mixture adheres to the surface of a solid with which the fluid is in contact. (This process should not be confused with *ab*sorption, in which a component of a gas mixture dissolves in a liquid solvent.) The solid is the **adsorbent**, and the species that adheres to the surface is the **adsorbate**. Good adsorbents such as activated carbon have extremely high specific surface areas (m^2 surface/g solid), enabling small quantities of adsorbent to remove large quantities of adsorbate from fluid mixtures. An **adsorption isotherm** is a plot or equation that relates the equilibrium amount of an adsorbate held by a given mass of adsorbent to the adsorbate partial pressure or concentration in the surrounding gas at a specified temperature.
- Material balance calculations on separation processes follow the same procedures used in Chapters 4 and 5. If the product streams leaving a unit include two phases in equilibrium, an equilibrium relationship for each species distributed between

the phases should be counted in the degree-of-freedom analysis and included in the calculations. If a species is distributed between gas and liquid phases (as in distillation, absorption, and condensation), use tabulated vapor–liquid equilibrium data, Raoult's law, or Henry's law. If a solid solute is in equilibrium with a liquid solution, use tabulated solubility data. If a solute is distributed between two immiscible liquid phases, use a tabulated distribution coefficient or equilibrium data. If an adsorbate is distributed between a solid surface and a gas phase, use an adsorption isotherm.

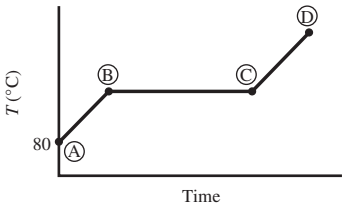
Note: This would be a good time to work through Interactive Tutorial #4.

WileyPLUS
Interactive Tutorial #4
Questions with Immediate Feedback

PROBLEMS

Unless otherwise instructed, use physical property data in this text when solving these problems.

6.1. Ten mL of pure liquid water in a cylinder with a movable piston is heated at a constant pressure of 1 atm from an initial temperature of 80°C. The temperature of the system is monitored, and the following behavior is observed:



(a) What is happening in steps AB, BC, and CD? What is the temperature corresponding to the horizontal portion of the curve?
(b) Estimate the volume occupied by the water at points B and C. (Assume the vapor follows the ideal-gas equation of state.)

6.2. A quantity of methyl acetate is placed in an open, transparent, three-liter flask and boiled long enough to purge all air from the vapor space. The flask is then sealed and allowed to equilibrate at 30°C, at which temperature methyl acetate has a vapor pressure of 269 mm Hg. Visual inspection shows 10 mL of liquid methyl acetate present.
(a) What is the pressure in the flask at equilibrium? Explain your reasoning.
(b) What is the total mass (grams) of methyl acetate in the flask? What fraction is in the vapor phase at equilibrium?
(c) The above answers would be different if the species in the vessel were *ethyl* acetate because methyl acetate and ethyl acetate have different vapor pressures. Give a rationale for that difference.

6.3. Ethyl alcohol has a vapor pressure of 20.0 mm Hg at 8.0°C and a normal boiling point of 78.4°C. Estimate the vapor pressure at 45°C using (a) the Antoine equation; (b) the Clausius–Clapeyron equation and the two given data points; and (c) linear interpolation between the two given points. Taking the first estimate to be correct, calculate the percentage error associated with the second and third estimates.

6.4. The vapor pressure of ethylene glycol at several temperatures is given below:

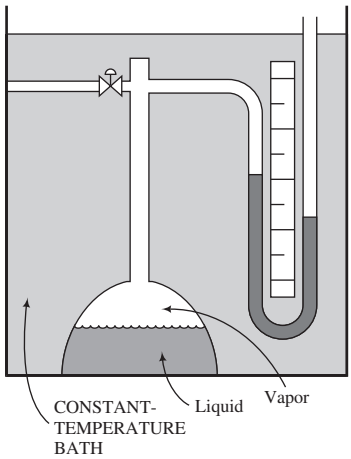
T(°C)	79.7	105.8	120.0	141.8	178.5	197.3
p^*(mm Hg)	5.0	20.0	40.0	100.0	400.0	760.0

(a) Construct a semilog plot of the vapor-pressure data and determine a linear expression for $\ln p^*$ as a function of $1/T$(K). Use the results to estimate the heat of vaporization (kJ/mol) of ethylene glycol, and then use that value in the Clausius–Clapeyron equation to estimate the vapor pressures at each of the temperatures given in the table.

(b) Repeat Part (a) using the Slope and Intercept functions of APEx to obtain the expression for $\ln p^*$ vs. $1/T$(K).

(c) Use the results from Part (b) to estimate vapor pressures of ethylene glycol at 50°C, 80°C, and 110°C. Also estimate the boiling point of this substance at system pressures of 760 mm Hg and 2000 mm Hg. Compare all five results with those obtained directly using APEx functions. In which of the estimates at the given temperatures and pressures would you have the least confidence? Explain your reasoning.

6.5. The apparatus shown here is used to measure the vapor pressure of ethylene diamine.



The system is loaded with pure ethylene diamine and the bath is adjusted to each of several known temperatures. The following readings are taken on a day when the atmospheric pressure is 758.9 mmHg:

	Mercury Level	
T(°C)	Right Arm (mm)	Left Arm (mm)
42.7	138	862
58.9	160	840
68.3	182	818
77.9	213	787
88.6	262	738
98.3	323	677
105.8	383	617

(a) Calculate p^* for ethylene diamine at each temperature.

(b) Use a semilog plot of p^* versus $1/T$ to estimate the normal boiling point and the heat of vaporization of ethylene diamine.

(c) Does the Clausius–Clapeyron equation appear to be justified for ethylene diamine in the temperature range covered by the data? Explain.

6.6. Estimate the vapor pressure of acetone (mm Hg) at 50°C (a) from data in *Perry's Chemical Engineers' Handbook* (Footnote 1) and the Clausius–Clapeyron equation, (b) from the Antoine equation using parameters from Table B.4, and (c) using the AntoineP function in APEx.

6.7. The vapor pressure of an organic solvent is 50 mm Hg at 25°C and 200 mm Hg at 45°C. The solvent is the only species in a closed flask at 35°C and is present in both liquid and vapor states. The volume of gas above the liquid is 150 mL.

(a) Estimate the amount of the solvent (mol) contained in the gas phase.

(b) What assumptions did you make? How would your answer change if the species *dimerized* (one molecule results from two molecules of the species combining)?

6.8. Liquid methyl ethyl ketone (MEK) is introduced into a vessel containing air. The system temperature is increased to 55°C, and the vessel contents reach equilibrium with some MEK remaining in the liquid state. The equilibrium pressure is 1200 mm Hg.

(a) Use the Gibbs phase rule to determine how many degrees of freedom exist for the system at equilibrium. State the meaning of your result in your own words.

(b) Mixtures of MEK vapor and air that contain between 1.8 mole% MEK and 11.5 mole% MEK can ignite and burn explosively if exposed to a flame or spark. Determine whether or not the given vessel constitutes an explosion hazard.

SAFETY

6.9. When a flammable liquid (e.g., gasoline) ignites, the substance actually burning is vapor generated from the liquid. If the concentration of the vapor in the air above the liquid exceeds a certain level (the *lower flammability limit*), the vapor will ignite if it is exposed to a spark or another ignition source. Once ignited, the heat released is likely to cause additional vaporization of the liquid, and the resulting fire may continue until all combustible material has been consumed.

(a) The *flash point* is defined as the minimum temperature at which a flammable liquid or volatile solid gives off sufficient vapor to form an ignitable mixture with air near the surface of the liquid or within a vessel (page 2-515, *Perry's Chemical Engineers' Handbook*, see Footnote 1). For example, the flash point of *n*-octane at 1.0 atm is 13°C (55°F), which means that dropping a match into an open container of octane is likely to start a fire in a laboratory, but not outside on a cold winter day. (Do not try it! One reference—L. Bretherick, *Bretherick's Handbook of Reactive Chemical Hazards*, 4th Edition, Butterworths, London, 1990, p. 1596—points out there is "usually a *fair* [our emphasis] correlation between flash point and probability of involvement in fire.")

Suppose you are keeping two solvents in your laboratory, one with a flash point of 15°C and the other with a flash point of 75°C. How do these solvents differ from the standpoint of safety? What differences, if any, should there be in how you treat them?

(b) The lower flammability limit (LFL) of methanol in air is 6.0 mole%. Calculate the temperature at which a saturated methanol–air mixture at 1 atm would have a composition corresponding to the LFL. What is the relationship of this value to the flash point, and what value would you assign the flash point of methanol?

(c) Give reasons why it would be unsafe to maintain an open container of methanol in an environment below the LFL (i.e., the value calculated in Part (b)) if there are ignition sources nearby. List common ignition sources that may be found in a laboratory.

6.10. A gas mixture contains 10.0 mole% H_2O(v) and 90.0 mole% N_2. The gas temperature and absolute pressure at the start of each of the three parts of this problem are 50°C and 500 mm Hg. Ideal-gas behavior may be assumed in every part of this problem.

(a) If some of the gas mixture is put in a cylinder and slowly cooled at constant pressure, at what temperature would the first drop of liquid form?

(b) If a 30.0-liter flask is filled with some of the gas mixture and sealed and 70% of the water vapor in the flask is condensed, what volume (cm^3) would be occupied by the liquid water? What would be the system temperature?

(c) If the gas mixture is stored in a rigid-walled cylinder and a low-pressure weather front moves in and the barometric (atmospheric) pressure drops, which of the following would change: (i) the gas density, (ii) the absolute pressure of the gas, (iii) the partial pressure of water in the gas, (iv) the gauge pressure of the gas, (v) the mole fraction of water in the gas, (vi) the dew-point temperature of the mixture?

Equipment Encyclopedia
manometer

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6.11. Pure chlorobenzene is contained in a flask attached to an open-end mercury manometer. When the flask contents are at 58.3°C, the height of the mercury in the arm of the manometer connected to the flask is 747 mm and that in the arm open to the atmosphere is 52 mm. At 110°C, the mercury level is 577 mm in the arm connected to the flask and 222 mm in the other arm. Atmospheric pressure is 755 mm Hg.

(a) Extrapolate the data using the Clausius–Clapeyron equation to estimate the vapor pressure of chlorobenzene at 130°C.

(b) Air saturated with chlorobenzene at 130°C and 101.3 kPa is cooled to 58.3°C at constant pressure. Estimate the percentage of the chlorobenzene originally in the vapor that condenses. (See Example 6.3-2.)

(c) Summarize the assumptions you made in doing the calculation of Part (b).

6.12. The weather report says the temperature is 86°F, the barometer is at 30.05 inches Hg, the relative humidity is 62%, and the dew point is 71°F. Estimate the mole fraction of water in the air, the molal humidity, absolute humidity, and percentage humidity in the air. Are the values given for relative humidity and dew point consistent?

6.13. In watching an airplane take off from a short runway, you overhear someone say he is concerned about the length of the runway because the temperature is so high and the humidity so low. You are not quite sure why these factors should be a cause for concern, so you return to your office and calculate air density at 90°F and 20% relative humidity and at 80°F and 50% relative humidity. You then search the Internet and find that $L = C\rho u^2 A$, where L is lift (the upward force provided by air flowing over and under a wing), C is a coefficient that depends on wing characteristics, ρ is the density of air, u is the velocity of air over the wing, and A is the wing area. Is the overheard concern justified? Explain your response.

6.14. Air at 50% relative humidity is cooled isobarically at 1 atm absolute from 90°C to 25°C.
- **(a)** Estimate the dew point and degrees of superheat of the air at 90°C.
- **(b)** How much water condenses (mol) per cubic meter of feed gas? (See Example 6.3-2.)
- **(c)** Suppose a sample of the 90°C air is put in a closed variable-volume chamber containing a mirror and the pressure is raised at constant temperature until a mist forms on the mirror. At what pressure (atm) would the mist form? (Assume ideal-gas behavior.)

ENVIRONMENTAL

6.15. In an attempt to conserve water and to be awarded LEED (Leadership in Energy and Environmental Design) certification, a 20,000-liter cistern has been installed during construction of a new building. The cistern collects water from an HVAC (heating, ventilation, and air-conditioning) system designed to provide 2830 cubic meters of air per minute at 22°C and 50% relative humidity after converting it from ambient conditions (31°C, 70% relative humidity). The collected condensate serves as the source of water for lawn maintenance. Estimate (a) the rate of intake of air at ambient conditions in cubic feet per minute and (b) the hours of operation required to fill the cistern.

6.16. Air containing 20.0 mole% water vapor at an initial pressure of 1 atm absolute is cooled in a 1-liter sealed vessel from 200°C to 15°C.
- **(a)** What is the pressure in the vessel at the end of the process? (*Hint:* The partial pressure of air in the system can be determined from the expression $p_{air} = n_{air}RT/V$ and $P = p_{air} + p_{H_2O}$. You may neglect the volume of the liquid water condensed, but you must show that condensation occurs.)
- **(b)** What is the mole fraction of water in the gas phase at the end of the process?
- **(c)** How much water (grams) condenses?

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6.17. Air at 90°C and 1.00 atm (absolute) contains 10.0 mole% water. A continuous stream of this air enters a compressor–condenser, in which the temperature is lowered to 15.6°C and the pressure is raised to 3.00 atm. The air leaving the condenser is then heated isobarically to 100°C. Calculate the fraction of water that is condensed from the air, the relative humidity of the air at 100°C, and the ratio (m^3 outlet air at 100°C)/(m^3 feed air) at 90°C.

BIOENGINEERING

6.18. When fermentation units are operated with high aeration rates, significant amounts of water can be evaporated into the air passing through the fermentation broth. Since fermentation can be adversely affected if water loss is significant, the air is humidified before being fed to the fermenter. Sterilized ambient air is combined with steam to form a saturated air–water mixture at 1 atm and 90°C. The mixture is cooled to the temperature of the fermenter (35°C), condensing some of the water, and the saturated air is fed to the bottom of the fermenter. For an air flow rate to the fermenter of 10 L/min at 35°C and 1 atm, estimate the rate at which steam must be added to the sterilized air and the rate (kg/min) at which condensate is collected upon cooling the air–steam mixture.

*__6.19.__ When you step out of a shower, the temperature in the bathroom is 71°F and the relative humidity is 96%. You notice that a barely perceptible amount of water has condensed on the inside of the bathroom window.

* Adapted from a problem contributed by Paul Blowers of the University of Arizona.

(a) Assuming that the air immediately adjacent to the glass has the same composition as the rest of the room air, estimate the temperature of the inside glass surface.

(b) What could you say about the inside surface temperature if the window were completely drenched with condensate?

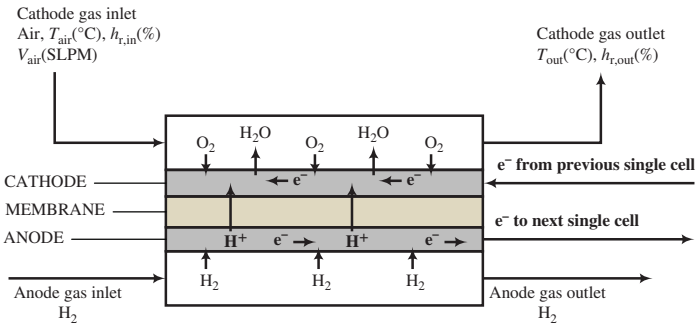
ALTERNATIVE ENERGY

*__6.20.__ A *fuel cell* is an electrochemical device in which hydrogen reacts with oxygen to produce water and DC electricity. A 1-watt proton-exchange membrane fuel cell (PEMFC) could be used for portable applications such as cellular telephones, and a 100-kW PEMFC could be used to power an automobile.

The following reactions occur inside the PEMFC:

Anode:	$H_2 \rightarrow 2H^+ + 2e^-$
Cathode:	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Overall:	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

A flowchart of a single cell of a PEMFC is shown below. The complete cell would consist of a stack of such cells in series, such as the one shown in Problem 9.19.



The cell consists of two gas channels separated by a membrane sandwiched between two flat carbon-paper electrodes—the anode and the cathode—that contain imbedded platinum particles. Hydrogen flows into the anode chamber and contacts the anode, where H_2 molecules are catalyzed by the platinum to dissociate and ionize to form hydrogen ions (protons) and electrons. The electrons are conducted through the carbon fibers of the anode to an external circuit, where they pass to the cathode of the next cell in the stack. The hydrogen ions permeate from the anode through the membrane to the cathode.

Humid air is fed into the cathode chamber, and at the cathode O_2 molecules are catalytically split to form oxygen atoms, which combine with the hydrogen ions coming through the membrane and electrons coming from the external circuit to form water. The water desorbs into the cathode gas and is carried out of the cell. The membrane material is a hydrophilic polymer that absorbs water molecules and facilitates the transport of the hydrogen ions from the anode to the cathode. Electrons come from the anode of the cell at one end of the stack and flow through an external circuit to drive the device that the fuel cell is powering, while the electrons coming from the device flow back to the cathode at the opposite end of the stack to complete the circuit.

It is important to keep the water content of the cathode gas between upper and lower limits. If the content reaches a value for which the relative humidity would exceed 100%, condensation occurs at the cathode (*flooding*), and the entering oxygen must diffuse through a liquid water film before it can react. The rate of this diffusion is much lower than the rate of diffusion through the gas film normally adjacent to the cathode, and so the performance of the fuel cell deteriorates. On the other hand, if there is not enough water in the cathode gas (less than 85% relative humidity), the membrane dries out and cannot transport hydrogen efficiently, which also leads to reduced performance.

A 400-cell 300-volt PEMFC operates at steady state with a power output of 36 kW. The air fed to the cathode side is at 20.0°C and roughly 1.0 atm (absolute) with a relative humidity of 70.0% and a volumetric flow rate of 4.00×10^3 SLPM (standard liters per minute). The gas exits at 60°C.

(a) Explain in your own words what happens in a single cell of a PEMFC.

(b) The stoichiometric hydrogen requirement for a PEMFC is given by $(n_{H_2})_{consumed} = IN/2F$, where I is the current in amperes (coulomb/s), N is the number of single cells in the fuel cell stack, and

* Adapted from a problem contributed by Jason Keith of Mississippi State University.

F is the Faraday constant, 96,485 coulombs of charge per mol of electrons. Derive this expression. (*Hint:* Recall that since the cells are stacked in series the same current flows through each one, and the same quantity of hydrogen must be consumed in each single cell to produce that current at each anode.)

(c) Use the expression of Part (b) to determine the molar rates of oxygen consumed and water generated in the unit with the given specifications, both in units of mol/min. (Remember that power = voltage × current.) Then determine the relative humidity of the cathode exit stream, $h_{r,out}$.

(d) Determine the minimum cathode inlet flow rate in SLPM to prevent the fuel cell from flooding ($h_{r,out} = 100\%$) and the maximum flow rate to prevent it from drying ($h_{r,out} = 85\%$).

SAFETY

6.21. A storage tank for liquid *n*-octane has a diameter of 30 ft and a height of 20 ft. During a typical 24-h period the level of liquid octane falls from 18 ft to 8 ft, after which fresh octane is pumped into the tank to return the level to 18 ft. As the level in the tank falls, nitrogen is fed into the free space to maintain the pressure at 16 psia; when the tank is being refilled, the pressure is maintained at 16 psia by discharging gas from the vapor space to the environment. The nitrogen in the tank may be considered saturated with octane vapor at all times. The average tank temperature is 90°F.

(a) What is the daily rate, in gallons and lb_m, at which octane is used?

(b) What is the variation in absolute pressure at the bottom of the tank in inches of mercury?

(c) How much octane is lost to the environment during a 24-h period?

(d) Why is nitrogen used in the vapor space of the tank when air would be cheaper?

(e) Suggest a means by which the octane can be recovered from the gas stream discharged to the atmosphere.

6.22. A 1000-gallon tank currently contains 100.0 gallons of liquid toluene and a gas saturated with toluene vapor at 85°F and 1 atm.

(a) What quantity of toluene (lb_m) will enter the atmosphere when the tank is filled and the gas displaced?

(b) Suppose that 90% of the displaced toluene is to be recovered by compressing the displaced gas to a total pressure of 5 atm and then cooling it isobarically to a temperature T(°F). Calculate T.

6.23. A gas mixture containing 85.0 mole% N_2 and the balance *n*-hexane flows through a pipe at a rate of 100.0 m^3/h. The pressure is 2.00 atm absolute and the temperature is 100°C.

(a) What is the molar flow rate of the gas in kmol/h?

(b) Is the gas saturated? If not, to what temperature (°C) would it have to be cooled at constant pressure in order to begin condensing hexane?

(c) To what temperature (°C) would the gas have to be cooled at constant pressure in order to condense 80% of the hexane?

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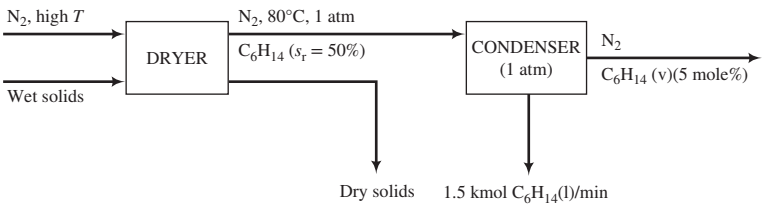
6.24. Recovery and processing of various oils are important elements of the agricultural and food industries. For example, soybean hulls are removed from the beans, which are then flaked and contacted with hexane. The hexane extracts soybean oil and leaves very little oil in the residual solids. The solids are dried at an elevated temperature, and the dried solids are used to feed livestock or further processed to extract soy protein. The gas stream leaving the dryer is at 80°C, 1 atm absolute, and 50% relative saturation.

(a) To recover hexane, the gas leaving the dryer is fed to a condenser, which operates at 1 atm absolute. The gas leaving the condenser contains 5.00 mole% hexane, and the hexane condensate is recovered at a rate of 1.50 kmol/min.



Calculate the condenser temperature and the required flow rate of fresh nitrogen to the dryer in standard cubic meters per minute (SCMM).

(b) In an alternative arrangement, the gas leaving the dryer is compressed to 10.0 atm and the temperature simultaneously is increased so that the relative saturation remains at 50%. The gas then is cooled at constant pressure to produce a stream containing 5.00 mole% hexane. Calculate the final gas temperature and the ratio of volumetric flow rates of the gas streams leaving and entering the condenser. State any assumptions you make.

(c) What would you need to know to determine which of processes (a) and (b) is more cost-effective?

SAFETY →

6.25. A 20,000-liter storage tank was taken out of service to repair and reattach a feed line damaged in a collision with a tanker. The tank was drained and then opened several days later for a welder to enter and perform the required work. No one realized, however, that 5 liters of liquid nonane (C_9H_{20}) remained in a collection sump at the bottom of the tank after the draining had been completed.

(a) Nonane has a lower explosive limit of 0.80 mole% and an upper explosive limit of 2.9 mole%[8] (i.e., nonane–air mixtures at 1 atm can explode when exposed to a spark or flame if the nonane mole fraction is between the two given values). Assume any liquid nonane that evaporates spreads uniformly throughout the tank. Is it possible for the average gas-phase composition in the tank to be within the explosive limits at any time? Even when the average composition falls outside those limits, why is an explosion still a possibility? (*Hint:* Think about that assumption.)

(b) Use the Antoine equation (6.1-4) to estimate the temperature at which the system would have to equilibrate in order for the gas in the tank to be at the lower explosive limit.

(c) Fortunately, a safety inspector examined the system before the welder began work and immediately canceled the work order. The welder was cited and fined for violating established safety procedures. One requirement was for the tank to be purged thoroughly with steam after being drained. What is the purpose of this requirement? (Why purge, and why with steam rather than air?) What other precautions should be taken to be sure that the welder is in no danger?

BIOENGINEERING →

6.26. An adult inhales approximately 12 times per minute, taking in about 500 mL of air with each inhalation. Oxygen and carbon dioxide are exchanged in the lungs, but there is essentially no exchange of nitrogen. The exhaled air has a mole fraction of nitrogen of 0.75 and is saturated with water vapor at body temperature, 37°C. If ambient conditions are 25°C, 1 atm, and 50% relative humidity, what volume of liquid water (mL) would have to be consumed over a two-hour period to replace the water loss from breathing? How much would have to be consumed if the person is on an airplane where the temperature, pressure, and relative humidity are respectively 25°C, 1 atm, and 10%?

ENVIRONMENTAL →

6.27. Recovering and reusing organic solvents is an important part of the operation of most chemical plants. The magnitude of these recovery efforts can be staggering: e.g., in recent years Eastman Chemical Company used 4.0 billion pounds of solvents annually and recovered 3.96 billion pounds (99%). Eastman's installation of a $26 million (in 1990 dollars) acetone-recovery system reduced acetone emissions by 50% in the division that had been responsible for most of these emissions.[9]

A gas stream containing 20.0 mole% acetone and the remainder nitrogen leaves a chemical plant at 90°C and 1 atm. In an acetone-recovery process, stream is cooled at constant pressure in a condenser, enabling some of the acetone vapor to be recovered as a liquid. The nitrogen and uncondensed acetone are discharged to the atmosphere.

(a) Give two major benefits of recovering the acetone.

(b) Two cooling fluids are available—cooling-tower water at 20°C and a refrigerant at −35°C. For each fluid, calculate the percentage acetone recovery [(mol acetone condensed/mol acetone fed to condenser) ×100%], assuming that the condenser temperature equals the coolant temperature.

(c) What more would you need to know to decide which coolant to use?

(d) In a real system, the condenser temperature could never be as low as the initial cooling fluid temperature. Why not? (*Hint:* In a condenser, heat is transferred from the process fluid to the cooling fluid.) Explain how this fact would affect the percentage solvent recovery.

6.28. On a hot summer day the temperature is 35°C, barometric pressure is 103 kPa, and the relative humidity is 90%. An air conditioner draws in outside air, cools it to 20°C, and delivers it at a rate of

[8] R. J. Lewis, *Hazardous Chemicals Desk Reference*, 6th Edition, John Wiley & Sons, New York, 2008, p. 1036.

[9] A Pollution Prevention Report from the Chemical Manufacturers Association. A Chemical Industry Progress Report (1988–1992). Responsible Care—A Public Commitment.

12,500 L/h. Calculate the rate of moisture condensation (kg/h) and the volumetric flow rate of the air drawn from the outside.

6.29. An air conditioner is designed to bring 10,000 ft^3/min of outside air (90°F, 29.8 inches Hg, 88% relative humidity) to 40°F, thereby condensing a portion of the water vapor, and then to reheat the air before releasing it into a room at 65°F. Calculate the rate of condensation (gallons H_2O/min) and the volumetric flow rate of the air delivered to the room. (*Suggestion:* On the flowchart, treat the cooling–condensation and the reheating as separate process steps.)

6.30. The air in a building is to be maintained at 25°C and 55% relative humidity by passing outside air through a water spray. The air enters the spray chamber at 32°C and 70% relative humidity, leaves the chamber cooled and saturated with water vapor, and is then reheated to 25°C. Estimate the temperature of the air leaving the spray chamber and the water (kg) added to or removed from (specify which) each kilogram of dry air processed.

6.31. A **hygrometer** is used to measure the moisture content of humid air. Calibration of the instrument leads to a straight line on a semilog plot of y, the mole fraction of water in air (logarithmic scale), versus H, the instrument reading (linear scale).

Room air is charged into the hygrometer sample chamber on a day when the temperature is 22°C, barometric pressure is 1.00 atm, and the relative humidity is 40%. The resulting meter reading is $H = 5.0$. A second measurement is then made by heating water to 50°C in a sealed flask containing air. The system is allowed to equilibrate at a pressure of 839 mm Hg with liquid still present in the flask, and a sample of the air above the liquid is withdrawn and injected into the sample chamber (which is heated to prevent condensation). The meter reading in this case is $H = 48$.

(a) Determine the expression for y as a function of H.

(b) Suppose you wish to condition air at 35°C and 1 atm to produce air at 22°C, 1 atm, and 40% relative humidity. The air conditioner first cools the air, condensing the necessary amount of water, and then reheats the remaining air to 22°C. A sample of the outside air is injected into the hygrometer chamber, and the resulting reading is $H = 30$. Calculate the temperature to which the air must be cooled before it is reheated and determine the amount of water condensed in kg/m^3 of delivered conditioned air.

Equipment Encyclopedia
condenser, refrigerator, compressor
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6.32. Recovery of a solvent vapor from a gas stream by condensation can be achieved by cooling the gas, by compressing it, or by a combination of these operations. The greater the compression, the less cooling is needed.

(a) A gas mixture at a pressure P_0 and temperature T_0 is the feed to a recovery process. A single condensable vapor and several noncondensable gases are present in the mixture, giving the feed a dew point of T_{d0}. A fraction f of the vapor is to be condensed. For a gas feed rate of $\dot{n}_0$, draw and label a flowchart. Then derive the following relationship for the final condenser pressure in terms of the final temperature T_f and the specified feed conditions and fractional solvent recovery:

$$P_f = \frac{p^*(T_f)[1 - f p^*(T_{d0})/P_0]}{(1-f)p^*(T_{d0})/P_0}$$

Also show that for a given final condenser pressure, the vapor pressure of the condensable component is given by

$$p^*(T)_f = \frac{P_f(1-f)p^*(T_{d0})}{P_0 - f p^*(T_{d0})}$$

(b) The cost of refrigeration equipment and the compressor can be estimated using the empirical formulas[10]

$$C_{refr}(\$/\text{kmol feed gas}) = 2000 + 27(\Delta T)^2$$
$$C_{comp}(\$/\text{kmol feed gas}) = 4500 + 5.58(\Delta P)$$

[10] These formulas are fictitious. Real cost-estimation formulas can be found in a number of texts including M. S. Peters, K. D. Timmerhaus, and R. West, *Plant Design and Economics for Chemical Engineers*, 5th Edition, McGraw-Hill, New York, 2003; W. D. Seider, J. D. Seader, D. R. Lewin, and S. Widagdo, *Product and Process Design Principles*, 3rd Edition, John Wiley & Sons, New York, 2009.

where $\Delta T(°C) = T_0 - T_f$ and $\Delta P(\text{mm Hg}) = P_f - P_0$. Prepare a spreadsheet having the form shown below to estimate the cost of a process in which ethyl benzene (also written as ethylbenzene) is recovered from a gaseous mixture of ethyl benzene and nitrogen. You may use APEx functions or the Antoine constants in Table B.4 in your calculations. Explore two regions of operation: The first should vary the final temperature between T1 = 45°C and T10 = 0°C in 5°C decrements, and the second should vary the final pressure between P1 = 1000 mm Hg and P10 = 10,000 mm Hg in 1000 mm Hg increments.

Condensation of Ethyl Benzene from Nitrogen											
Variations in Final Temperature											
Run	T0(C)	P0(mm Hg)	Td0(C)	p*(Td0) (mm Hg)	f	Tf(C)	p*(Tf) (mm Hg)	Pf(mm Hg)	Cref	Ccomp	Ctot
T1	50	765	40	21.5	0.95	45	27.6	19,139	2675	107,027	109,702
T2	50	765	40	21.5	0.95	40					
Topt	50	765	40	21.5	0.95	Tinitial					
Variations in Final Pressure											
Run	T0(C)	P0(mm Hg)	Td0(C)	p*(Td0) (mm Hg)	f	Pf(mm Hg)	p*(Tf) (mm Hg)	Tf(C)	Cref	Ccomp	Ctot
P1	50	765	40	21.5	0.95	1000	1.4	−3.7	79,778	5811	85,590
P2	50	765	40	21.5	0.95	2000					
Popt	50	765	40	21.5	0.95	Pinitial					

The row shown above for Run T1 contains results for a feed gas at 50°C and 765 mm Hg with a dew point of 40°C, from which 95% of the ethylbenzene is to be recovered by cooling the mixture to 45°C. The output shows that the mixture must be compressed to 19,139 mm Hg to achieve the desired recovery, and that the costs of refrigeration and compression and the total cost ($/kmol feed gas) are, respectively, $2675, $107,027, and $109,702. (We recognize that the significant figures shown are excessive, but leave them in the spreadsheet.)

(c) When you have constructed the spreadsheet and duplicated the results shown for Run T1, copy that row into the next 9 rows and change the values in the first and seventh columns to correspond to the requested run numbers and final temperature. Note what happens to the calculated values of P_f, C_{refr}, C_{comp}, and C_{tot} as you move from Run T1 to Run T10. Now, copy the row for Run T10 into the next row of the spreadsheet and label it Topt. Use Solver to minimize the total cost by varying the final temperature.

(d) Repeat the procedures from Part (c) but this time vary the final pressure, P_f. Use Solver again to minimize total cost, this time by adjusting P_f. You should obtain the same values for Run Popt as were determined in Run Topt.

(e) Summarize the effects of T_f and P_f on one another and on the refrigeration and compression costs. Explain why the total cost has a minimum.

6.33. A gas stream containing 40.0 mole% hydrogen, 35.0% carbon monoxide, 20.0% carbon dioxide, and 5.0% methane is cooled from 1000°C to 10°C at a constant absolute pressure of 35 atm. Gas enters the cooler at 120 m^3/min, and upon leaving the cooler, is fed to an absorber where it is contacted with refrigerated liquid methanol that enters the absorber at a molar flow rate 1.2 times that of the inlet gas and at −15°C. Essentially all of the CO_2 is absorbed, as is 98% of the methane and an inconsequential amount of the other components of the feed gas. The gas leaving the absorber is saturated with methanol at −12°C and is fed to a reactor for further processing.

(a) Calculate the volumetric flow rate of methanol entering the absorber (m^3/min) and the molar flow rate of methanol in the gas leaving the absorber. *Do not assume ideal-gas behavior when doing PVT calculations.*

SAFETY

(b) List and explain at least three hazards associated with the system described.

(c) One of the possible uses of the product gas is as a feed to a reactor in which the water–gas shift reaction takes place: $H_2 + CO_2 \rightleftharpoons H_2O + CO$. Explain the effect of removing CO_2 before introducing the feed to the reactor.

Equipment Encyclopedia
dryer
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6.34. You were recently hired as a process engineer by a pulp and paper manufacturing firm. Your new boss calls you in and tells you about a pulp dryer designed to reduce the moisture content of 1500 kg/min of wet pulp from 0.9 kg H_2O/kg dry pulp to 0.15 wt% H_2O. The design called for drawing atmospheric air at 90% relative humidity, 25°C, 760 mm Hg into a blower that forces the air through a heater and into the dryer. When the operation was put into service, weather conditions were exactly as assumed in the design, and measurements showed that the air leaving the dryer was at 80°C and a gauge pressure of 10 mm Hg. However, there was no way to check the operation of the blower to see if it was delivering the specified volumetric flow rate of air. Your boss wants to check that value and asks you to devise a method for doing so. You go back to your office, sketch the process, and determine that you can estimate the air flow rate from the given information if you also know the moisture content of the air leaving the dryer.

(a) Propose a method to estimate the moisture content of the exit air.

(b) Suppose your measurement is carried out and you learn that the exit air at 10 mm Hg gauge has a dew point of 40°C. Use that information and the mass of water removed from the wet pulp to determine the volumetric flow rate (m^3/min) of air entering the system.

Equipment Encyclopedia
dryer
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6.35. In the manufacture of an active pharmaceutical ingredient (API), the API goes through a final purification step in which it is crystallized, filtered, and washed. The washed crystals contain 47% water. They are fed to a tunnel dryer and leave the dryer at a rate of 165 kg/h containing 5% adhered moisture. Dry air enters the dryer at 145°F and 1 atm, and the outlet air is at 130°F and 1 atm with a relative humidity of 50%. Calculate the rate (kg/h) at which the API enters the dryer and the volumetric flow rate (ft^3/h) of inlet air.

Equipment Encyclopedia
extractor, dryer, condenser
www.wiley.com/college/felder

6.36. *n*-Hexane is used to extract oil from soybeans. (See Problem 6.24.) The solid residue from the extraction unit, which contains 0.78 kg liquid hexane/kg dry solids, is contacted in a dryer with nitrogen that enters at 85°C. The solids leave the dryer containing 0.05 kg liquid hexane/kg dry solids, and the gas leaves the dryer at 80°C and 1.0 atm with a relative saturation of 70%. The gas is then fed to a condenser in which it is compressed to 5.0 atm and cooled to 28°C, enabling some of the hexane to be recovered as condensate.

(a) Calculate the fractional recovery of hexane (kg condensed/kg fed in wet solids).

(b) A proposal has been made to split the gas stream leaving the condenser, combining 90% of it with fresh makeup nitrogen, heating the combined stream to 85°C, and recycling the heated stream to the dryer inlet. What fraction of the fresh nitrogen required in the process of Part (a) would be saved by introducing the recycle? What costs would be incurred by introducing the recycle?

Equipment Encyclopedia
dryer, condenser, heat exchanger
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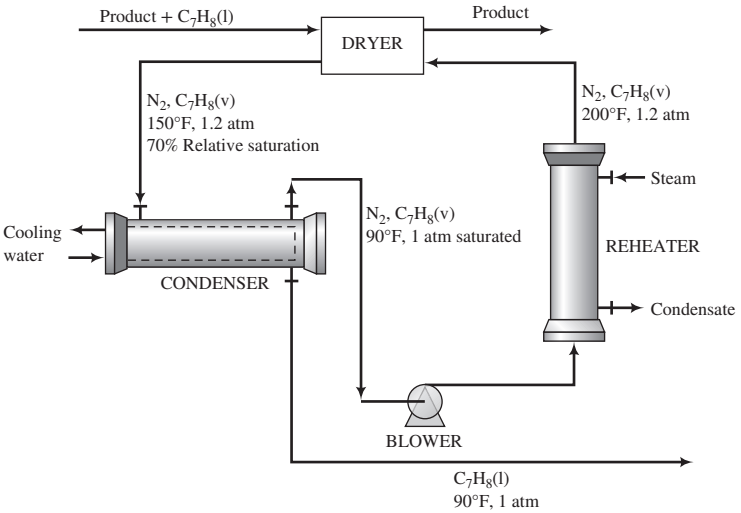
6.37. In the final stage of the manufacturing process for a solid organic product, the product is cleaned with liquid toluene and then dried in a process whose flowchart is shown on the next page.[11]

The wet product enters the dryer at a rate of 300 lb_m/h containing 0.200 lb_m toluene/lb_m dry solids. A stream of nitrogen at 200°F, 1.2 atm, and containing a small amount of toluene vapor also enters the dryer. (A higher temperature would cause the product to soften and degrade.) Heat is transferred in the dryer from the gas to the wet solids, causing most of the toluene to evaporate. The final product contains 0.020 lb_m toluene/lb_m dry solids. Gas leaves the dryer at 150°F and 1.2 atm with a relative saturation of 70% and passes through a water-cooled condenser. Gas and liquid streams leave the condenser in equilibrium at 90°F and 1 atm. The gas is reheated to 200°F and reenters the dryer.

[11] Adapted from *Professional Engineering Examinations*, Vol. 1 (1965–1971), National Council of Engineering Examiners, p. 60.

(a) Briefly explain this process in your own words. In your explanation, include the purposes of the condenser and the nitrogen reheater and a likely reason that nitrogen rather than air is used as the recirculating gas. What do you suppose happens to the liquid toluene leaving the condenser?



(b) Calculate the compositions (component mole fractions) of the gas streams entering and leaving the dryer, the circulation rate of dry nitrogen (lb_m/h), and the volumetric flow rate of gas entering the dryer (ft^3/h).

(c) Explain why the actual process has a small make-up nitrogen stream blended with the feed to the blower.

6.38. *n*-Hexane is burned with excess air. An analysis of the product gas yields the following *dry-basis* molar composition: 6.9% CO_2, 2.1% CO, 0.265% C_6H_{14} (+ O_2 and N_2). The stack gas emerges at 760 mm Hg. Calculate the percentage conversion of hexane, the percentage excess air fed to the burner, and the dew point of the stack gas, taking water to be the only condensable species.

6.39. A fuel gas containing methane and ethane is burned with air in a furnace, producing a stack gas at 300°C and 105 kPa (absolute). You analyze the stack gas and find that it contains no unburned hydrocarbons, oxygen, or carbon monoxide. You also determine the dew-point temperature.

(a) Estimate the range of possible dew-point temperatures by determining the dew points when the feed is either pure methane or pure ethane.

(b) Estimate the fraction of the feed that is methane if the measured dew-point temperature is 59.5°C.

(c) What range of measured dew point temperatures would lead to calculated methane mole fractions within 5% of the value determined in Part (b)?

6.40. A mixture of propane and butane is burned with air. Partial analysis of the stack gas produces the following dry-basis volume percentages: 0.0527% C_3H_8, 0.0527% C_4H_{10}, 1.48% CO, and 7.12% CO_2. The stack gas is at an absolute pressure of 780 mm Hg and the dew point of the gas is 46.5°C. Calculate the molar composition of the fuel.

Equipment Encyclopedia
absorber

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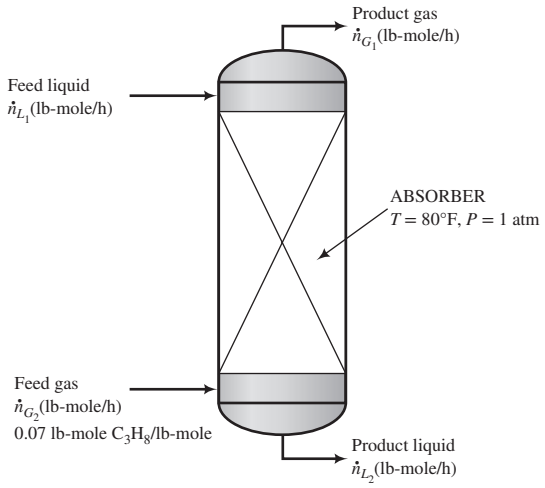
6.41. An important parameter in the design of gas absorbers is the ratio of the flow rate of the feed liquid to that of the feed gas. The lower the value of this ratio, the lower the cost of the solvent required to process a given quantity of gas but the taller the absorber must be to achieve a specified separation.

Propane is recovered from a 7 mole% propane–93% nitrogen mixture by contacting the mixture with liquid *n*-decane. An insignificant amount of decane is vaporized in the process, and 98.5% of the propane entering the unit is absorbed.



(a) The highest possible propane mole fraction in the exiting liquid is that in equilibrium with the propane mole fraction in the feed gas (a condition requiring an infinitely tall column). Using Raoult's law to relate the mole fractions of propane in the feed gas and liquid, calculate the ratio $(\dot{n}_{L_1}/\dot{n}_{G_2})$ corresponding to this limiting condition.

(b) Suppose the actual feed ratio $(\dot{n}_{L_1}/\dot{n}_{G_2})$ is 1.2 times the value calculated in Part (a) and the percentage of the entering propane absorbed is the same (98.5%). Calculate the mole fraction of propane in the exiting liquid.

(c) What are the costs and benefits associated with increasing $(\dot{n}_{L_1}/\dot{n}_{G_2})$ from its minimum value [the value calculated in Part (a)]? What would you have to know to determine the most cost-effective value of this ratio?

Equipment Encyclopedia
stripper

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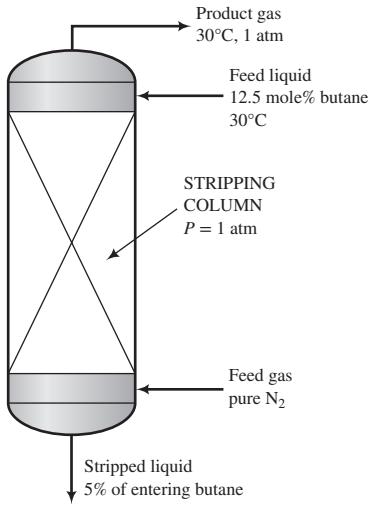
6.42. A liquid stream consisting of 12.5 mole% *n*-butane and the balance a heavy nonvolatile hydrocarbon is fed to the top of a stripping column, where it is contacted with an upward-flowing stream of nitrogen. The residual liquid leaves the bottom of the column containing all of the heavy hydrocarbon, 5% of the butane entering the column, and a negligible amount of dissolved nitrogen.



(a) The highest possible butane mole fraction in the exiting gas is that in equilibrium with the butane in the entering liquid (a condition that would require an infinitely tall column to achieve). Using Raoult's law to relate the mole fractions of butane in the entering liquid and exiting gas, calculate the molar feed-stream ratio (mol gas fed/mol liquid fed) corresponding to this limiting condition.

(b) Suppose the actual mole fraction of butane in the exit gas is 80% of its theoretical maximum value and the percentage stripped (95%) is the same as in Part (a). Calculate the ratio (mol gas fed/mol liquid fed) for this case.

(c) Increasing the nitrogen feed rate for a given liquid feed rate and butane recovery decreases the cost of the process in one way and increases it in another. Explain. What would you have to know to determine the most cost-effective value of the gas/liquid feed ratio?

Equipment Encyclopedia
compressor
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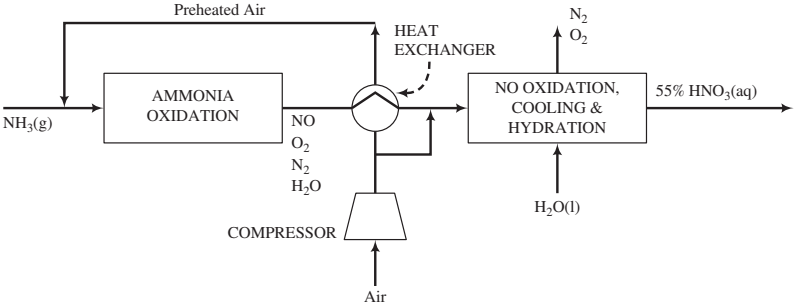
6.43. Nitric acid is a chemical intermediate primarily used in the synthesis of ammonium nitrate, which is used in the manufacture of fertilizers. The acid also is important in the production of other nitrates and in the separation of metals from ores.

Nitric acid may be produced by oxidizing ammonia to nitric oxide over a platinum–rhodium catalyst, then oxidizing the nitric oxide to nitrogen dioxide in a separate unit where it is absorbed in water to form an aqueous solution of nitric acid.



The reaction sequence is as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$4NO + 2O_2 \rightarrow 4NO_2$$
$$4NO_2 + 2H_2O(l) + O_2 \rightarrow 4HNO_3(aq)$$

where, unless otherwise specified, the species are gases. A side reaction in which ammonia is oxidized to form nitrogen and water can lower product yield:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Ammonia vapor produced by vaporizing pure liquid ammonia at 820 kPa absolute is mixed with air, and the combined stream enters the ammonia oxidation unit. Air at 30°C, 1 atm absolute, and 50% relative humidity is compressed and fed to the process. A fraction of the air is sent to the cooling and hydration units, while the remainder is passed through a heat exchanger and mixed with the ammonia. The total oxygen fed to the process is the amount stoichiometrically required to convert all of the ammonia to HNO_3, while the fraction sent to the ammonia oxidizer corresponds to the stoichiometric amount required to convert ammonia to NO.

The ammonia reacts completely in the oxidizer, with 97% forming NO and the rest forming N_2. Only a negligible amount of NO_2 is formed in the oxidizer. However, the gas leaving the oxidizer is subjected to a series of cooling and hydration steps in which the NO is completely oxidized to NO_2, which in turn combines with water (some of which is present in the gas from the oxidizer and the rest is added) to form a 55 wt% aqueous solution of nitric acid. The product gas from the process may be taken to contain only N_2 and O_2.

(a) Taking a basis of 100 kmol of ammonia fed to the process, calculate (i) the volumes (m^3) of the ammonia vapor and air fed to the process using the compressibility-factor equation of state; (ii) the amount (kmol) and composition (in mole fractions) of the gas leaving the oxidation unit; (iii) the required volume of liquid water (m^3) that must be fed to the cooling and hydration units; and (iv) the fraction of the air fed to the ammonia oxidizer.

(b) Scale the results from Part (a) to a new basis of 100 metric tons per hour of 55% nitric acid solution.

Exploratory Exercises—Research and Discover

ENVIRONMENTAL

(c) Nitrogen oxides (collectively referred to as NO_x) are a category of pollutants that are formed in many ways, including processes like that described in this problem. List the annual emission rates of the

three largest sources of NO_x emissions in your home region. What are the effects of exposure to excessive concentrations of NO_x?

(d) A platinum–rhodium catalyst is used in ammonia oxidation. Explain the function of the catalyst, describe its structure, and explain the relationship of the structure to the function.

6.44. A dry gas containing 10.0% NH_3 by volume is contacted with water at 10°C and 1 atm in a single-stage bubble contactor. The effluent liquid and gas streams may be considered to be in equilibrium with each other. A small slip stream taken from the effluent liquid is fed to a continuous densitometer, which indicates that the liquid density is 0.9534 g/mL.

(a) Using tabulated data from *Perry's Chemical Engineers' Handbook*,[12] estimate the percentage of the ammonia in the feed that is removed in the contactor.

(b) Why is it important to maintain the slip stream and densitometer chamber at a known temperature at or below the temperature of the contactor?

6.45. Sulfur trioxide (SO_3) dissolves in and reacts with water to form an aqueous solution of sulfuric acid (H_2SO_4). The vapor in equilibrium with the solution contains both SO_3 and H_2O. If enough SO_3 is added, all of the water reacts and the solution becomes pure H_2SO_4. If still more SO_3 is added, it dissolves to form a solution of SO_3 in H_2SO_4, called **oleum** or **fuming sulfuric acid**. The vapor in equilibrium with oleum is pure SO_3. Twenty percent oleum by definition contains 20 kg of dissolved SO_3 and 80 kg of H_2SO_4 per hundred kilograms of solution. Alternatively, the oleum composition can be expressed as % SO_3 by mass, with the constituents of the oleum considered to be SO_3 and H_2O.

(a) Prove that a 15.0% oleum contains 84.4% SO_3.

(b) Suppose a gas stream at 40°C and 1.2 atm containing 90 mole% SO_3 and 10% N_2 contacts a liquid stream of 98 wt% H_2SO_4 (aq), producing 15% oleum. Tabulated equilibrium data indicate that the partial pressure of SO_3 in equilibrium with this oleum is 1.15 mm Hg. Calculate (i) the mole fraction of SO_3 in the outlet gas if this gas is in equilibrium with the liquid product at 40°C and 1 atm, and (ii) the ratio (m^3 gas feed)/(kg liquid feed).

6.46. State whether you would use Raoult's law or Henry's law to perform vapor–liquid equilibrium calculations for each component in the following liquid mixtures: (a) water and dissolved nitrogen; (b) hexane, octane, and decane; and (c) CO_2 and water in club soda or any other carbonated beverage.

6.47. A gas containing nitrogen, benzene, and toluene is in equilibrium with a liquid mixture of 40 mole% benzene–60 mole% toluene at 100°C and 10 atm. Estimate the gas-phase composition (mole fractions) using Raoult's law. State your assumptions. Why would you have confidence in the accuracy of Raoult's law?

6.48. Using Raoult's law or Henry's law for each substance (whichever one you think appropriate), calculate the pressure and gas-phase composition (mole fractions) in a system containing a liquid that is 0.3 mole% N_2 and 99.7 mole% water in equilibrium with nitrogen gas and water vapor at 80°C.

6.49. The pressure in a vessel containing methane and water at 70°C is 10 atm. At the given temperature, the Henry's law constant for methane is 6.66×10^4 atm/mole fraction. Estimate the mole fraction of methane in the liquid.

6.50. A correlation for methane solubility in seawater[13] is given by the equation

$$\ln \beta = -67.1962 + 99.1624\left(\frac{100}{T}\right) + 27.9015 \ln\left(\frac{T}{100}\right) + S\left[-0.072909 + 0.041674\left(\frac{T}{100}\right) - 0.0064603\left(\frac{T}{100}\right)^2\right]$$

where β is volume of gas in mL at STP per unit volume (mL) of water when the partial pressure of methane is 760 mm Hg, T is temperature in Kelvin, and S is salinity in parts per thousand (ppt) by weight. At conditions of interest, the average salinity is 35 ppt, the temperature is 42°F, and the average density of seawater is 1.027 g/cm^3.

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[12] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008, pp. 2-91, 2-92, and 2-104.

[13] S. Yamamoto, J. B. Alcauskas, and T. E. Crozier, *J. Chem. Eng. Data*, **21**, 78(1976).

(a) Estimate the mole fraction of methane in seawater for equilibrium at the given conditions. Use a mean molecular weight of 18.4 g/mol for seawater. What is the Henry's law constant at this temperature and salinity?
(b) What does the above equation say about the effect of S on methane solubility?
(c) Use the Henry's law constant from Part (a) to estimate methane solubility at the given temperature and salinity, but 5000 ft below the ocean surface. (*Hint:* Estimate the pressure at that depth.)

Exploratory Exercise—Research and Discover

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(d) At the low temperatures and high pressures associated with the depths described in Part (c), methane can combine with water to form *methane hydrates*, which may affect both energy availability and the environment. Explain (i) how such behavior would influence the results in Part (c) and (ii) how dissolution of methane in seawater might affect energy availability and the environment.

BIOENGINEERING

6.51. When air (≈21 mole% O_2, 79% N_2) is placed in contact with 1000 cm^3 of liquid water at body temperature, 36.9°C, and 1 atm absolute, approximately 14.1 standard cubic centimeters [cm^3(STP)] of gas are absorbed in the water at equilibrium. Subsequent analysis of the liquid reveals that 33.4 mole% of the dissolved gas is oxygen and the balance is nitrogen.
(a) Estimate the Henry's law coefficients (atm/mole fraction) of oxygen and nitrogen at 36.9°C.
(b) An adult absorbs approximately 0.4 g O_2/min in the blood flowing though the lungs. Assuming that blood behaves like water and that it enters the lungs free of oxygen, estimate the flow rate of blood into the lungs in L/min.
(c) The actual flow rate of blood into the lungs is roughly 5 L/min. Identify the assumptions made in the calculation of Part (b) that are likely causes of the discrepancy between the calculated and actual blood flows.

6.52. The constituent partial pressures of a gas in equilibrium with a liquid solution at 30°C and 1 atm containing 2 lb_m SO_2/100 lb_m H_2O are $p_{H_2O} = 31.6$ mm Hg and $p_{SO_2} = 176$ mm Hg. The balance of the gas is air.
(a) Calculate the partial pressure of air. If you make any assumptions, state what they are.
(b) Suppose the only data available on this system gave $p_{SO_2} = 176$ mm Hg, but there was no information given on the equilibrium partial pressure of water. Use Raoult's law to estimate a value for this quantity. Assuming that the value given in the problem statement is correct, what percentage error results from using Raoult's law?
(c) The same system was examined in Example 6.4-1. What percentage errors in the two calculated quantities would result from using Raoult's law for the partial pressure of water?

6.53. The **solubility coefficient** of a gas may be defined as the number of cubic centimeters (STP) of the gas that dissolves in 1 cm^3 of a solvent under a partial pressure of 1 atm. The solubility coefficient of CO_2 in water at 20°C is 0.0901 cm^3 CO_2(STP)/cm^3 H_2O(l).
(a) Calculate the Henry's law constant in atm/mole fraction for CO_2 in H_2O at 20°C from the given solubility coefficient.
(b) How many grams of CO_2 can be dissolved in a 12-oz bottle of soda at 20°C if the gas above the soda is pure CO_2 at a gauge pressure of 2.5 atm (1 liter = 33.8 fluid ounces)? Assume the liquid properties are those of water.
(c) What volume would the dissolved CO_2 occupy if it were released from solution at body temperature and pressure—37°C and 1 atm?

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6.54. The sulfur dioxide content of a stack gas is monitored by passing a sample stream of the gas through an SO_2 analyzer. The analyzer reading is 1000 ppm SO_2 (parts per million on a molar basis). The sample gas leaves the analyzer at a rate of 1.50 L/min at 30°C and 10.0 mm Hg gauge and is bubbled through a tank containing 140 liters of initially pure water. In the bubbler, SO_2 is absorbed and water evaporates. The gas leaving the bubbler is in equilibrium with the liquid in the bubbler at 30°C and 1 atm absolute. The SO_2 content of the gas leaving the bubbler is periodically monitored with the SO_2 analyzer, and when it reaches 100 ppm SO_2 the water in the bubbler is replaced with 140 liters of fresh water.
(a) Speculate on why the sample gas is not just discharged directly into the atmosphere after leaving the analyzer. Assuming that the equilibrium between SO_2 in the gas and dissolved SO_2 is described by Henry's law, explain why the SO_2 content of the gas leaving the bubbler increases

with time. What value would it approach if the water were never replaced? Explain. (The word "solubility" should appear in your explanation.)

(b) Use the following data for aqueous solutions of SO_2 at 30°C[14] to estimate the Henry's law constant in units of mm Hg/mole fraction:

g SO_2 dissolved/100 g H_2O(l)	0.0	0.5	1.0	1.5	2.0
p_{SO_2}(mm Hg)	0.0	37.1	83.7	132	183

(c) Estimate the SO_2 concentration of the bubbler solution (mol SO_2/liter), the total moles of SO_2 dissolved, and the molar composition of the gas leaving the bubbler (mole fractions of air, SO_2, and water vapor) at the moment when the bubbler solution must be changed. Make the following assumptions:

- The feed and outlet streams behave as ideal gases.
- Dissolved SO_2 is uniformly distributed throughout the liquid.
- The liquid volume remains essentially constant at 140 liters.
- The water lost by evaporation is small enough for the total moles of water in the tank to be considered constant.
- The distribution of SO_2 between the exiting gas and the liquid in the vessel at any instant of time is governed by Henry's law, and the distribution of water is governed by Raoult's law (assume $x_{H_2O} \approx 1$).

(d) Suggest changes in both scrubbing conditions and the scrubbing solution that might lead to an increased removal of SO_2 from the feed gas.

6.55. A vapor stream that is 65 mole% styrene and 35 mole% toluene is in equilibrium with a liquid mixture of the same two species. The pressure in the system is 150 mm Hg absolute. Use Raoult's law to estimate the composition of the liquid and the system temperature.

6.56. A gas containing nitrogen, benzene, and toluene is in equilibrium with a liquid consisting of 35 mole% benzene and 65 mole% toluene at 85°C and 10 atm. Estimate the gas composition (mole fractions) using Raoult's law and assuming ideal-gas behavior.

6.57. A liquid mixture containing 50 mole% propane, 30% *n*-butane, and 20% isobutane is stored in a rigid container at 77°F. The container has a maximum allowable working pressure of 400 psig. The head space above the liquid contains only vapors of the three hydrocarbons.

(a) A form of the Antoine equation for which constants for the three components are available[15] is $\log_{10} p^* = A - B/(T + C)$ where p^* is in bar and T is in kelvin. The constants and the data range from which they were obtained are given in the following table:

Component	A	B	C	Range (K)
propane	4.53678	1149.360	24.906	278–361
n-butane	4.35576	1175.581	–2.070	273–425
isobutane	4.32810	1132.108	0.918	261–408

Using these values and Raoult's law, show that use of the container at the given temperature is safe.

SAFETY

(b) Assume that upon heating there is little change in the liquid composition, and obtain a rough estimate of the temperature above which the maximum allowable pressure would be exceeded. Explain why the assumption regarding no change in liquid composition is reasonable.

6.58. A closed system contains an equimolar mixture of *n*-pentane and isopentane.

(a) Suppose the system is initially all liquid at 120°C and a high pressure, and the pressure is gradually reduced at a constant temperature. Estimate the pressures at which the first bubble of vapor forms and at which the last drop of liquid evaporates. Also calculate the liquid and vapor compositions (mole fractions) at those two conditions. (*Suggestion:* Use a spreadsheet.)

[14] A. E. Rabe and J. F. Harris, *J. Chem. Eng. Data*, **8**, 333(1963).

[15] http://webbook.nist.gov/cgi/.

(b) Now suppose the system starts as a vapor at 1200 mm Hg gauge and a high temperature, and the temperature is gradually reduced at constant pressure. Estimate the temperatures at which the first drop of liquid forms and at which the last bubble of vapor condenses. Also calculate the liquid and vapor compositions (mole fractions) at those two conditions.

6.59. Nitrogen is bubbled through a liquid mixture that initially contains equimolar amounts of benzene and toluene. The system pressure is 3 atm and the temperature is 80°C. The nitrogen flow rate is 10.0 standard liters per minute. The gas leaving the bubbler is saturated with benzene and toluene vapors.
(a) Estimate the initial rates (mol/min) at which benzene and toluene leave the bubbler.
(b) How will the mole fractions of benzene and toluene in the liquid change with time (increase, decrease, or remain constant)? Explain your answer.
(c) How will the mole fractions of benzene and toluene in the exiting gas change with time (increase, decrease, or remain constant)? Explain your answer.

6.60. Calculate the following:
(a) The bubble-point temperature of an equimolar mixture of liquid *n*-hexane and *n*-heptane at 1.0 atm and the composition (mole fractions) of the vapor in equilibrium with this mixture.
(b) The dew-point temperature of a gas mixture with a molar composition of 30% *n*-hexane, 30% *n*-heptane, and 40% air at 1 atm and the composition (mole fractions) of the liquid in equilibrium with this mixture.

6.61. A liquid mixture contains N components (N may be any number from 2 to 10) at pressure P(mm Hg). The mole fraction of the ith component is $x_i (i = 1, 2, \ldots, N)$, and the vapor pressure of that component is given by the Antoine equation (see Table B.4) with constants A_i, B_i, and C_i. Raoult's law may be applied to each component.
(a) Write the equations you would use to calculate the bubble-point temperature of the mixture, ending with an equation of the form $f(T) = 0$. (The value of T that satisfies this equation is the bubble-point temperature.) Then write the equations for the component mole fractions $(y_1, y_2, \ldots, y_N)$ in the first bubble that forms, assuming that the temperature is now known.
(b) Prepare a spreadsheet to perform the calculations of Part (a). The spreadsheet should include a title line for identification of the problem and a row that has entries for the given pressure and an estimate of the system temperature. Be sure to label these variables and show the units in which each is expressed. Adjacent columns should be headed Species, p_i^*, x_i, p_i, and y_i. Values of vapor pressures at the estimated temperature should be calculated using the physical property database in APEx, and Raoult's law should be used to determine partial pressures. The final row in the table should have the sums of the vapor mole fractions and partial pressures. Place a convergence function $f(T) = P - \Sigma p_i$ below the table so that Goal Seek can be used to vary the estimated T until $f(T) = 0$. Test the spreadsheet by calculating the bubble-point temperature for a liquid mixture containing 22.6 mole% benzene, 22.6% ethylbenzene, 22.3% toluene, and the balance styrene at pressures of 250 mm Hg, 760 mm Hg, and 7500 mm Hg. Identify any concerns you may have about the calculated results.
(c) It is determined that instead of styrene, the balance of the above mixture in Part (b) is propylbenzene. Upon entering the name "propylbenzene" in the APEx AntoineP estimator, you probably get the error message #VALUE!, which means that this substance is not in the APEx database. Poling et al. (see Footnote 2, p. A.57) provide constants for the vapor pressure of propylbenzene corresponding to the following expression of the Antoine equation:

$$\log_{10} p^*(\text{bar}) = A - B/[T(^\circ\text{C}) + C],$$

where $A = 4.07664$, $B = 1491.8$, and $C = 207.25$; the correlation is valid over the range 324 K–461 K. Modify the spreadsheet to incorporate this expression, and estimate the bubble-point temperature of the mixture at a pressure of 760 mm Hg.

6.62. A vapor mixture of *n*-butane (B) and *n*-hexane (H) contains 50.0 mole% butane at 120°C and 1.0 atm. A stream of this mixture flowing at a rate of 150.0 L/s is cooled and compressed, causing some but not all of the vapor to condense. (Treat this process as a single-unit operation.) Liquid and vapor product streams emerge from the process in equilibrium at T(°C) and 1100 mm Hg. The vapor product contains 60.0 mole% butane.

(a) Draw and label a flowchart. Perform a degree-of-freedom analysis to show that you have enough information to determine the required final temperature (T), the composition of the liquid product (component mole fractions), and the molar flow rates of the liquid and vapor products from the given information and Antoine expressions for the vapor pressures $p_B^*(T)$ and $p_H^*(T)$. *Just identify the equations—for example, mole balance on butane or Raoult's law for hexane—but don't write them yet.*

(b) Write in order the equations you would use to determine the quantities listed in Part (a) and also the fractional condensation of *hexane* (mol H condensed/mol H fed). In each equation, circle the variable for which you would solve. Do no algebra or calculations.

(c) Complete the calculations either manually or with an equation-solving program.

(d) State three assumptions you made that could lead to errors in the calculated quantities.

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distillation column

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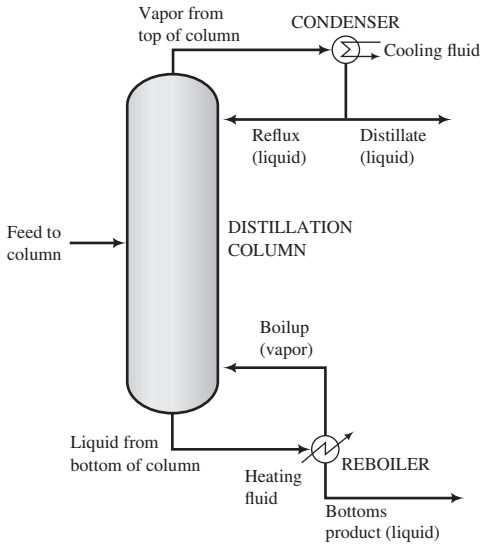
6.63. The feed to a distillation column (sketched below) is a 45.0 mole% *n*-pentane–55.0 mole% *n*-hexane liquid mixture. The vapor stream leaving the top of the column, which contains 98.0 mole% pentane and the balance hexane, goes to a total condenser (which means all the vapor is condensed). Half of the liquid condensate is returned to the top of the column as *reflux* and the rest is withdrawn as overhead product (*distillate*) at a rate of 85.0 kmol/h. The distillate contains 95.0% of the pentane fed to the column. The liquid stream leaving the bottom of the column goes to a *reboiler*. Part of the stream is vaporized; the vapor is returned to the bottom of the column as *boilup*, and the residual liquid is withdrawn as *bottoms product*.

(a) Calculate the molar flow rate of the feed stream and the molar flow rate and composition of the bottoms product stream.

(b) Estimate the temperature of the vapor entering the condenser, assuming that it is saturated (at its dew point) at an absolute pressure of 1 atm and that Raoult's law applies to both pentane and hexane. Then estimate the volumetric flow rates of the vapor stream leaving the column and of the liquid distillate product. State any assumptions you make.

(c) Estimate the temperature of the reboiler and the composition of the vapor boilup, again assuming operation at 1 atm.



(d) Calculate the minimum diameter of the pipe connecting the column and the condenser if the maximum allowable vapor velocity in the pipe is 10 m/s. Then list all the assumptions underlying the calculation of that number.

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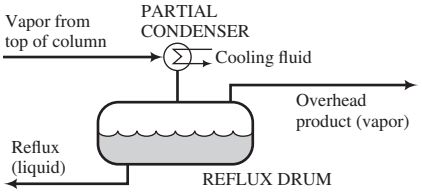
6.64. The vapor leaving the top of a distillation column goes to a condenser in which either total or partial condensation takes place. If a *total condenser* is used, a portion of the condensate is returned to the top of the column as *reflux* and the remaining liquid is taken off as the *overhead product* (or *distillate*). (See Problem 6.63.) If a *partial condenser* is used, the liquid condensate is returned as reflux and the uncondensed vapor is taken off as the overhead product.



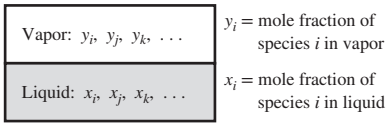
The overhead product from an *n*-butane–*n*-pentane distillation column is 96 mole% butane. The temperature of the cooling fluid limits the condenser temperature to 40°C or higher.

(a) Using Raoult's law, estimate the minimum pressure at which the condenser can operate as a partial condenser (i.e., at which it can produce liquid for reflux) and the minimum pressure at which it can operate as a total condenser. In terms of dew point and bubble point, what do each of these pressures represent for the given temperature?

(b) Suppose the condenser operates as a total condenser at 40°C, the production rate of overhead product is 75 kmol/h, and the mole ratio of reflux to overhead product is 1.5:1. Calculate the molar flow rates and compositions of the reflux stream and the vapor feed to the condenser.

(c) Suppose now that a partial condenser is used, with the reflux and overhead product in equilibrium at 40°C and the overhead product flow rate and reflux-to-overhead product ratio having the values given in Part (b). Calculate the operating pressure of the condenser and the compositions of the reflux and vapor feed to the condenser.

6.65. Vapor–liquid equilibrium calculations can sometimes be simplified through the use of a quantity called the **relative volatility**, which may be defined in terms of the following depiction of vapor and liquid phases in equilibrium:



The relative volatility of species i to species j is

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{y_i/y_j}{x_i/x_j}$$

If α_{ij} is much greater than 1, species i is much more volatile than species j (i.e., it has a much greater tendency to vaporize at the system temperature and pressure); conversely, if $\alpha_{ij} \ll 1$, species i is much less volatile than species j. The closer α_{ij} is to 1, the more difficult it is to separate species i from species j by a process such as distillation or partial condensation of a vapor mixture.

(a) Show that the relative volatility of species A to species B, α_{AB}, equals the ratio of vapor pressures at the system temperature, p^*_A/p^*_B, if both species obey Raoult's law and follow ideal-gas behavior.

(b) Determine the relative volatility of styrene to ethylbenzene at 85°C and the relative volatility of benzene to ethylbenzene at the same temperature. Which pair would you classify as more difficult to separate by distillation?

(c) Show that for a binary mixture of i and j

$$y_i = \frac{\alpha_{ij}x_i}{1 + (\alpha_{ij} - 1)x_i}$$

(d) Apply the equation from Part (c) to a benzene–ethylbenzene system at 85°C, using it to estimate the mole fractions of benzene in the vapor phase in equilibrium with liquids having benzene mole fractions of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0. Then calculate the total system pressure for each of these six conditions.

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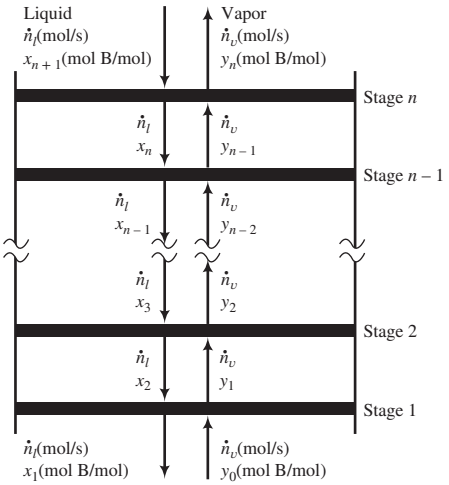
6.66. A **stage** of a separation process is defined as an operation in which components of one or more feed streams divide themselves between two phases, and the phases are taken off separately. In an **ideal stage** or **equilibrium stage**, the effluent (exit) streams are in equilibrium with each other.

Distillation columns often consist of a series of vertically distributed stages. Vapor flows upward and liquid flows downward between adjacent stages; some of the liquid fed to each stage vaporizes,

and some of the vapor fed to each stage condenses. A representation of a section of a distillation column is shown below. (See Problem 4.42 for a more realistic representation.)

Consider a distillation column operating at 0.4 atm absolute in which benzene and styrene are being separated. A vapor stream containing 65 mole% benzene and 35 mole% styrene enters stage 1 at a rate of 200 mol/h, and liquid containing 55 mole% benzene and 45 mole% styrene leaves this stage at a rate of 150 mol/h. You may assume (1) the stages are ideal, (2) Raoult's law can be used to relate the compositions of the streams leaving each stage, and (3) the total vapor and liquid molar flow rates do not change by a significant amount from one stage to the next.



(a) How would you expect the mole fraction of benzene in the liquid to vary from one stage to another, beginning with stage 1 and moving up the column? In light of your answer and considering that the pressure remains essentially constant from one stage to another, how would you then expect the temperature to vary at progressively higher stages? Briefly explain.

(b) Estimate the temperature at stage 1 and the compositions of the vapor stream leaving this stage and the liquid stream entering it. Then repeat these calculations for stage 2.

(c) Describe how you would calculate the number of ideal stages required to reduce the styrene content of the vapor to less than 5 mole%.

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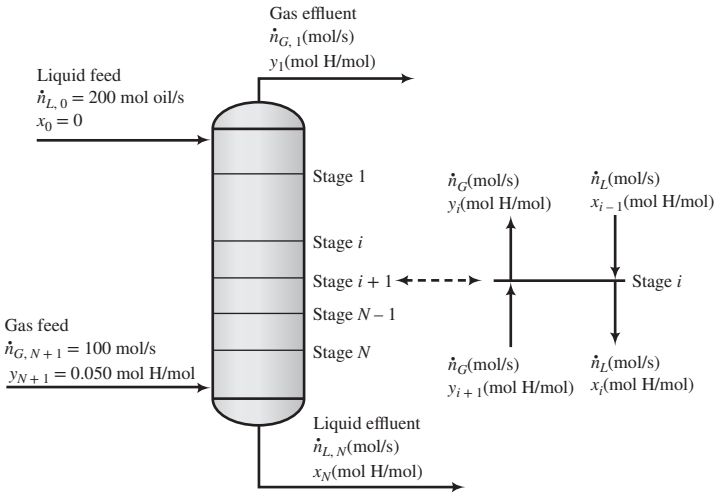
6.67. The following diagram shows a staged absorption column in which *n*-hexane (H) is absorbed from a gas into a heavy oil.



A gas feed stream containing 5.0 mole% hexane vapor and the balance nitrogen enters at the bottom of an absorption column at a basis rate of 100 mol/s, and a nonvolatile oil enters the top of the column in a ratio 2 mol oil fed/mol gas fed. The absorber consists of a series of ideal stages (see Problem 6.66), arranged so that gas flows upward and liquid flows downward. The liquid and gas streams leaving each stage are in equilibrium with each other (by the definition of an ideal stage), with compositions related by Raoult's law. The absorber operates at an approximately constant temperature T(°C) and 760 mm Hg. Of the hexane entering the column, 99.5% is absorbed and leaves in the liquid column effluent. At the given conditions it may be assumed that N_2 is insoluble in the oil and that none of the oil vaporizes.

(a) Calculate the molar flow rates and mole fractions of hexane in the gas and liquid streams leaving the column. Then calculate the average values of the liquid and gas molar flow rates in the column, $\dot{n}_L$(mol/s) and $\dot{n}_G$(mol/s). For simplicity, in subsequent calculations use the average values for liquid and gas molar flow rates *within* the column, but the actual values for the corresponding flow rates entering and leaving the column.

(b) Considering the bottom stage to be ideal, estimate the mole fractions of hexane in the gas leaving that stage (y_N) and in the liquid entering it (x_{N-1}) if the column temperature is 50°C.

(c) Suppose that x_i and y_i are the mole fractions of hexane in the liquid and gas streams leaving stage i. Derive the following equations from an equilibrium relationship and a mass balance around a section of the column encompassing stage i and the bottom of the column:

$$y_i = x_i p_i^*(T)/P \tag{1}$$

$$x_{i-1} = \left(x_N n_{L,N} + y_i \dot{n}_G - y_{N+1}\dot{n}_{G+1}\right)/\dot{n}_L \tag{2}$$

Verify that these equations yield the answers you calculated in Part (b).

(d) Examine the effect of operating temperature on the column by estimating the number of ideal stages necessary to achieve the desired separation. In the calculations, which will be done using a spreadsheet, take the pressure in the column to be constant at 760 torr, but consider three different operating temperatures: 30°C, 50°C, and 70°C. The calculations will follow a stage-to-stage strategy beginning at the bottom of the column and repeatedly applying Equations (1) and (2) until the mole fraction of hexane in the vapor leaving the column is less than or equal to that calculated in Part (a). You may use APEx or the Antoine equation and Table B.4 to estimate the hexane vapor pressure. The calculations for the case of $T = 30$°C illustrate how to proceed; for this case, $y_{N-1} < y_1 = 0.00263$ after only two stages.

Hexane Absorption								
P(torr) =	760	yN+1 =	0.05	x0 =	0	nG,N+1(mol/s) =	100	
Fraction removal =	0.95	y1 =	0.00263	xN =		nL,0(mol/s) =	200	
						nG(mol/s) =		
						nL(mol/s) =		
T(C) =	30		T(C) =	50		T(C) =	70	
p*(torr) =	187.1		p*(torr) =			p*(torr) =		
i	xi × 10^3	yi × 10^3	i	xi × 10^3	yi × 10^3	i	xi × 10^3	yi × 10^3
N+1		50.00			50.00			50.00
N	24.27	5.976						
N–1	2.754	0.678						

When you set up your spreadsheet, you should be able to accomplish many of your calculations simply by copying cells from one location to another. In any case, *do not go beyond 25 stages* for any temperature, whether or not you achieve the required separation.

(e) You can see that the number of stages required increases as the column temperature increases. In fact, there is a maximum temperature beyond which the required separation cannot be achieved. At that temperature, the entering gas and leaving liquid are approximately in equilibrium, so that $x_N p^*(T) = y_{N+1} P$. Use either APEx or the Antoine equation to estimate the maximum temperature at which the separation can be achieved.

6.68. A vapor mixture containing 30 mole% benzene and 70% toluene at 1 atm is cooled isobarically in a closed container from an initial temperature of 115°C. Use the *Txy* diagram of Figure 6.4-1 to answer the following questions.

(a) At what temperature does the first drop of condensate form? What is its composition?

(b) At one point during the process the system temperature is 100°C. Determine the mole fractions of benzene in the vapor and liquid phases and the ratio (total moles in vapor/total moles in liquid) at this point.

(c) At what temperature does the last bubble of vapor condense? What is its composition?

6.69. Three gram-moles of benzene and 7 gram-moles of toluene are placed in a closed cylinder equipped with a piston. The cylinder is immersed in a bath of boiling water that maintains the temperature at 100°C. The force exerted on the piston can be varied to adjust the cylinder pressure to any desired value. The pressure is initially 1000 mm Hg and is gradually lowered to 600 mm Hg. Use the *Pxy* diagram of Figure 6.4-1 to convince yourself that the cylinder initially contains only liquid benzene and toluene and to answer the following questions.

(a) At what pressure does the first vapor bubble form? What is its composition?

(b) At what pressure does the last droplet of liquid evaporate? What is its composition?

(c) What are the liquid and vapor compositions in equilibrium with each other when the pressure is 750 mm Hg? What is the ratio (moles vapor/mole liquid) at this point?

(d) Estimate the volume of the cylinder contents when the pressure is (i) 1000 mm Hg, (ii) 750 mm Hg, and (iii) 600 mm Hg.

6.70. This problem deals with two-phase mixtures of benzene and toluene at equilibrium. The vapor phase may be assumed ideal and Raoult's law can be used for all system compositions. Use APEx and Solver (and not Figure 6.4-1) for the requested calculations.

(a) Use the Gibbs phase rule to show that there are two degrees of freedom for the system.

(b) For $T = 25$°C and $P = 50$ mm Hg, estimate the liquid and vapor compositions.

(c) For $T = 25$°C and $x_B = 0.500$, estimate the pressure and vapor composition.

(d) For $P = 100$ mm Hg and $x_B = 0.500$, estimate the temperature and vapor composition.

(e) For $P = 100$ mm Hg and $y_B = 0.500$, estimate the temperature and liquid composition.

(f) For $x_B = 0.55$ and $y_B = 0.8$, estimate the temperature and pressure.

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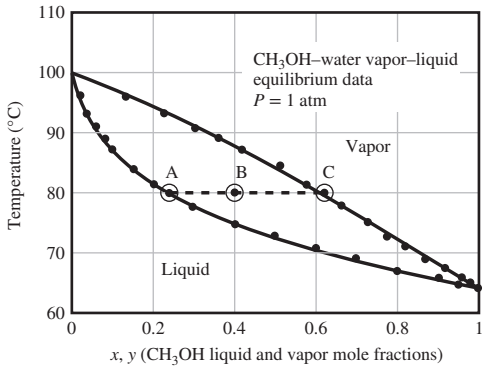
6.71. A methanol–water feed stream is introduced to a vaporizer in which a molar fraction f of the feed is vaporized. The feed has a methanol mole fraction of $x_F = 0.4$, and the vaporizer operates at a pressure of 1 atm absolute and 80°C. Vapor and liquid leaving the device are in equilibrium at the temperature and pressure of the system and have methanol mole fractions of y and x, respectively.

A *Txy* diagram for methanol–water mixtures at 1 atm absolute is shown below. The feed to the vaporizer and the liquid and vapor product streams are shown as points B, A, and C, respectively.



(a) Prove that f can be determined from the equation

$$f = \frac{\text{moles of vapor}}{\text{moles of liquid}} = \frac{x_F - x}{y - x_F}$$

Use this result to determine f for the specific conditions cited above ($x_F = 0.4$, $T = 80°C$).

(b) Use the *Txy* diagram to estimate the minimum and maximum temperatures at which the given feed stream could be separated into vapor and liquid fractions at 1 atm. In each case, what fraction of the feed would be vaporized?

(c) The vapor at C is sent to a condenser operated at constant pressure (1 atm). The liquid and vapor product streams leaving the condenser are in equilibrium and in a ratio of 1 mol vapor/1 mol liquid. Estimate the temperature and compositions of the two streams leaving the condenser.

6.72. Vapor–liquid equilibrium data for mixtures of acetone (A) and ethanol at 1 atm are given in the following table:

T(°C)	78.3	67.3	65.9	63.6	61.8	60.4	59.1	58.0	57.0	56.1
x_A	0.000	0.250	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.000
y_A	0.000	0.478	0.524	0.605	0.674	0.739	0.802	0.865	0.929	1.000

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(a) Use the given data to construct a *Txy* diagram for this system. Use the diagram to solve Parts (b)–(d).

(b) A thermocouple inserted into a two-phase mixture of acetone and ethanol at equilibrium reads 62.1°C. The system pressure is 1 atm. Estimate the mole fractions of acetone in the liquid and vapor phases.

(c) An equimolar mixture of acetone and ethanol is fed to an evacuated vessel and allowed to come to equilibrium at 65°C and 1.00 atm absolute. State a quick way to show that the system has two phases. Estimate (i) the molar compositions of each phase, (ii) the percentage of the total moles in the vessel that are in the vapor phase, and (iii) the percentage of the vessel volume occupied by the vapor phase.

(d) A liquid mixture containing 40.0 mole% acetone and 60.0% ethanol is fed to a continuous flash evaporator. Vapor and product streams leave the unit in equilibrium at 1.00 atm. The molar flow rate of the vapor product stream is 20% of the molar flow rate of the feed stream. Estimate the operating temperature of the evaporator and the compositions of the liquid and vapor product streams.

(e) Use Raoult's law and either APEx or Table B.4 to estimate the bubble-point temperature and vapor composition in equilibrium with an equimolar liquid mixture of acetone and ethanol. Calculate the percentage errors in the estimated values of T_{bp} and y. Propose a reason why Raoult's law produces poor estimates for this system. (*Suggestion:* Consider the molecular structure of the two components.)

6.73. In this problem you will use a spreadsheet to create a *Txy* diagram for the benzene-chloroform system at 1 atm. Once the spreadsheet has been created, it can be used as a template for vapor–liquid equilibrium calculations for other species. The calculations will be based on Raoult's law (i.e., $y_i P = x_i p_i^*$), although we recognize that this relationship may not produce accurate results for benzene-chloroform mixtures.

(a) Begin by establishing bounds on the system behavior. Look up the normal boiling points of chloroform and benzene and, without performing any calculations, sketch the expected shape of a *Txy* diagram for these two species at 1 atm.

(b) Using APEx or Table B.4, estimate the normal boiling points of the two species and compare them to the results in Part (a).

(c) Prepare a spreadsheet that has a title row "*Txy* Diagram for Ideal Binary Solution of Chloroform and Benzene." In the first cell of Row 2, place the label "*P* (mm Hg) =" and in the adjacent cell enter the system pressure, which for this case is 760. In Row 3 place headings for columns: xC, xB, T, p*C, p*B, P, yC, yB, and yC + yB. Not all of these columns are essential, but when filled they will give a complete picture of the system and a final check of the calculations. Carry out the following procedures in each subsequent row:

- Enter values for the mole fraction of chloroform (the first entry should be 1.000 and the last should be 0.000).

- Calculate the mole fraction of benzene by subtracting the value in the previous cell from 1.000.
- Enter an estimate of the equilibrium temperature that is between the two pure-component boiling points.
- Use APEx or Table B.4 to estimate p^*C and p^*B from the estimated temperature.
- Calculate pC and pB from Raoult's law.
- Calculate $P = p_C + p_B$ and apply the Goal Seek tool to adjust the value of T until $P = 760$ mm Hg.
- Calculate yC and yB from the partial pressures and P.
- Sum yC and yB to be sure they equal 1.000.

Once you have completed a row for the first value of xC, you should be able to copy formulas into subsequent rows. When the calculation has been completed for all rows (i.e., xC = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0), draw the Txy diagram.

(d) Explain what you did in the bulleted sequence of steps in Part (c) giving relevant relationships among system variables. The phrase "bubble point" should appear in your explanation.

(e) The following vapor–liquid equilibrium data have been obtained for mixtures of chloroform (C) and benzene (B) at 1 atm.

T(°C)	80.6	79.8	79.0	77.3	75.3	71.9	68.9	61.4
x_C	0.00	0.08	0.15	0.29	0.44	0.66	0.79	1.00
y_C	0.00	0.10	0.20	0.40	0.60	0.80	0.90	1.00

Plot these data on the graph generated in Part (c). Estimate the percentage errors in the Raoult's law values of the bubble-point temperature and vapor mole fraction for $x_C = 0.44$, taking the tabulated values to be correct. Why does Raoult's law give poor estimates for this system?

6.74. A mixture of benzene and toluene is in a tank whose pressure is maintained at 2.0 atm. Observation through a sight glass on the vessel shows that half of the tank volume is occupied by liquid. Analysis shows that the liquid contains 50.0 wt% benzene and the balance toluene. Raoult's law applies at all compositions, and the density of the liquid is essentially independent of temperature. Estimate (a) the temperature and (b) the fraction of the system mass in the liquid phase.

6.75. A liquid mixture containing 40.0 mole% methanol and 60.0 mole% 1-propanol is placed in an open vessel and heated slowly. Estimate the temperature at which the mixture begins to boil. List assumptions made in your calculations. If heat is supplied continuously, how will the liquid temperature and composition change with time? What is the temperature when the liquid contains 15 mole% methanol?

Equipment Encyclopedia
evaporator

www.wiley.com/college/felder

6.76. A liquid mixture containing 35.0 mole% acetone and 65.0 mole% water is to be partially vaporized to produce a vapor that is 70.0 mole% acetone and a residual liquid that is 30.0 mole% acetone.

(a) Suppose the process is to be carried out continuously, and at steady state the feed rate to the evaporator is 10.0 kmol/h. Calculate the molar flow rates of the product streams and the temperature (°C) and pressure (mm Hg) of the system.

(b) Suppose the vaporization unit has been built, operations have begun, and the product stream flow rates and compositions are measured. The measured acetone content of the vapor stream is 70.0 mole %, and the product stream flow rates have the values calculated in Part (a). However, the liquid product stream is found to contain 22.3 mole% acetone. Your colleague suggests that the analytical lab made a mistake in determining the composition of the liquid. Give at least five other possible reasons for the discrepancy. [Think about assumptions made in obtaining the solution to Part (a).]

Equipment Encyclopedia
reactor, condenser, distillation column

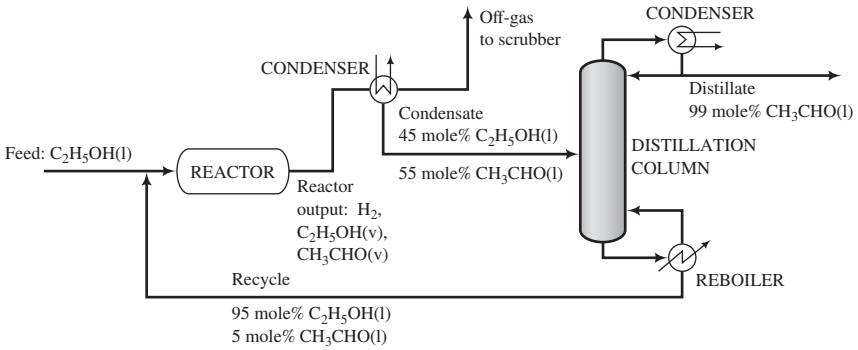
www.wiley.com/college/felder

6.77. Acetaldehyde is synthesized by the catalytic dehydrogenation of ethanol:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

Fresh feed (pure ethanol) is blended with a recycle stream (95 mole% ethanol and 5% acetaldehyde), and the combined stream is heated and vaporized, entering the reactor at 280°C. Gases leaving the reactor are cooled to −40°C to condense the acetaldehyde and unreacted ethanol. Off-gas from the condenser is sent to a scrubber, where the uncondensed organic compounds are removed and hydrogen is recovered as a by-product. The condensate from the condenser, which is 45 mole%

ethanol, is sent to a distillation column that produces a distillate containing 99 mole% acetaldehyde and a bottoms product that constitutes the recycle blended with fresh feed to the process. The production rate of the distillate is 1000 kg/h. The pressure throughout the process may be taken as 1 atm absolute.

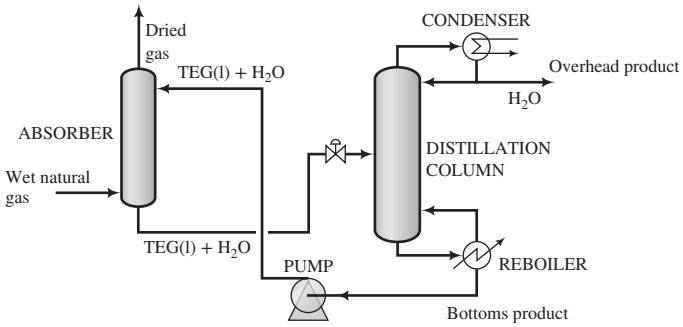


(a) Calculate the molar flow rates (kmol/h) of the fresh feed, the recycle stream, and the hydrogen in the off-gas. Also determine the volumetric flow rate (m^3/h) of the feed to the reactor. (*Suggestion:* Use Raoult's law in the analysis of the condenser.)

(b) Estimate (i) the overall and single-pass conversions of ethanol and (ii) the rates (kmol/h) at which ethanol and acetaldehyde are sent to the scrubber.

6.78. Dehydration of natural gas is necessary to prevent the formation of gas hydrates, which can plug valves and other components of a gas pipeline, and also to reduce potential corrosion problems. Water removal can be accomplished as shown in the following schematic diagram:

Equipment Encyclopedia
absorber, distillation column, pump
www.wiley.com/college/felder



Natural gas containing 80 lb_m $H_2O/10^6$ SCF gas [SCF = ft^3 (STP)] enters the bottom of an absorber at a rate of 4.0×10^6 SCF/day. A liquid stream containing triethylene glycol (TEG, molecular weight = 150.2) and a small amount of water is fed to the top of the absorber. The absorber operates at 500 psia and 90°F. The dried gas leaving the absorber contains 10 lb_m $H_2O/10^6$ SCF gas. The solvent leaving the absorber, which contains all the TEG–water mixture fed to the column plus all the water absorbed from the natural gas, goes to a distillation column. The overhead product stream from the distillation column contains only liquid water. The bottoms product stream, which contains TEG and water, is the stream recycled to the absorber.

(a) Draw and completely label a flowchart of this process. Calculate the mass flow rate (lb_m/day) and volumetric flow rate (ft^3/day) of the overhead product from the distillation column.

(b) The greatest possible amount of dehydration is achieved if the gas leaving the absorption column is in equilibrium with the solvent entering the column. If the Henry's law constant for water in TEG at 90°F is 0.398 psia/mol fraction, what is the maximum allowable mole fraction of water in the solvent fed to the absorber?

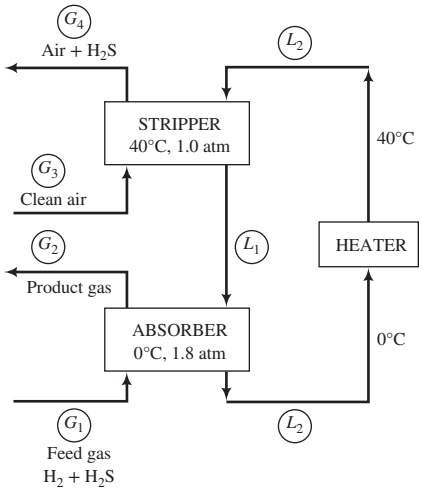
(c) A column of infinite height would be required to achieve equilibrium between the gas and liquid at the top of the absorber. For the desired separation to be achieved in practice, the mole fraction of water in the entering solvent must be less than the value calculated in Part (b). Suppose it is 80% of

that value and the flow rate of TEG in the recirculating solvent is 37 lb_m TEG/lb_m water absorbed in the column. Calculate the flow rate (lb_m/day) of the solvent stream entering the absorber and the mole fraction of water in the solvent stream leaving the absorber.

(d) What is the purpose of the distillation column in the process? (*Hint:* Think about how the process would operate without it.)

Equipment Encyclopedia
stripper, heater, absorber
www.wiley.com/college/felder

6.79. A two-unit process is used to separate H_2S from a gas containing 96% H_2 and 4% H_2S by volume. The H_2S is absorbed in a solvent, which is then regenerated by air in a stripping column. The Henry's law constant for the absorption of H_2S in the solvent at 0°C is 22 atm/mole fraction.



Data on Process Streams

G_1: 100 mol/h
96% H_2, 4% H_2S, 1.8 atm

G_2: 99.9% H_2, 0.1% H_2S

G_3: 200 mol air/h

G_4: 40°C, 1 atm

L_1: 0.200 mole% H_2S

L_2: Assume at equilibrium with G_1 at 0°C

(a) Briefly explain in your own words the functions of the three process units. Include in your explanation the purpose of the air in the stripper and the reason the stripper operates at a higher temperature than the absorber.

(b) Calculate the molar flow rate of pure solvent and the volumetric flow rate of the gas at G_4, neglecting evaporation of solvent in both columns. (See flowchart.)

Exploratory Exercise—Research and Discover

ENVIRONMENTAL

(c) The objective of the process described above is to produce purified hydrogen. However, in doing so the process also generates an effluent stream containing H_2S. Identify at least three concerns with simply releasing this stream into the air. Suggest an add-on to the process that allays as many of these concerns as possible. Calculate the mass per 100 mol of G_1 of any reactant required by the add-on. Identify any new concerns created by the add-on.

6.80. The solubility of sodium bicarbonate in water is 11.1 g $NaHCO_3$/100 g H_2O at 30°C and 16.4 g $NaHCO_3$/100 g H_2O at 60°C. If a saturated solution of $NaHCO_3$ at 60°C is cooled and comes to equilibrium at 30°C, what percentage of the dissolved salt crystallizes?

Equipment Encyclopedia
crystallizer
www.wiley.com/college/felder

6.81. An aqueous solution of potassium hydroxide (KOH) is fed to an evaporative crystallizer at a rate of 875 kg/h. The crystallizer operates at 10°C and produces crystals of $KOH \cdot 2H_2O$. Water evaporated from the crystallizer flows to a condenser, and the resulting condensate is collected in a tank. During a 30-minute period, 73.8 kg of water is collected. Five-gram samples of the feed to the crystallizer and the liquid removed with the crystals are taken for analysis and subsequently titrated with 0.85 M H_2SO_4. It is found that 22.4 mL of the H_2SO_4 solution is required for the feed and 26.6 mL is required for the product liquid.

(a) What fraction of the KOH in the feed is crystallized?

(b) Later you learn that a solution in equilibrium with $KOH \cdot 2H_2O$ crystals at 10°C has a concentration of 103 kg KOH/100 kg H_2O. How would this information cause you to reconsider the procedure by which a sample of the mother liquor was obtained? (*Hint:* Consider removing a slurry sample—i.e., one containing both solution and $KOH \cdot 2H_2O$ crystals—that is maintained at 10°C, but that initially had a solute concentration of 121 kg KOH/100 kg H_2O. What would that concentration be after the sample is stored for several hours?)

6.82. A salt A is soluble in a solvent S. A conductivity meter used to measure the solute concentration in A–S solutions is calibrated by dissolving a known quantity of A in S, adding more S to bring the solution volume to a fixed value, and noting the conductivity meter reading. The data given below are taken at 30°C:

Solute Dissolved (g)	Solution Volume (mL)	Meter Reading R
0	100.0	0
20.0	100.0	30
30.0	100.0	45

The following experiment is performed. One hundred sixty grams of A is dissolved in S at 30°C. S is added until a final solution volume of 500 mL is obtained. The solution is cooled slowly to 0°C while being stirred and is maintained at this temperature long enough for crystallization to be complete. The concentration of A in the supernatant liquid is then measured with the conductivity meter, yielding $R = 17.5$. The solution is next reheated in small temperature increments. The last crystal is observed to dissolve at 10.2°C. A specific gravity of 1.10 may be assumed for all A–S solutions.

(a) Derive an expression for C(g A/mL solution) in terms of R.

(b) Calculate the solubilities (g A/100 g S) at 10.2°C and 0°C and the mass of solid crystals in the beaker at 0°C.

(c) If half the solvent in the flask were to evaporate at 0°C, how much more A would come out of solution?

Equipment Encyclopedia
crystallizer

www.wiley.com/college/felder

6.83. An aqueous solution containing 35 wt% $MgSO_4$ is fed to an evaporative crystallizer operating at 50°F. The vapor generated is 20% by mass of the feed. The solution, which contains 23 wt% $MgSO_4$, and the crystals suspended in it are in equilibrium.

(a) Based on the information in Table 6.5-1, what is the composition of the crystalline product?

(b) For a crystal production rate of 1000 kg/h, estimate (i) the required feed and vapor flow rates in kg/h, and (ii) the rate at which $MgSO_4$ could be recovered from the crystals if all the water is removed from them by drying.

Equipment Encyclopedia
crystallizer

www.wiley.com/college/felder

6.84. A solution containing 100 lb_m KNO_3/100 lb_m H_2O at 80°C is fed to a cooling crystallizer operated at 25°C. Slurry from the crystallizer (KNO_3 crystals suspended in saturated solution) is fed to a filter, where the crystals are separated from the solution. Use the solubility data in Figure 6.5-1 to determine the production rate of crystals (lb_m/lb_m feed) and the solid-to-liquid mass ratio (lb_m crystals/lb_m liquid) in the slurry leaving the crystallizer.

Equipment Encyclopedia
crystallizer, filter, pump

www.wiley.com/college/felder

6.85. A 10.0 wt% aqueous solution of sodium chloride is fed to an evaporative crystallizer operated under a partial vacuum. Evaporation of water concentrates the remaining solution beyond its saturation point at the crystallizer temperature and causes crystallization of NaCl. The crystallizer product is a slurry of solute crystals suspended in a saturated solution at 80°C. The unit is to produce 1000 kg NaCl(s)/h. The solubility of NaCl in water is given by Figure 6.5-1.

(a) Derive expressions for the required rate of evaporation of water (kg/h) and the mass flow rate of solution in the exit slurry in terms of the mass flow rate of the feed stream to the crystallizer. Determine the minimum possible feed rate (explain why it is the minimum rate) and the corresponding values of the evaporation rate and exit solution flow rate.

(b) The pump that conveys the exit slurry from the crystallizer to a downstream filter cannot handle material containing more than 40 wt% solids. Determine the maximum feed rate to the crystallizer and the corresponding evaporation rate.

Equipment Encyclopedia
evaporator, crystallizer, dryer

www.wiley.com/college/felder

6.86. Potassium dichromate ($K_2Cr_2O_7$) is to be recovered from a 21 wt% aqueous solution in a continuous crystallization operation. The solution is joined by a recycle stream and fed to a vacuum evaporator where water is removed and the remaining solution is cooled to 30°C, at which temperature the solubility of the salt is 0.20 kg $K_2Cr_2O_7$/kg H_2O. The solution and suspended potassium dichromate crystals flow to a centrifuge. The crystals and 5.0% of the solution constitute the solids recovered from the centrifuge, and the remaining solution is recycled to the evaporator. The solids, which contain 90 wt% crystals and 10% entrained solution, are fed to a dryer, where they are contacted with hot air. The remaining water in

the solids is evaporated, leaving pure potassium dichromate crystals. The air leaves the dryer at 90°C and 1 atm with a dew point of 39.2°C. For a production rate of 1000 kg solid $K_2Cr_2O_7$/h, calculate the required feed rate (kg/h) of 21% solution, the rate of evaporation of water in the evaporator (kg/h), the flow rate (kg/h) of the recycle stream, and the feed rate of air (standard liters/h).

BIOENGINEERING

6.87. Various *amino acids* have utility as food additives and in medical applications. They are often synthesized by fermentation using a specific microorganism to convert a substrate (e.g., a sugar) into the desired product. Small quantities of other species also may be formed and must be removed to meet product specifications. For example, isoleucine (Ile), which has a molecular weight of 131.2, is an essential amino acid[16] produced by fermentation, and other amino acids such as leucine and valine also are found in the fermentation broth. The broth is subjected to several processing steps to remove these and other impurities, but final processing by crystallization is required to meet stringent specifications on purity. The strategy is to crystallize the hydrated acid form of Ile (Ile·HCl·H_2O), whose crystals exclude other amino acids, and then to redissolve, neutralize, and crystallize the final Ile product.

In a batch process designed to manufacture 2500 kg of Ile per batch, an aqueous feed solution containing 35 g Ile/dL and much lower concentrations of leucine and valine is fed to the final purification stages. The pH of the solution is 1.1 and its specific gravity is 1.02. The solution is heated to 60°C and 35-wt% HCl solution is added in a ratio of 0.4 kg per kg of feed. The addition of HCl causes the formation of crystals of Ile·HCl·H_2O, and the production of these crystals is further increased by slowly lowering the temperature to 20°C. At the final crystallizer conditions the Ile solubility is 5 g Ile/100 g solution. The resulting slurry is sent to a centrifuge where the crystals are separated from the liquid solution and the crystal cake is washed with water. The solids leaving the centrifuge contain 12% free water (i.e., not part of the crystal structure) and 88% pure crystals of Ile·HCl·H_2O.

The washed crystals are redissolved in water to form a solution that is 4.0 g Ile/dL with a specific gravity of 1.1. The solution is sent to an ion exchange unit where HCl is removed. Upon leaving the ion exchange unit the solution has a pH of about 5.5. It is sent to a second crystallizer where the temperature is gradually reduced to 10°C and the Ile solubility is 3.4 g Ile/100 g H_2O. The crystals are separated from the slurry by centrifugation, washed with pure water, and sent to a dryer for final processing.

(a) Construct a labeled flowchart for the process.

(b) Choosing a basis of 1 kg of feed solution, estimate (i) the mass of HCl solution added to the system, (ii) the water added to redissolve the Ile·HCl·H_2O crystals, (iii) the mass of HCl removed in the ion exchange unit, and (iv) the mass of final Ile product.

(c) Scale the quantities calculated in Part (b) to the production rate of 2500 kg Ile/batch.

(d) Estimate the active volume (in liters) of each of the crystallizers.

Exploratory Exercise—Research and Discover

(e) Amino acids are amphoteric, which means they can either donate or accept a proton (H^+). At low pH they tend to accept a proton and become acidic while at high pH they tend to donate a proton and become basic. They also are known as *zwitterions* because their ends are oppositely charged, even though the overall molecule is neutral. Isoleucine is reported to have an isoelectric point (pI) of 6.02 and pK_a values of 2.36 and 9.60. Look up the meaning of these terms and prepare a plot showing how these values are used in plotting the distribution of Ile between acid, zwitterionic (neutral), and basic forms as a function of pH. Explain why such a distribution is important in carrying out the separations described in the process.

BIOENGINEERING

6.88. Serine (Ser, molecular weight = 105.1 g/mol) is a nonessential amino acid (see Footnote 16) produced by fermentation. As with many other fermentation products, substantial downstream processing is required to meet specifications on product purity. Crystallization from an aqueous solution is useful in meeting those specifications. The following table shows how serine solubility in water varies with temperature:

T(°C)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	45.0	50.0
Solubility[17] (g Ser/100 g H_2O)	18.45	22.71	26.88	30.22	35.91	39.40	44.34	50.77	53.76

[16] Designating an amino acid as essential means it is not manufactured by the body and must be obtained in other ways (i.e., through food or the use of dietary supplements). Nonessential amino acids are manufactured by the body.

[17] H. Charmolue, M.S. Thesis, Georgia Institute of Technology, 1990.

(a) Prepare a plot of solubility as a function of temperature that can be used for interpolation.

(b) An aqueous solution of serine containing 60 g Ser/100 g H_2O is pumped into a batch cooling crystallizer, and the temperature is reduced slowly to 10°C, causing the formation of crystals of the monohydrated salt Ser·H_2O. Using the given solubility data, estimate the mass of crystals produced per unit mass of feed solution and the fraction of serine fed that is recovered as crystalline product.

(c) The molecular structure of serine makes it much more hydrophilic than other amino acids, and therefore its solubility is about an order of magnitude greater than that of most other amino acids. The addition of methanol to reduce the solubility in the solution has been suggested. Experimental data show that the solubility of Ser as a function of methanol content is given by the correlation $S/S_0 = \exp(-4.8x_M)$ where x_M is the mass fraction of methanol in a methanol–water solvent mixture, S_0 (g/g solvent) is serine solubility in water at a given temperature, and S is the solubility in the methanol–water solvent.

In an alternative to the processing scheme described in Part (b), sufficient methanol is added to the crystallizer after it has reached 10°C to produce a final solution that has a methanol-to-water mass ratio of 55:45, and the resulting system is allowed to come to equilibrium. Estimate the mass of crystals produced per unit mass of feed solution and the fraction of serine fed that is recovered as crystalline product.

Exploratory Exercises—Research and Discover

(d) Explain why serine is more hydrophilic than most other amino acids.

(e) Sketch a flowchart for a process in which the methanol fed to the crystallizer in Part (c) is recycled, and suggest why this design might be preferable to the one without recycle.

Equipment Encyclopedia
reactor, filter

www.wiley.com/college/felder

6.89. Sodium bicarbonate is synthesized by reacting sodium carbonate with carbon dioxide and water at 70°C and 2.0 atm gauge pressure:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

An aqueous solution containing 7.00 wt% sodium carbonate and a gas stream containing 70.0 mole% CO_2 and the balance air are fed to the reactor. All of the sodium carbonate and some of the carbon dioxide in the feed react. The gas leaving the reactor, which contains the air and unreacted CO_2, is saturated with water vapor at the reactor conditions. A liquid–solid slurry of sodium bicarbonate crystals in a saturated aqueous solution containing 2.4 wt% dissolved sodium bicarbonate and a negligible amount of dissolved CO_2 leaves the reactor and is pumped to a filter. The wet filter cake contains 86 wt% sodium bicarbonate crystals and the balance saturated solution, and the filtrate also is saturated solution. The production rate of solid crystals is 500 kg/h.

Suggestion: Although the problems to be given can be solved in terms of the product flow rate of 500 kg $NaHCO_3$(s)/h, it might be easier to assume a different basis and then scale the process to the desired production rate of crystals.

(a) Calculate the composition (component mole fractions) and volumetric flow rate (m^3/min) of the gas stream leaving the reactor.

(b) Calculate the feed rate of gas to the process in standard cubic meters/min [m^3(STP)/min].

(c) Calculate the flow rate (kg/h) of the liquid feed to the process. What more would you need to know to calculate the volumetric flow rate of this stream?

(d) The filtrate was assumed to leave the filter as a saturated solution at 70°C. What would be the effect on your calculations if the temperature of the filtrate actually dropped to 50°C as it passed through the filter?

(e) The reactor pressure of 2 atm gauge was arrived at in an optimization study. What benefit do you suppose would result from increasing the pressure? What penalty would be associated with this increase? The term "Henry's law" should appear in your explanation. (*Hint:* The reaction occurs in the liquid phase and the CO_2 enters the reactor as a gas. What step must precede the reaction?)

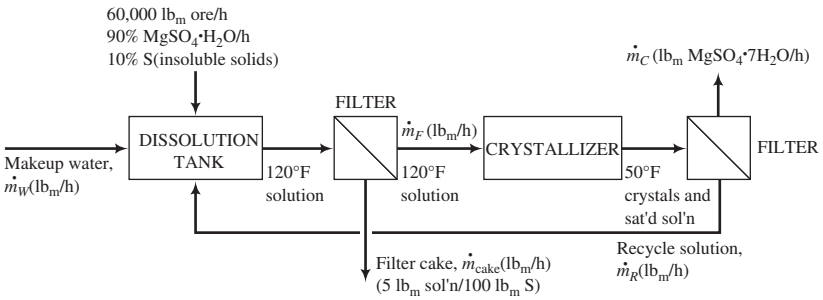
Equipment Encyclopedia
filter, crystallizer

www.wiley.com/college/felder

6.90. An ore containing 90 wt% $MgSO_4 \cdot H_2O$ and the balance insoluble minerals is fed to a dissolution tank at a rate of 60,000 lb_m/h along with fresh water and a recycle stream. The tank contents are heated to 120°F, causing all of the magnesium sulfate monohydrate in the ore to dissolve, forming a solution 10°F above saturation. The resulting slurry of the insoluble minerals in $MgSO_4$ solution is pumped to a heated filter, where a wet filter cake is separated from a solids-free filtrate. The filter

cake retains 5 lb_m of solution per 100 lb_m of solids. The filtrate is sent to a crystallizer in which the temperature is reduced to 50°F, producing a slurry of $MgSO_4 \cdot 7H_2O$ crystals in a saturated solution that is sent to another filter. The product filter cake contains all of the crystals and entrained solution in a ratio of 5 lb_m solution per 100 lb_m crystals. The filtrate from this filter is returned to the dissolution tank as the recycle stream.

Solubility data: Saturated magnesium sulfate solutions at 110°F and 50°F contain 32 wt% $MgSO_4$ and 23 wt% $MgSO_4$, respectively.



(a) Explain why the solution is first heated (in the dissolution tank) and filtered and then cooled (in the crystallizer) and filtered.

(b) Calculate the production rate of crystals and the required feed rate of fresh water to the dissolution tank. (*Note:* Don't forget to include water of hydration when you write a mass balance on water.)

(c) Calculate the ratio lb_m recycle/lb_m makeup water.

Equipment Encyclopedia
reactor, crystallizer, filter
@
www.wiley.com/college/felder
ENVIRONMENTAL

6.91. An aqueous waste stream leaving a process contains 10.0 wt% sulfuric acid and 1 kg nitric acid per kg sulfuric acid. The flow rate of sulfuric acid in the waste stream is 1000 kg/h. The acids are neutralized before being sent to a wastewater treatment facility by combining the waste stream with an aqueous slurry of solid calcium carbonate that contains 2 kg of recycled liquid per kg solid calcium carbonate. (The source of the recycled liquid will be given later in the process description.)

The following neutralization reactions occur in the reactor:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$
$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$

The sulfuric and nitric acids and calcium carbonate fed to the reactor are completely consumed. The carbon dioxide leaving the reactor is compressed to 30 atm absolute and 40°C and sent elsewhere in the plant. The remaining reactor effluents are sent to a crystallizer operating at 30°C, at which temperature the solubility of calcium sulfate is 2.0 g $CaSO_4$/1000 g H_2O. Calcium sulfate crystals form in the crystallizer and all other species remain in solution.

The slurry leaving the crystallizer is filtered to produce (i) a filter cake containing 96% calcium sulfate crystals and the remainder entrained saturated calcium sulfate solution, and (ii) a filtrate solution saturated with $CaSO_4$ at 30°C that also contains dissolved calcium nitrate. The filtrate is split, with a portion being recycled to mix with the solid calcium carbonate to form the slurry fed to the reactor, and the remainder being sent to the wastewater treatment facility.

(a) Draw and completely label a flowchart for this process.

(b) Speculate on why the acids must be neutralized before being sent to the wastewater treatment facility.

(c) Calculate the mass flow rates (kg/h) of the calcium carbonate fed to the process and of the filter cake; also determine the mass flow rates and compositions of the solution sent to the wastewater facility and of the recycle stream. (*Caution:* If you write a water balance around the reactor or the overall system, remember that water is a reaction product and not just an inert solvent.)

(d) Calculate the volumetric flow rate (L/h) of the carbon dioxide leaving the process at 30 atm absolute and 40°C. Do not assume ideal-gas behavior.

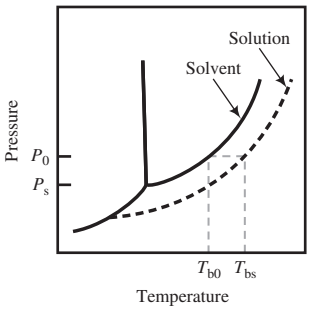
(e) The solubility of $Ca(NO_3)_2$ at 30°C is 152.6 kg $Ca(NO_3)_2$ per 100 kg H_2O. What is the maximum ratio of nitric acid to sulfuric acid in the feed that can be tolerated without encountering difficulties associated with contamination of the calcium sulfate by-product by $Ca(NO_3)_2$?

6.92. A solution of diphenyl (MW = 154.2) in benzene is formed by mixing 56.0 g diphenyl with 550.0 mL of benzene. Estimate the effective vapor pressure of the solution at 30°C and the melting and boiling points of the solution at 1 atm.

6.93. An aqueous solution of urea (MW = 60.06) freezes at −4.6°C and 1 atm. Estimate the normal boiling point of the solution; then calculate the mass of urea (grams) that would have to be added to 1.00 kg of solution to raise the normal boiling point by 3°C.

6.94. A solution is prepared by dissolving 0.5150 g of a solute (MW = 110.1) in 100.0 g of an organic solvent (MW = 94.10). The solution is observed to have a freezing point 0.41°C below that of the pure solvent. A second solution is prepared by dissolving 0.4460 g of a solute having an unknown molecular weight in 95.60 g of the original solvent. A freezing point depression of 0.49°C is observed. Determine the molecular weight of the second solute and the heat of fusion (kJ/mol) of the solvent. The melting point of the pure solvent is −5.000°C.

6.95. Derive Equation 6.5-4 for the boiling-point elevation of a dilute solution of a nonvolatile solute with mole fraction x in a solvent that has a pure-component vapor pressure $p_s^*(T)$. To do so, suppose that when the pressure is P_0, the pure solvent boils at temperature T_{b0} [so that $P_0 = p_s^*(T_{b0})$] and when the solvent is in the solution it boils at $T_{bs} > T_{b0}$. Further suppose that at temperature T_{b0} the effective vapor pressure of the solvent is $P_s = (p_s^*)_e(T_{b0}) < P_0$. (See diagram.)



The procedure is as follows.

(a) Write the Clausius–Clapeyron equation (Equation 6.1-3) for P_s (the effective solvent vapor pressure at T_{b0}) and then for P_0 (the effective solvent vapor pressure at T_{bs}), assuming that at the low solute concentrations in question the heat of vaporization is the same at both temperatures. Subtract the two equations. Simplify the equation algebraically, assuming that T_{b0} and T_{bs} are close enough together to say that $T_{b0}T_{bs} \approx T_{b0}^2$.

(b) Substitute the Raoult's law expression (Equation 6.5-2) for $P_s = (p_s^*)_e(T_{b0})$. Observe that if $x \ll 1$ (which it is for highly dilute solutions), then $\ln(1 - x) \approx -x$. The desired result follows.

MATERIALS

6.96. The separation of aromatic compounds from paraffins is essential in producing many polyesters that are used in a variety of products. When aromatics and paraffins have the same number of carbon atoms, they often have similar vapor pressures, which makes them difficult to separate by distillation. Extraction is a viable alternative, as illustrated by the following simple system.

Sulfolane (an industrial solvent) and octane may be considered completely immiscible. At 25°C, the ratio of the mass fraction of xylene in the octane-rich phase to the mass fraction of xylene in the sulfolane-rich phase is 0.25. One hundred kg of pure sulfolane are added to 100 kg of a mixture containing 75 wt% octane and 25% xylene, and the resulting system is allowed to equilibrate. How much xylene transfers to the sulfolane phase?

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6.97. A stream of 5.00 wt% oleic acid in cottonseed oil enters an extraction unit at a rate of 100.0 kg/h. The unit operates as a single equilibrium stage (the streams leaving the unit are in equilibrium) at 85°C. At this temperature, propane and cottonseed oil are essentially immiscible, the vapor pressure of propane is 34 atm, and the distribution coefficient (oleic acid mass fraction in propane/oleic acid mass fraction in cottonseed oil) is 0.15.

(a) Calculate the rate at which liquid propane must be fed to the unit to extract 90% of the oleic acid.

(b) Estimate the minimum operating pressure of the extraction unit. Explain your answer.

(c) High-pressure operation is costly and introduces potential safety hazards. Suggest two possible reasons for using propane as the solvent when other less volatile hydrocarbons are equally good solvents for oleic acid.

6.98. Benzene and hexane are being considered as solvents to extract acetic acid from aqueous mixtures. At 30°C, distribution coefficients for the two solvents are $K_B = 0.098$ mass fraction acetic acid in benzene/mass fraction acetic acid in water and $K_H = 0.017$ mass fraction acetic acid in hexane/mass fraction acetic acid in water.

(a) Based on the distribution coefficients only, which of the two solvents would you use and why? Demonstrate the logic of your decision by comparing the quantities of the two solvents required to reduce the acetic acid content in 100 kg of an aqueous solution from 30 wt% to 10 wt%.

(b) What other factors may be important in choosing between benzene and cyclohexane?

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6.99. Acetone is to be extracted with *n*-hexane from a 40.0 wt% acetone–60.0 wt% water mixture at 25°C. The acetone distribution coefficient (mass fraction acetone in the hexane-rich phase/mass fraction acetone in the water-rich phase) is 0.34.[18] Water and hexane may be considered immiscible. Three different processing alternatives are to be considered: a two-stage process and two single-stage processes.

(a) In the first stage of the proposed two-stage process, equal masses of the feed mixture and pure hexane are blended vigorously and then allowed to settle. The organic phase is withdrawn and the aqueous phase is mixed with 75% of the amount of hexane added in the first stage. The mixture is allowed to settle and the two phases are separated. What percentage of the acetone in the original feed solution remains in the water at the end of the process?

(b) Suppose all of the hexane added in the two-stage process of Part (a) is instead added to the feed mixture and the process is carried out in a single equilibrium stage. What percentage of the acetone in the feed solution remains in the water at the end of the process?

(c) Finally, suppose a single-stage process is used but it is desired to reduce the acetone content of the water to the final value of Part (a). How much hexane must be added to the feed solution?

(d) Under what circumstances would each of the three processes be the most cost-effective? What additional information would you need to make the choice?

BIOENGINEERING

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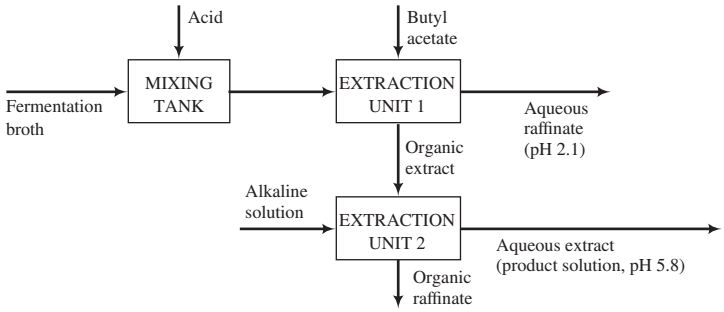
6.100. Penicillin is produced by fermentation and recovered from the resulting aqueous broth by extraction with butyl acetate. The penicillin distribution coefficient K (mass fraction of penicillin in the butyl acetate phase/mass fraction of penicillin in the water phase) depends strongly on the pH in the aqueous phase:

pH	2.1	4.4	5.8
K	25.0	1.38	0.10

This dependence provides the basis for the process to be described. Water and butyl acetate may be considered immiscible.

The extraction is performed in the following three-unit process:



- After filtration, broth from a fermentor containing dissolved penicillin, other soluble impurities, and water is acidified in a mixing tank. The acidified broth, which contains 1.5 wt% penicillin, is

[18] *Perry's Chemical Engineers' Handbook,* 8th Edition, McGraw-Hill, New York, 2008, p. 15-30.

contacted with liquid butyl acetate in an extraction unit consisting of a mixer, in which the aqueous and organic phases are brought into intimate contact with each other, followed by a settling tank, in which the two phases separate under the influence of gravity. The pH of the aqueous phase in the extraction unit equals 2.1. In the mixer 90% of the penicillin in the feed broth transfers from the aqueous phase to the organic phase.

- The two streams leaving the settler are in equilibrium with each other—that is, the ratio of the penicillin mass fractions in the two phases equals the value of K corresponding to the pH of the aqueous phase (= 2.1 in Unit 1). The impurities in the feed broth remain in the aqueous phase. The *raffinate* (by definition, the product stream containing the feed-solution solvent) leaving Extraction Unit 1 is sent elsewhere for further processing, and the organic *extract* (the product stream containing the extracting solvent) is sent to a second mixer–settler unit.
- In the second unit, the organic solution fed to the mixing stage is contacted with an alkaline aqueous solution that adjusts the pH of the aqueous phase in the unit to 5.8. In the mixer, 90% of the penicillin entering in the organic feed solution transfers to the aqueous phase. Once again, the two streams emerging from the settler are in equilibrium. The aqueous extract is the process product.

(a) Taking a basis of 100 kg of acidified broth fed to the first extraction unit, draw and completely label a flowchart of this process and carry out the degree-of-freedom analysis to show that all labeled variables can be determined. (*Suggestion:* Consider the combination of water, impurities, and acid as a single species and the alkaline solution as a second single species, since the components of these "pseudospecies" always stay together in the process.)

(b) Calculate the ratios (kg butyl acetate required/kg acidified broth) and (kg alkaline solution required/kg acidified broth) and the mass fraction of penicillin in the product solution.

(c) Briefly explain the following:

(i) What is the likely reason for transferring most of the penicillin from an aqueous phase to an organic phase and then transferring most of it back to an aqueous phase, when each transfer leads to a loss of some of the drug?

(ii) What is the purpose of acidifying the broth prior to the first extraction stage, and why is the extracting solution added to the second unit a base?

(iii) Why are the two "raffinates" in the process the aqueous phase leaving the first unit and the organic phase leaving the second unit, and vice versa for the "extracts"? (Look again at the definitions of these terms.)

(d) An alternative process for recovering the penicillin from the fermentation broth might involve evaporation to dryness. In that case, all the water simply is evaporated. Give two possible reasons for rejection of this alternative.

6.101. A mixture of 20 wt% water, 33% acetone, and the remainder methyl isobutyl ketone is brought to equilibrium at 25°C. If the total mass of the system is 1.2 kg, use the data in Figure 6.6-1 to estimate the composition and mass of each phase of the mixture.

6.102. Five kilograms of a 30 wt% acetone–70% water mixture is added to 3.5 kg of a 20 wt% acetone–80% MIBK mixture at 25°C. Use Figure 6.6-1 to estimate the mass and composition of each phase of the resulting mixture.

6.103. An aqueous acetone solution is fed at a rate of 32.0 lb_m/h to a stirred tank. A stream of pure methyl isobutyl ketone is also fed to the tank, and the resulting mixture is sent to a settler operating at 25°C. One of the phases formed has a flow rate of 41.0 lb_m/h and contains 70 wt% MIBK. Use Figure 6.6-1 to determine the flow rate and composition of the second product stream and the rate at which MIBK is fed to the unit.

6.104. Two systems contain water, acetone, and methyl isobutyl ketone in equilibrium at 25°C. The first system contains equal masses of the three species, and the second one contains 9.0% acetone, 21.0% water, and 70.0% MIBK by mass. Let $x_{a,aq}$ and $x_{a,org}$, respectively, denote the mass fractions of acetone in the aqueous phase (the phase that contains most of the water in the system) and the organic phase (the phase that contains most of the MIBK), and let $x_{w,aq}$ and $x_{w,org}$ denote the mass fractions of water in the two phases.

(a) Use Figure 6.6-1 to estimate the mass and composition (component mass fractions) of each phase of the mixtures in System 1 and in System 2.

(b) Determine the distribution coefficient of acetone in the organic phase relative to the aqueous phase in each system, $K_a = x_{a,org}/x_{a,aq}$. If a process is being designed to extract acetone from one of the two solvents (water and MIBK) to the other one, when would a high value of K_a be desirable and when would a low value be desirable?

(c) Determine the *selectivity*, β_{aw}, of acetone relative to water in the two systems, where

$$\beta_{aw} = \frac{(\text{mass fraction acetone/mass fraction water})_{\text{extract phase}}}{(\text{mass fraction acetone/mass fraction water})_{\text{raffinate phase}}}$$

What would be the value of β_{aw} if water and MIBK were completely immiscible?

(d) Express the selectivity, β_{aw}, in terms of the distribution coefficients of acetone and water, K_a and K_w. [Start with the formula given in Part (c).] If MIBK is being used to extract acetone from an aqueous phase, under what circumstances might it be important to have a very high value of β_{aw}, even if it means that less acetone is being extracted?

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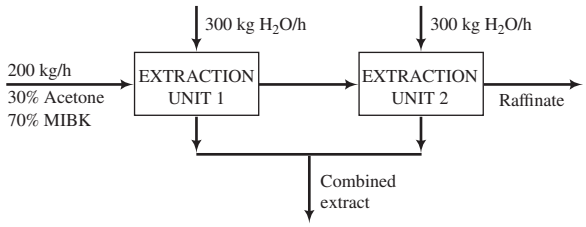
6.105. Water is used to extract acetone from a 30 wt% acetone–70% MIBK mixture flowing at a rate of 200 kg/h. Two equilibrium stages at 25°C are used as shown in the following diagram. If 300 kg H_2O/h is fed to each extraction unit, what fraction of the acetone in the feed solution would be removed and what would be the composition of the combined extract?



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6.106. Air at 25°C and 1 atm with a relative humidity of 25% is to be dehumidified in an adsorption column packed with silica gel. The equilibrium adsorptivity of water on silica gel is given by the expression[19]

$$X^*(\text{kg water/100 kg silica gel}) = 12.5\,\frac{p_{H_2O}}{p^*_{H_2O}}$$

where p_{H_2O} is the partial pressure of water in the gas contacting the silica gel and $p^*_{H_2O}$ is the vapor pressure of water at the system temperature. Air is fed to the column at a rate of 1.50 L/min until the silica gel is saturated (i.e., until it reaches equilibrium with the feed air), at which point the flow is stopped and the silica gel regenerated.

(a) Calculate the minimum amount of silica gel needed in the column if regeneration is to take place no more frequently than every two hours. State any assumptions you make.

(b) Briefly describe this process in terms that a high school student would have no trouble understanding. (What is the process designed to do, what happens within the column, and why is regeneration of the column packing necessary?)

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6.107. A 50.0-L tank contains an air–carbon tetrachloride gas mixture at an absolute pressure of 1 atm, a temperature of 34°C, and a relative saturation of 30%. Activated carbon is added to the tank to remove the CCl_4 from the gas by adsorption and the tank is then sealed. The volume of added activated carbon may be assumed negligible in comparison to the tank volume.

(a) Calculate p_{CCl_4} at the moment the tank is sealed, assuming ideal-gas behavior and neglecting adsorption that occurs prior to sealing.

(b) Calculate the total pressure in the tank and the partial pressure of carbon tetrachloride at a point when half of the CCl_4 initially in the tank has been adsorbed. *Note:* It was shown in Example 6.7-1 that at 34°C

$$X^*\left(\frac{\text{g } CCl_4 \text{ adsorbed}}{\text{g carbon}}\right) = \frac{0.0762 p_{CCl_4}}{1 + 0.096 p_{CCl_4}}$$

where p_{CCl_4} is the partial pressure (in mm Hg) of carbon tetrachloride in the gas contacting the carbon.

[19] R. Yang, *Gas Separation by Adsorption Processes*, Butterworths, London, 1987, p. 13.

(c) How much activated carbon must be added to the tank to reduce the mole fraction of CCl_4 in the gas to 0.001?

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6.108. The following equilibrium data[20] have been obtained for the adsorption of nitrogen dioxide, NO_2, on silica gel at 25°C and 1 atm:

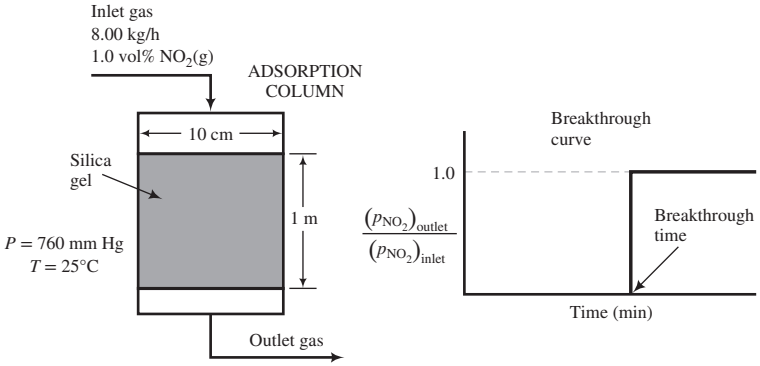
p_{NO_2} (mm Hg)	0	2	4	6	8	10	12
X^* (kg NO_2/100 kg silica gel)	0	0.4	0.9	1.65	2.60	3.65	4.85

(a) Confirm that these data are reasonably correlated by the **Freundlich isotherm**

$$X^* = K_F p_{NO_2}^{\beta}$$

and determine the values of K_F and β that provide the best correlation. (Use one of the methods introduced in Section 2.7c.)

(b) The adsorption column shown in the figure below has an internal diameter of 10.0 cm and a bed height of 1.00 m. The bed of silica gel has a bulk density of 0.75 kg/L. The adsorber is to remove NO_2 from a stream containing 1.0 mole% NO_2 and the balance air that enters the adsorber at 8.00 kg/h. The pressure and temperature throughout the column are maintained at 1 atm and 25°C. Past experience with this system has shown that a plot of the partial-pressure ratio $[(p_{NO_2})_{outlet}/(p_{NO_2})_{inlet}]$ versus time produces a **breakthrough curve** with the following appearance.



Using the isotherm derived in Part (a), determine the time (in min) required for breakthrough of the NO_2.

(c) Silica gel in the column can be *regenerated* (i.e., adsorbed NO_2 can be removed so that the silica gel column can be reused) by elevating the bed temperature and/or purging the bed with clean air. Suppose such a regeneration process requires 1.5 hours to accomplish. Process shutdowns can be avoided by installing several silica gel columns in parallel, using one to carry out the purification while the others are being regenerated. What is the minimum number of columns required to achieve continuous process operation?

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6.109. Various amounts of activated carbon were added to a fixed amount of raw cane sugar solution (48 wt% sucrose in water) at 80°C. A colorimeter was used to measure the color of the solutions, R, which is proportional to the concentration of trace unknown impurities in the solution. The following data were obtained (adapted from the reference in Footnote 20, p. 652):

kg carbon/kg dry sucrose	0	0.005	0.010	0.015	0.020	0.030
R (color units/kg sucrose)	20.0	10.6	6.0	3.4	2.0	1.0

The reduction in color units is a measure of the mass of impurities (the adsorbate) adsorbed on the carbon (the adsorbent).

[20] Adapted from R. E. Treybal, *Mass-Transfer Operations*, 3rd Edition, McGraw-Hill, New York, 1980, p. 308.

(a) The general form of the **Freundlich isotherm** is

$$X_i^* = K_F c_i^\beta$$

where X_i^* is the mass of i adsorbed/mass of adsorbent and c_i is the concentration of i in solution. Demonstrate that the Freundlich isotherm may be formulated for the system described above as

$$\vartheta = K'_F R^\beta$$

where ϑ is the % removal of color/[mass of carbon/mass of dissolved sucrose]. Then determine K'_F and β by fitting this expression to the given data, using one of the methods in Section 2.7.

(b) Calculate the amount of carbon that would have to be added to a vat containing 1000 kg of the 48 wt% sugar solution at 80°C for a reduction in color content to 2.5% of the original value.

PART 3 Energy Balances

CHAPTER 7

Energy and Energy Balances

Energy is expensive. We have not yet learned how to use efficiently the seemingly endless supply of "free" energy provided by the sun, winds, and tides. Nuclear power generation is feasible, but the need for safe disposal of radioactive wastes from nuclear reactors is a serious unresolved problem, and there are not nearly enough waterfalls and dams to provide sufficient hydroelectric power to meet the world's energy needs. This leaves us with fuel combustion—burning a combustible gas, oil, or solid fuel, and using the energy released as a source of thermal or (indirectly) electrical energy.

Process industries have always recognized that wasting energy leads to reduced profits, but throughout much of the last century the cost of energy was often an insignificant part of the overall process cost, and gross operational inefficiencies were tolerated. Beginning in the 1970s, a series of sharp increases in the price of natural gas and petroleum raised the cost of energy severalfold and intensified the need to eliminate unnecessary energy consumption. If a plant uses more energy than its competitors, its product could be priced out of the marketplace.

As an engineer designing or operating a process, one of your principal jobs would be to account carefully for the energy that flows into and out of each process unit and to determine the overall energy requirement for the process. You would do this by writing **energy balances** on the process, in much the same way that you write material balances to account for the mass flows to and from the process and its units. Typical problems that may be solved using energy balances include the following:

1. How much power (energy/time) is required to pump 1250 m^3/h of water from a storage vessel to a process unit? (The answer determines the size of the required pump motor.)

2. How much energy is required to convert 2000 kg of water at 30°C to steam at 180°C?

3. A hydrocarbon mixture is distilled, producing a liquid and a vapor stream, each with a known or calculable flow rate and composition. The energy input to the distillation column is provided by condensing saturated steam at a pressure of 15 bar. At what rate must steam be supplied to process 2000 mol/h of the feed mixture?

4. A highly exothermic chemical reaction A → B takes place in a continuous reactor. If a 75% conversion of A is to be achieved, at what rate must energy be transferred from the reactor to keep the contents below a specified temperature?

5. How much coal must be burned each day to produce enough energy to generate the steam to run the turbines to produce enough electricity to meet the daily power requirements of a city of 500,000 people?

6. A chemical process consists of four reactors, 25 pumps, and a number of compressors, distillation columns, mixing tanks, evaporators, filter presses, and other materials handling and separation units. Each individual unit either requires or releases energy.

(a) How can the process operation be designed to minimize the total energy requirement? (For example, can the energy released by an energy-emitting process unit be transferred to an energy-absorbing process unit?)

(b) What is the total energy requirement for the final process design, and how much will it cost to provide this energy? (The answer could determine whether or not the process is economically feasible.)

In this chapter we show how energy balances are formulated and applied. Section 7.1 defines the types of energy a process system can possess and the ways in which energy can be transferred to and from a system. Section 7.2 reviews the procedure for calculating the kinetic energy and gravitational potential energy of a process stream. Sections 7.3 and 7.4 derive the general energy balance for closed (batch) systems and open (semibatch and continuous) systems, and various applications of these equations are illustrated in Sections 7.5 through 7.7.

7.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- List and define in your own words the three components of the total energy of a process system and the two forms of energy transfer between a system and its surroundings. State the conditions under which heat and work are positive. Convert a quantity of energy or power (energy/time) expressed in any unit (e.g., J, dyne·cm, Btu, ft·lb_f/h, kW, hp) to its equivalent in any other dimensionally consistent units.
- Calculate the kinetic energy of a body of mass m moving with velocity u or the rate of transport of kinetic energy by a stream moving with mass flow rate $\dot{m}$ and velocity u. Calculate the gravitational potential energy of a body of mass m at elevation z or the rate of transport of gravitational potential energy by a stream moving with mass flow rate $\dot{m}$ at elevation z, where z is height above a reference plane at which potential energy is defined to equal zero.
- Define the terms **closed process system, open process system, isothermal process**, and **adiabatic process**. Write the first law of thermodynamics (the energy balance) for a closed process system and state the conditions under which each of the five terms in the balance can be neglected. Given a description of a closed process system, simplify the energy balance and solve it for whichever term is not specified in the process description.
- Define the terms **flow work, shaft work, specific internal energy, specific volume**, and **specific enthalpy**. Write the energy balance for an open process system in terms of enthalpy and shaft work and state the conditions under which each of the five terms can be neglected. Given a description of an open process system, simplify the energy balance and solve it for whichever term is not specified in the process description.
- State why the actual values of $\hat{U}$ and $\hat{H}$ can never be known for a given species in a specified **state** (temperature, pressure, and phase) and define the concept of a **reference state**. Explain in your own terms the statement, "The specific enthalpy of CO(g) at 100°C and 0.5 atm relative to CO(g) at 500°C and 1 atm is −12,141 J/mol." (Your explanation should involve a process in which carbon monoxide gas goes from one state to another.)
- Explain why the reference state used to generate a table of specific internal energies or enthalpies is irrelevant if one is only interested in calculating ΔU or ΔH for a process. (The term "state property" should appear in your explanation.)
- Given a process in which a specified mass m of a species goes from one state to another and tabulated values of $\hat{U}$ or $\hat{H}$ for the species at the initial and final states are available, calculate ΔU or ΔH. Given values of $\hat{V}$ at each state, calculate ΔH from the previously calculated ΔU or vice versa. Carry out the corresponding calculations to determine $\Delta \dot{U}$ and $\Delta \dot{H}$ for a stream with mass flow rate $\dot{m}$ going from one state to another.
- Use the saturated and superheated steam tables (Tables B.5, B.6, and B.7) to determine (a) whether water at a specified temperature and pressure is liquid, saturated vapor, or superheated vapor; (b) the specific volume, specific internal energy, and specific enthalpy of liquid water or steam at a specified temperature and pressure; (c) the vapor pressure of water

at a specified temperature; (d) the boiling point of water at a specified pressure; and (e) the dew point of superheated steam at a specified pressure.

- Explain the significance of the specific internal energies and enthalpies tabulated in the steam tables (B.5, B.6, and B.7), remembering that we can never know the true values of either variable in a given state. Given any process in which a specified mass (or mass flow rate) of water changes from one state to another, use the steam tables to calculate ΔU (or $\Delta \dot{U}$) and/or ΔH (or $\Delta \dot{H}$).
- Given a description of any nonreactive process for which tabulated specific internal energies or specific enthalpies are available at all input and output states for all process species, (a) draw and completely label a flowchart, including Q and W (or $\dot{Q}$ and $\dot{W}_s$ for an open system) if their values are either specified or called for in a problem statement; (b) perform a degree-of-freedom analysis; and (c) write the necessary equations (including the appropriately simplified energy balance) to determine all requested variables.
- Starting with the open system balance equation, derive the steady-state mechanical energy balance equation (Equation 7.7-2) for an incompressible fluid and simplify the equation further to derive the Bernoulli equation. List all the assumptions made in the derivation of the latter equation.
- Given fluid conditions (pressure, flow rate, velocity, elevation) at the inlet and outlet of an open system and values of friction loss and shaft work within the system, substitute known quantities into the mechanical energy balance (or the Bernoulli equation if friction loss and shaft work can be neglected) and solve the equation for whichever variable is unknown.

7.1 FORMS OF ENERGY: THE FIRST LAW OF THERMODYNAMICS

The total energy of a system has three components:

1. **Kinetic energy:** Energy due to the translational motion of the system as a whole relative to some frame of reference (usually the earth's surface) or to rotation of the system about some axis. In this text, we will deal only with translational kinetic energy.
2. **Potential energy:** Energy due to the position of the system in a potential field (such as a gravitational or electromagnetic field). In this text, we will deal only with gravitational potential energy.
3. **Internal energy:** All energy possessed by a system other than kinetic and potential energy, such as energy due to the motion of molecules relative to the center of mass of the system, to the rotational and vibrational motion and the electromagnetic interactions of the molecules, and to the motion and interactions of the atomic and subatomic constituents of the molecules.

Suppose a process system is **closed**, meaning that no mass is transferred across its boundaries while the process is taking place. Energy may be transferred between such a system and its surroundings in two ways:

1. As **heat**, or energy that flows as a result of temperature difference between a system and its surroundings. The direction of flow is always from a higher temperature to a lower one. *Heat is defined as positive when it is transferred to the system from the surroundings.*
2. As **work**, or energy that flows in response to any driving force other than a temperature difference, such as a force, a torque, or a voltage. For example, if a gas in a cylinder expands and moves a piston against a restraining force, the gas does work on the piston (energy is transferred as work from the gas to its surroundings, which include the piston). *In this text, work—like heat—is defined as positive if it is transferred to the system from the surroundings.*

(*Note:* The opposite sign convention is sometimes used. The choice is arbitrary, as long as it is used consistently; however, to avoid confusion when reading thermodynamics references, you should be sure which convention has been adopted.)

The terms "work" and "heat" refer only to energy that is being transferred: you can speak of the heat or work added to a system or given off by a system, but it is meaningless to speak of the heat or work possessed by or contained within a system.

Energy, like work, has units of force times distance: for example, joules (N·m), ergs (dyne·cm), and ft·lb_f. It is also common to use energy units defined in terms of the amount of heat that must be transferred to a specified mass of water to raise the temperature of the water by a specified temperature interval at a constant pressure of 1 atm. The most common of these units are tabulated here.

Unit	Symbol	Mass of Water	Temperature Interval
Kilogram-calorie or kilocalorie	kcal	1 kg	15°C to 16°C
Gram-calorie or calorie	cal	1 g	15°C to 16°C
British thermal unit	Btu	1 lb_m	60°F to 61°F

Conversion between these and other energy units may be performed using the conversion factors in the table on the inside front cover.

The principle that underlies all energy balances is the law of conservation of energy, which states that energy can neither be created nor destroyed. This law is also called the **first law of thermodynamics**. In its most general form, the first law states that the rate at which energy (kinetic + potential + internal) is carried into a system by the input streams, plus the rates at which it enters as heat and work, minus the rate at which it is transported out of the system by the output streams, equals the rate of accumulation of energy in the system. (That is, accumulation = input − output, as would be expected.)

Instead of presenting the equation in its most general form at this point, we will build up to it in stages. The next section reviews how to evaluate the kinetic and potential energies of an object and shows how the calculation can readily be extended to determine the rates at which kinetic and potential energies are transported by a flowing stream. Section 7.3 presents an integrated form of the transient balance equation that describes the behavior of a system between an initial state and a final state. This form of the equation is particularly useful for analyzing batch process systems. In Section 7.4 the first law is developed for a continuous steady-state process.

Most process systems are conveniently analyzed using one of the two forms of the energy balance equation presented in Sections 7.3 and 7.4. To perform energy balance calculations on other types of processes, such as semibatch processes or continuous processes that are being started up or shut down, the full transient energy balance equation is required. This equation is discussed in an introductory fashion in Chapter 10. A more thorough treatment of the full equation is deferred to thermodynamics courses and texts.

Test Yourself

(Answers, p. 658)

1. What forms of energy may a system possess? In what forms may energy be transferred to and from a closed system?
2. Why is it meaningless to speak of the heat possessed by a system?
3. Suppose the initial energy of a system (internal + kinetic + potential) is E_i, the final energy is E_f, an amount of energy Q is transferred from the environment to the system as heat, and an amount W is transferred from the environment to the system as work. According to the first law of thermodynamics, how must E_i, E_f, Q, and W be related?

7.2 KINETIC AND POTENTIAL ENERGY

The kinetic energy, E_k(J), of an object of mass m(kg) moving with velocity u(m/s) relative to the surface of the earth is

$$E_k = \tfrac{1}{2}mu^2 \qquad \textbf{(7.2-1a)}$$

If a fluid enters a system with a mass flow rate $\dot{m}$(kg/s) and uniform velocity u(m/s), then

$$\dot{E}_k = \tfrac{1}{2}\dot{m}u^2 \qquad \textbf{(7.2-1b)}$$

$\dot{E}_k$(J/s) may be thought of as the rate at which kinetic energy is transported into the system by the fluid.

Example 7.2-1 Kinetic Energy Transported by a Flowing Stream

Water flows into a process unit through a 2-cm ID pipe at a rate of 2.00 m^3/h. Calculate $\dot{E}_k$ for this stream in joules/second.

Solution First calculate the linear velocity (which equals the volumetric flow rate divided by the cross-sectional area of the pipe) and the mass flow rate of the fluid:

$$u = \frac{2.00\ \text{m}^3}{\text{h}} \left| \frac{100^2\ \text{cm}^2}{1^2\ \text{m}^2} \right| \frac{}{\pi(1)^2\ \text{cm}^2} \left| \frac{1\ \text{h}}{3600\ \text{s}} \right. = 1.77\ \text{m/s}$$

$$\dot{m} = \frac{2.00\ \text{m}^3}{\text{h}} \left| \frac{1000\ \text{kg}}{\text{m}^3} \right| \frac{1\ \text{h}}{3600\ \text{s}} = 0.556\ \text{kg/s}$$

Then, from Equation 7.2-1b

$$\dot{E}_k = \frac{0.556\ \text{kg/s}}{2} \left| \frac{(1.77)^2\ \text{m}^2}{\text{s}^2} \right| \frac{1\ \text{N}}{1\ \text{kg}\cdot\text{m/s}^2} = 0.870\ \text{N}\cdot\text{m/s} = \boxed{0.870\ \text{J/s}}$$

The gravitational potential energy of an object of mass m is

$$E_p = mgz \qquad \textbf{(7.2-2a)}$$

where g is the acceleration of gravity and z is the height of the object above a reference plane at which E_p is arbitrarily defined to be zero. If a fluid enters a system with a mass flow rate $\dot{m}$ and an elevation z relative to the potential energy reference plane, then

$$\dot{E}_p = \dot{m}gz \qquad \textbf{(7.2-2b)}$$

$\dot{E}_p$(J/s) may be thought of as the rate at which gravitational potential energy is transported into the system by the fluid. Since we are normally interested in the *change* in potential energy when a body or fluid moves from one elevation to another [$\dot{E}_{p2} - \dot{E}_{p1} = \dot{m}g(z_2 - z_1)$], the elevation chosen as the reference plane does not matter.

Example 7.2-2 Potential Energy Increase of a Flowing Fluid

Crude oil is pumped at a rate of 15.0 kg/s from a point 220 meters below the earth's surface to a point 20 meters above ground level. Calculate the attendant rate of increase of potential energy.

Solution Let subscripts 1 and 2 denote the first and second points, respectively:

Equipment Encyclopedia
pump
www.wiley.com/college/felder

$$\Delta \dot{E}_p = \dot{E}_{p2} - \dot{E}_{p1} = \dot{m}g(z_2 - z_1)$$

$$= \frac{15.0\ \text{kg}}{\text{s}} \left| \frac{9.81\ \text{m}}{\text{s}^2} \right| \frac{1\ \text{N}}{1\ \text{kg}\cdot\text{m/s}^2} \Big| [20 - (-220)]\ \text{m}$$

$$= 35{,}300\ \text{N}\cdot\text{m/s} = \boxed{35{,}300\ \text{J/s}}$$

The answer could also have been expressed as 35,300 W or 35.3 kW. A pump would have to deliver at least this much power to raise the oil at the given rate.

Test Yourself

(Answers, p. 658)

A gas flows through a long pipe of constant diameter. The outlet of the pipe is higher than the inlet, and the pressure of the gas at the outlet is less than the inlet pressure. The gas temperature is constant throughout the pipe and the system is at steady state.

1. How do the mass flow rates at the inlet and outlet compare? The densities? The volumetric flow rates? (Assume ideal-gas behavior.)
2. Is the change in potential energy of the gas from inlet to outlet positive, negative, or zero? What about the change in kinetic energy?

7.3 ENERGY BALANCES ON CLOSED SYSTEMS

A system is termed **open** or **closed** according to whether or not mass crosses the system boundary during the period of time covered by the energy balance. A batch process system is, by definition, closed, and semibatch and continuous systems are open.

An integral energy balance may be derived for a closed system between two instants of time. Since energy can neither be created nor destroyed, the generation and consumption terms of the general balance (4.2-1) drop out, leaving

$$\text{accumulation} = \text{input} - \text{output} \qquad \textbf{(7.3-1)}$$

In deriving the integral mass balance for a closed system in Section 4.2c we eliminated the input and output terms, since by definition no mass crosses the boundaries of a closed system. It is possible, however, for energy to be transferred across the boundaries as heat or work, so that the right side of Equation 7.3-1 may not be eliminated automatically. As with mass balances, however, the accumulation term equals the final value of the balanced quantity (in this case, the system energy) minus the initial value of this quantity. Equation 7.3-1 may therefore be written

$$\left\{\begin{matrix}\text{final system}\\ \text{energy}\end{matrix}\right\} - \left\{\begin{matrix}\text{initial system}\\ \text{energy}\end{matrix}\right\} = \begin{matrix}\text{net energy transferred to}\\ \text{the system (in} - \text{out)}\end{matrix} \qquad \textbf{(7.3-2)}$$

Now

$$\text{initial system energy} = U_i + E_{ki} + E_{pi}$$
$$\text{final system energy} = U_f + E_{kf} + E_{pf}$$
$$\text{energy transferred} = Q + W$$

where the subscripts i and f refer to the initial and final states of the system and U, E_k, E_p, Q, and W represent internal energy, kinetic energy, potential energy, and heat and work transferred to the system from its surroundings. Equation 7.3-2 then becomes

$$(U_f - U_i) + (E_{kf} - E_{ki}) + (E_{pf} - E_{pi}) = Q + W \qquad \textbf{(7.3-3)}$$

or, if the symbol Δ is used to signify (final − initial),

$$\boxed{\Delta U + \Delta E_k + \Delta E_p = Q + W} \qquad \textbf{(7.3-4)}$$

Equation 7.3-4 is the basic form of the first law of thermodynamics for a closed system. When applying this equation to a given process, you should be aware of the following points:

1. The internal energy of a system depends almost entirely on the chemical composition, state of aggregation (solid, liquid, or gas), and temperature of the system materials. It is independent of pressure for ideal gases and nearly independent of pressure for liquids and solids. *If no temperature changes, phase changes, or chemical reactions occur in a closed system and if pressure changes are less than a few atmospheres, then* $\Delta U \approx 0$.
2. *If a system is not accelerating, then* $\Delta E_k = 0$. *If a system is not rising or falling, then* $\Delta E_p = 0$.
3. *If a system and its surroundings are at the same temperature or the system is perfectly insulated, then* $Q = 0$. The process is then termed **adiabatic**.
4. Work done on or by a closed system is accomplished by movement of the system boundary against a resisting force or the passage of an electrical current or radiation across the system boundary. Examples of the first type of work are motion of a piston or rotation of a shaft that projects through the system boundary. *If there are no moving parts or electrical currents or radiation at the system boundary, then* $W = 0$.

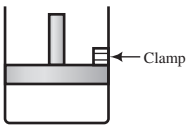
Test Yourself

(Answers, p. 658)

1. What do the terms closed system and open system mean? What is an adiabatic process?
2. If 250 J is added to a system as heat, what is the value of Q in the energy balance equation? If 250 J of work is done by the system, what is the value of W?
3. If a closed system has an internal energy of 100 kcal at the beginning of a process and 50 kcal at the end, what is ΔU?
4. Under what circumstances might U be considered independent of pressure for a pure substance?

Example 7.3-1 Energy Balance on a Closed System

A gas is contained in a cylinder fitted with a movable piston.

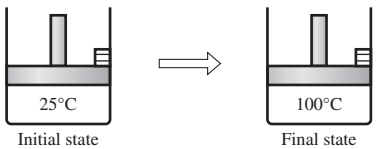


The initial gas temperature is 25°C.

The cylinder is placed in boiling water with the piston held in a fixed position. Heat in the amount of 2.00 kcal is transferred to the gas, which equilibrates at 100°C (and a higher pressure). The piston is then released, and the gas does 100 J of work in moving the piston to its new equilibrium position. The final gas temperature is 100°C.

Write the energy balance equation for each of the two stages of this process, and in each case solve for the unknown energy term in the equation. In solving this problem, consider the gas in the cylinder to be the system, neglect the change in potential energy of the gas as the piston moves vertically, and assume the gas behaves ideally. Express all energies in joules.

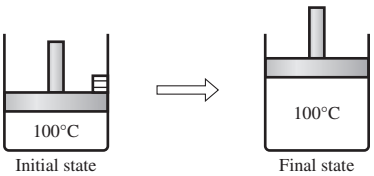
Solution **1.**



$$\Delta U + \Delta E_k + \Delta E_p = Q + W \quad \text{(Equation 7.3-4)}$$
$$\Delta E_k = 0 \quad \text{(the system is stationary)}$$
$$\Delta E_p = 0 \quad \text{(no vertical displacement)}$$
$$W = 0 \quad \text{(no moving boundaries)}$$
$$\Delta U = Q$$
$$Q = 2.00\ \text{kcal}$$
$$\Delta U = \frac{2.00\ \text{kcal}}{} \left| \frac{10^3\ \text{cal}}{\text{kcal}} \right| \frac{1\ \text{J}}{0.23901\ \text{cal}} = \boxed{8370\ \text{J} = \Delta U}$$

The gas thus gains 8370 J of internal energy in going from 25 to 100°C.

2.



$$\Delta U + \Delta E_k + \Delta E_p = Q + W$$
$$\Delta E_k = 0 \quad \text{(the system is stationary at the initial and final states)}$$
$$\Delta E_p = 0 \quad \text{(assumed negligible by hypothesis)}$$
$$\Delta U = 0 \quad (U \text{ depends only on } T \text{ for an ideal gas, and } T \text{ does not change})$$
$$0 = Q + W$$
$$W = -100\ \text{J} \quad \text{(Why is it negative?)}$$
$$\boxed{Q = 100\ \text{J}}$$

Thus an additional 100 J of heat is transferred to the gas as it expands and reequilibrates at 100°C.

7.4 ENERGY BALANCES ON OPEN SYSTEMS AT STEADY STATE

An open process system by definition has mass crossing its boundaries as the process occurs. Work must be done on such a system to push mass in, and work is done on the surroundings by mass that emerges. Both work terms must be included in the energy balance.

In Section 7.4a we outline the calculation of the work (or more precisely, the rate of energy transferred as work) required to move fluid through a continuous process system, and in Section 7.4b we review the concepts of intensive and extensive variables introduced in Chapter 6 and introduce the concept of specific properties of a substance. Section 7.4c uses the results of the two preceding sections to derive the energy balance for an open system at steady state.

7.4a Flow Work and Shaft Work

The net rate of work done on an open system by its surroundings may be written as

$$\dot{W} = \dot{W}_s + \dot{W}_{fl} \qquad \textbf{(7.4-1)}$$

where

$\dot{W}_s$ = **shaft work**, or rate of work done on the process fluid by a moving part within the system (e.g., a pump rotor)

$\dot{W}_{fl}$ = **flow work**, or rate of work done on the fluid at the system inlet minus the rate of work done by the fluid at the system outlet

To derive an expression for $\dot{W}_{fl}$, we consider the single-inlet–single-outlet system shown here.

Fluid at a pressure $P_{in}(N/m^2)$ enters a pipe at a volumetric flow rate $\dot{V}_{in}(m^3/s)$ and exits at a pressure $P_{out}(N/m^2)$ and volumetric flow rate $\dot{V}_{out}(m^3/s)$. The fluid that enters the system does work on the fluid just ahead of it at a rate

$$\dot{W}_{in}(N \cdot m/s) = P_{in}(N/m^2)\dot{V}_{in}(m^3/s) \tag{7.4-2}$$

while the fluid leaving the system performs work on the surroundings at a rate

$$\dot{W}_{out} = P_{out}\dot{V}_{out} \tag{7.4-3}$$

The net rate at which work is done on the system at the inlet and outlet is therefore

$$\dot{W}_{fl} = P_{in}\dot{V}_{in} - P_{out}\dot{V}_{out} \tag{7.4-4}$$

If several input and output streams enter and leave the system, the $P\dot{V}$ products for each stream must be summed to determine $\dot{W}_{fl}$.

Test Yourself

(Answers, p. 658)

An incompressible liquid flows through a straight horizontal pipe. Friction of the fluid within the pipe causes a small amount of heat to be transferred from the fluid; to compensate, flow work must be done on the fluid to move it through the system (so that $\dot{W}_{fl}$ is greater than zero).

1. How are $\dot{V}_{in}$ and $\dot{V}_{out}$ related, where $\dot{V}$ is the volumetric flow rate of the liquid? (Remember, the fluid is incompressible.)
2. How must the pressures P_{in} and P_{out} be related? ($P_{in} > P_{out}, P_{in} = P_{out},$ or $P_{in} < P_{out}$?)

7.4b Specific Properties and Enthalpy

As we observed in Section 6.2, the properties of a process material are either extensive (proportional to the quantity of the material) or intensive (independent of the quantity). Mass, number of moles, and volume (or mass flow rate, molar flow rate, and volumetric flow rate for a continuous stream), and kinetic energy, potential energy, and internal energy (or the rates of transport of these quantities by a continuous stream) are extensive properties, while temperature, pressure, and density are intensive.

A **specific property** is an intensive quantity obtained by dividing an extensive property (or its flow rate) by the total amount (or flow rate) of the process material. Thus, if the volume of a fluid is 200 cm^3 and the mass of the fluid is 200 g, the **specific volume** of the fluid is 1 cm^3/g. Similarly, if the mass flow rate of a stream is 100 kg/min and the volumetric flow rate is 150 L/min, the specific volume of the stream material is (150 L/min/100 kg/min) = 1.5 L/kg; if the rate at which kinetic energy is transported by this stream is 300 J/min, then the **specific kinetic energy** of the stream material is (300 J/min)/(100 kg/min) = 3 J/kg. *We will use the symbol ˆ to denote a specific property:* $\hat{V}$ will denote specific volume, $\hat{U}$ specific internal energy, and so on.

If the temperature and pressure of a process material are such that the specific internal energy of the material is $\hat{U}$(J/kg), then a mass m(kg) of this material has a total internal energy

$$U(J) = m(kg)\hat{U}(J/kg) \tag{7.4-5}$$

Similarly, a continuous stream of this material with a mass flow rate $\dot{m}$(kg/s) transports internal energy at a rate

$$\dot{U}(J/s) = \dot{m}(kg/s)\hat{U}(J/kg) \tag{7.4-6}$$

A property that occurs in the energy balance equation for open systems (Section 7.4c) is the **specific enthalpy**, defined as

$$\hat{H} \equiv \hat{U} + P\hat{V} \tag{7.4-7}$$

where P is total pressure and $\hat{U}$ and $\hat{V}$ are specific internal energy and specific volume. The gas constants tabulated on the inside back cover provide a convenient source for the conversion factors needed to evaluate $\hat{H}$ from Equation 7.4-7, as the following example shows.

Example 7.4-1 Calculation of Enthalpy

The specific internal energy of helium at 300 K and 1 atm is 3800 J/mol, and the specific molar volume at the same temperature and pressure is 24.63 L/mol. Calculate the specific enthalpy of helium at this temperature and pressure, and the rate at which enthalpy is transported by a stream of helium at 300 K and 1 atm with a molar flow rate of 250 kmol/h.

Solution

$$\hat{H} = \hat{U} + P\hat{V} = 3800\ \text{J/mol} + (1\ \text{atm})(24.63\ \text{L/mol})$$

To convert the second term to joules we need the factor J/(L·atm). From the gas constant table on the inside back cover,

$$0.08206\ \text{L·atm/(mol·K)} = 8.314\ \text{J/(mol·K)}$$

Dividing the right side by the left side yields the desired factor:

$$\frac{8.314\ \text{J/mol·K}}{0.08206\ \text{L·atm/(mol·K)}} = 101.3\ \text{J/(L·atm)}$$

Therefore,

$$\hat{H} = 3800\ \text{J/mol} + \frac{24.63\ \text{L·atm}}{\text{mol}}\left|\frac{101.3\ \text{J}}{1\ \text{L·atm}}\right. = \boxed{6295\ \text{J/mol}}$$

If $\dot{n} = 250$ kmol/h

$$\dot{H} = \dot{n}\hat{H} = \frac{250\ \text{kmol}}{\text{h}}\left|\frac{10^3\ \text{mol}}{\text{kmol}}\right|\frac{6295\ \text{J}}{\text{mol}} = \boxed{1.57 \times 10^9\ \text{J/h}}$$

The enthalpy function is important in the analysis of open systems, as we will show in the next section. It can also be shown, however, that *if a closed system expands (or contracts) against a constant external pressure, ΔE_k and ΔE_p are negligible, and the only work done by or on the system is the work of the expansion, then the energy balance equation reduces to $Q = \Delta H$*. A proof of this statement is required in Problem 7.17.

Test Yourself

(Answers, p. 658)

The specific internal energy of a fluid is 200 cal/g.

1. What is the internal energy of 30 g of this fluid?
2. If the fluid leaves a system at a flow rate of 5 g/min, at what rate does it transport internal energy out of the system?
3. What would you need to know to calculate the specific enthalpy of this fluid?

7.4c The Steady-State Open-System Energy Balance

The first law of thermodynamics for an open system at steady state has the form

$$\text{input} = \text{output} \tag{7.4-8}$$

(Why do the accumulation, generation, and consumption terms of the general balance equation vanish?) "Input" here signifies the total rate of transport of kinetic energy, potential energy, and internal energy by all process input streams plus the rate at which energy is transferred in as heat and work, and "output" is the total rate of energy transport by the output streams.

If $\dot{E}_j$ denotes the total rate of energy transport by the jth input or output stream of a process, and $\dot{Q}$ and $\dot{W}$ are again defined as the rates of flow of heat into and work on the process, then Equation 7.4-8 may be written

$$\dot{Q} + \dot{W} + \sum_{\substack{\text{input}\\\text{streams}}} \dot{E}_j = \sum_{\substack{\text{output}\\\text{streams}}} \dot{E}_j$$

$$\Downarrow$$

$$\sum_{\substack{\text{output}\\\text{streams}}} \dot{E}_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{E}_j = \dot{Q} + \dot{W} \qquad \textbf{(7.4-9)}$$

If $\dot{m}_j$, $\dot{E}_{kj}$, $\dot{E}_{pj}$, and $\dot{U}_j$ are the flow rates of mass, kinetic energy, potential energy, and internal energy for the jth process stream, then the total rate at which energy is transported into or out of the system by this stream is

$$\dot{E}_j = \dot{U}_j + \dot{E}_{kj} + \dot{E}_{pj}$$

$$\Downarrow \quad \dot{U}_j = \dot{m}_j \hat{U}_j$$

$$\Downarrow \quad \dot{E}_{kj} = \dot{m}_j u_j^2/2$$

$$\Downarrow \quad \dot{E}_{pj} = \dot{m}_j g z_j$$

$$\dot{E}_j = \dot{m}_j \left(\hat{U}_j + \frac{u_j^2}{2} + g z_j \right) \qquad \textbf{(7.4-10)}$$

where u_j is the velocity of the jth stream and z_j is the height of this stream relative to a reference plane at which $E_p = 0$.

The total work $\dot{W}$ done on the system equals the shaft work $\dot{W}_s$ plus the flow work $\dot{W}_{fl}$ (Equation 7.4-1). If $\dot{V}_j$ is the volumetric flow rate of the jth stream and P_j is the pressure of this stream as it crosses the system boundary, then as was shown in Section 7.4a,

$$\dot{W}_{fl} = \sum_{\substack{\text{input}\\\text{streams}}} P_j \dot{V}_j - \sum_{\substack{\text{output}\\\text{streams}}} P_j \dot{V}_j$$

$$\Downarrow \quad \dot{V}_j = \dot{m}_j \hat{V}_j$$

$$\dot{W} = \dot{W}_s + \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j P_j \hat{V}_j - \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j P_j \hat{V}_j \qquad \textbf{(7.4-11)}$$

Substituting the expression for $\dot{E}_j$ of Equation 7.4-10 and that for $\dot{W}$ of Equation 7.4-11 into Equation 7.4-9 and bringing the $P\hat{V}$ terms to the left side yields

$$\sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j \left[\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + g z_j \right] - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j \left[\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + g z_j \right] = \dot{Q} + \dot{W}_s \qquad \textbf{(7.4-12)}$$

Equation 7.4-12 could be used for all steady-state open-system energy balance problems. As a rule, however, the term $\hat{U}_j + P_j \hat{V}_j$ is combined and written as $\hat{H}_j$, the variable previously defined as

the specific enthalpy. In terms of this variable, Equation 7.4-12 becomes

$$\sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j \left(\hat{H}_j + \frac{u_j^2}{2} + g z_j \right) - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j \left(\hat{H}_j + \frac{u_j^2}{2} + g z_j \right) = \dot{Q} + \dot{W}_s \tag{7.4-13}$$

Finally, let us use the symbol Δ to denote total output minus total input, so that

$$\Delta \dot{H} = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j \hat{H}_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j \hat{H}_j \tag{7.4-14a}$$

$$\Delta \dot{E}_k = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j u_j^2/2 - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j u_j^2/2 \tag{7.4-14b}$$

$$\Delta \dot{E}_p = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j g z_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j g z_j \tag{7.4-14c}$$

In terms of these quantities, Equation 7.4-13 becomes

$$\boxed{\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} + \dot{W}_s} \tag{7.4-15}$$

Equation 7.4-15 states that the net rate at which energy is transferred to a system as heat and/or shaft work ($\dot{Q} + \dot{W}_s$) equals the difference between the rates at which the quantity (enthalpy + kinetic energy + potential energy) is transported into and out of the system ($\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p$). We will use this equation as the starting point for most energy-balance calculations on open systems at steady state.

Notice that if a process has a single input stream and a single output stream and there is no accumulation of mass in the system (so that $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$), the expression for $\Delta \dot{H}$ of Equation 7.4-14a simplifies to

$$\Delta \dot{H} = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = \dot{m} \Delta \hat{H} \tag{7.4-16}$$

Also notice that if a specific variable has the same value for all input and output streams, the corresponding term of Equation 7.4-15 drops out of the equation. For example, if $\hat{H}_j$ is the same for all streams, then from Equation 7.4-14a

$$\Delta \dot{H} = \hat{H} \left[\sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j \right] \tag{7.4-17}$$

But from a total mass balance the quantity in brackets (which is simply total mass in minus total mass out) equals zero, and hence $\Delta \dot{H} = 0$, as claimed.

Test Yourself

(Answers, p. 658)

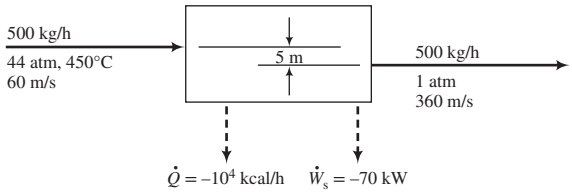
How would you simplify Equation 7.4-15 in each of the following cases?

1. There are no moving parts in the system.
2. The system and its surroundings are at the same temperature.
3. The linear velocities of all streams are the same.
4. All streams enter and leave the process at a single height.

Example 7.4-2 Energy Balance on a Turbine

Five hundred kilograms per hour of steam drives a turbine. The steam enters the turbine at 44 atm and 450°C at a linear velocity of 60 m/s and leaves at a point 5 m below the turbine inlet at atmospheric pressure and a velocity of 360 m/s. The turbine delivers shaft work at a rate of 70 kW, and the heat loss from the turbine is estimated to be 10^4 kcal/h. Calculate the specific enthalpy change associated with the process.

Solution



From Equation 7.4-15

$$\Delta\dot{H} = \dot{Q} + \dot{W}_s - \Delta\dot{E}_k - \Delta\dot{E}_p$$

Normally, heat, work, and kinetic and potential energy terms are determined in different units. To evaluate $\Delta\dot{H}$, we will convert each term to kW (kJ/s) using conversion factors given on the inside front cover, first noting that $\dot{m} = (500\text{ kg/h}/3600\text{ s/h}) = 0.139$ kg/s.

$$\Delta\dot{E}_k = \frac{\dot{m}}{2}(u_2^2 - u_1^2) = \frac{0.139\text{ kg/s}}{2}\left|\frac{1\text{ N}}{1\text{ kg}\cdot\text{m/s}^2}\right|\frac{(360^2 - 60^2)\text{ m}^2}{\text{s}^2}\left|\frac{1\text{ W}}{1\text{ N}\cdot\text{m/s}}\right|\frac{1\text{ kW}}{10^3\text{ W}}$$
$$= 8.75\text{ kW}$$

$$\Delta\dot{E}_p = \dot{m}g(z_2 - z_1) = \frac{0.139\text{ kg/s}}{}\left|\frac{9.81\text{ N}}{\text{kg}}\right|\frac{(-5)\text{ m}}{}\left|\frac{1\text{ kW}}{10^3\text{ N}\cdot\text{m/s}}\right. = -6.81\times10^{-3}\text{ kW}$$

$$\dot{Q} = \frac{-10^4\text{ kcal}}{\text{h}}\left|\frac{1\text{ J}}{0.239\times10^{-3}\text{ kcal}}\right|\frac{1\text{ h}}{3600\text{ s}}\left|\frac{1\text{ kW}}{10^3\text{ J/s}}\right. = -11.6\text{ kW}$$

$$\dot{W}_s = -70\text{ kW}$$

$$\Downarrow$$

$$\Delta\dot{H} = \dot{Q} + \dot{W}_s - \Delta\dot{E}_k - \Delta\dot{E}_p = -90.3\text{ kW}$$

But

$$\Delta\dot{H} = \dot{m}(\hat{H}_2 - \hat{H}_1) \quad \text{(from Equation 7.4-16)}$$

$$\Downarrow$$

$$\hat{H}_2 - \hat{H}_1 = \Delta\dot{H}/\dot{m}$$
$$= \frac{-90.3\text{ kJ/s}}{0.139\text{ kg/s}} = \boxed{-650\text{ kJ/kg}}$$

7.5 TABLES OF THERMODYNAMIC DATA

7.5a Reference States and State Properties

It is not possible to know the absolute value of $\hat{U}$ or $\hat{H}$ for a process material, but you can determine the *change* in $\hat{U}(\Delta\hat{U})$ or in $\hat{H}(\Delta\hat{H})$ corresponding to a specified change of state (temperature, pressure, and phase). This may be done, for example, by bringing a known mass m of a substance through the specified change of state in such a way that all terms of the energy

balance except ΔU (i.e., heat, work, and changes in potential and kinetic energies) are known. Once $\Delta\hat{U}(= \Delta U/m)$ has been determined, $\Delta\hat{H}$ for the same change in state can be calculated as $\Delta\hat{U} + \Delta P\hat{V}$.

A convenient way to tabulate measured changes in $\hat{U}$ or $\hat{H}$ is to choose a temperature, pressure, and state of aggregation as a **reference state**, and to list $\Delta\hat{U}$ or $\Delta\hat{H}$ for changes from this state to a series of other states. Suppose, for example, that the enthalpy changes for carbon monoxide going from a reference state of 0°C and 1 atm to two other states are measured, with the following results:

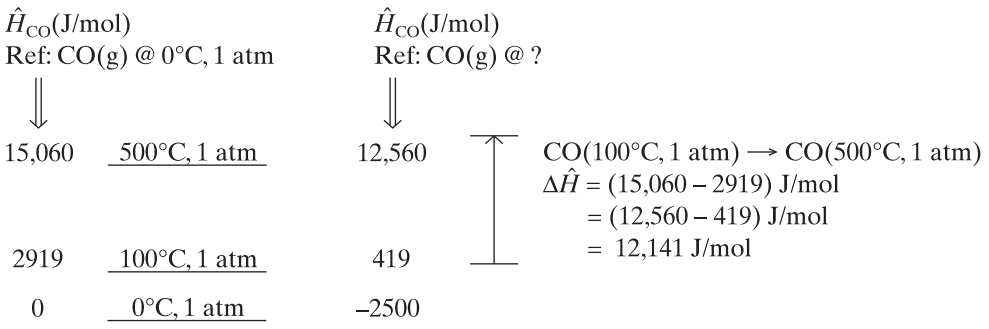
$$\text{CO(g, 0°C, 1 atm)} \rightarrow \text{CO(g, 100°C, 1 atm)}: \quad \Delta\hat{H}_1 = 2919\ \text{J/mol}$$
$$\text{CO(g, 0°C, 1 atm)} \rightarrow \text{CO(g, 500°C, 1 atm)}: \quad \Delta\hat{H}_2 = 15{,}060\ \text{J/mol}$$

Since $\hat{H}$ cannot be known absolutely, for convenience we may assign a value $\hat{H}_0 = 0$ to the reference state; then $\Delta\hat{H}_1 = \hat{H}_1 - 0 = \hat{H}_1$, $\Delta\hat{H}_2 = \hat{H}_2$, and so on. A table may then be constructed for CO at 1 atm:

T(°C)	$\hat{H}$(J/mol)
0	0
100	2919
500	15,060

Note that the value 2919 J/mol for $\hat{H}$ at 100°C does *not* mean that the absolute value of the specific enthalpy of CO at 100°C and 1 atm is 2919 J/mol—we cannot know the absolute value of $\hat{H}$—but rather means that the *change* in $\hat{H}$ when CO goes from the reference state to 100°C and 1 atm is 2919 J/mol. We then say *the specific enthalpy of CO at 100°C and 1 atm relative to CO at 0°C and 1 atm is 2919 J/mol.*

Some enthalpy tables give the reference states on which the listed values of $\hat{H}$ are based and others do not; however, you do not have to know the reference state to calculate $\Delta\hat{H}$ for the transition from one tabulated state to another. If $\hat{H}_1$ is the specific enthalpy at state 1 and $\hat{H}_2$ is that at state 2, then $\Delta\hat{H}$ for the transition from state 1 to state 2 equals $\hat{H}_2 - \hat{H}_1$, regardless of the reference state on which $\hat{H}_1$ and $\hat{H}_2$ are based. (*Caution:* If two different tables are used, be sure $\hat{H}_1$ and $\hat{H}_2$ are based on the same reference state.) For example, $\Delta\hat{H}$ for CO going from 100 to 500°C at 1 atm is (15,060 − 2919) J/mol = 12,141 J/mol. If another reference state had been used to generate the specific enthalpies of CO at 100°C and 500°C, $\hat{H}_1$ and $\hat{H}_2$ would have different values but $\hat{H}_2 - \hat{H}_1$ would still be 12,141 J/mol. (See diagram below.)



This convenient result is a consequence of the fact that $\hat{H}$, like $\hat{U}$, is a **state property**, or a property of a system component whose value depends only on the state of the system (temperature,

pressure, phase, and composition) and not on how the system reached that state.[1] We will have more to say about this concept in Chapter Eight.

Example 7.5-1 Use of Tabulated Enthalpy Data

The following entries are taken from a data table for saturated methyl chloride:

State	T(°F)	P(psia)	$\hat{V}$(ft^3/lb$_m$)	$\hat{H}$(Btu/lb$_m$)
Liquid	−40	6.878	0.01553	0.000
Vapor	0	18.90	4.969	196.23
Vapor	50	51.99	1.920	202.28

1. What reference state was used to generate the given enthalpies?
2. Calculate $\Delta\hat{H}$ and $\Delta\hat{U}$ for the transition of saturated methyl chloride vapor from 50°F to 0°F.
3. What assumption did you make in solving question 2 regarding the effect of pressure on specific enthalpy?

Solution

1. Liquid at −40°F and 6.878 psia (the state at which $\hat{H} = 0$). You do not need this information to solve Part 2.
2. $\Delta\hat{H} = \hat{H}(0°\text{F}) - \hat{H}(50°\text{F}) = (196.23 - 202.28) = -6.05\ \text{Btu/lb}_m$

$$\Delta\hat{U} = \Delta\hat{H} - \Delta P\hat{V} = \Delta\hat{H} - (P_{\text{final}}\hat{V}_{\text{final}} - P_{\text{initial}}\hat{V}_{\text{initial}})$$

$$= -6.05\ \text{Btu/lb}_m$$

$$- \frac{[(18.90)(4.969) - (51.99)(1.920)]\ \text{ft}^3\cdot\text{psia/lb}_m \mid 1.987\ \text{Btu}}{10.73\ \text{ft}^3\cdot\text{psia}}$$

$$= \boxed{-4.96\ \text{Btu/lb}_m}$$

The value of the conversion factor Btu/(ft^3·psia) was obtained from the table of gas constants in back of the book. (Verify it!)

3. $\hat{H}$ was assumed independent of P.

Tables of enthalpies and other state properties of many substances may be found in tables B5-B9 of this text and *Perry's Chemical Engineers' Handbook*[2] on pp. 2-208 through 2-418.

Test Yourself

(Answers, p. 658)

1. What is a state property?
2. The enthalpy of a vapor A relative to liquid A at 0°C and 1 atm is 5000 J/kg at 0°C and 1 atm, and 7500 J/kg at 30°C and 1 atm.
   - **(a)** What is $\hat{H}$ of A(l) at 0°C and 1 atm?
   - **(b)** What is the approximate value of $\hat{H}$ for A(v) at 0°C and 5 atm?
   - **(c)** What is $\Delta\hat{H}$ for the process

$$\text{A(v, 30°C, 1 atm)} \rightarrow \text{A(v, 0°C, 1 atm)}$$

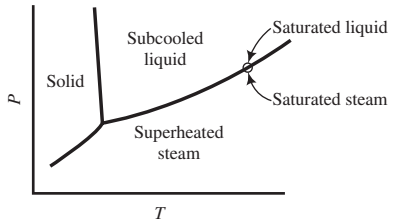
   - **(d)** Does the answer depend on the reference state used to generate the table of enthalpies? Why not?

[1] We will not prove our claim that $\hat{U}$ and $\hat{H}$ satisfy this condition. All texts on thermodynamics discuss this point in detail.

[2] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008.

7.5b Steam Tables

Recall the phase diagram for water (Figure 6.1-1*a*), which has the following appearance:



Pure water may coexist as liquid and vapor only at temperature–pressure pairs that fall on the vapor–liquid equilibrium (VLE) curve. At points above the VLE curve (but to the right of the solid–liquid equilibrium curve), water is a **subcooled liquid**. At points on the VLE curve, water may be **saturated liquid** or **saturated steam** (vapor) or a mixture of both. At points below the VLE curve, water is **superheated steam**.

For many years, compilations of physical properties of liquid water, saturated steam, and superheated steam issued in **steam tables** have been standard references for mechanical and chemical engineers involved with steam cycles for electrical power generation. Steam tables are contained in Tables B.5–B.7 of this text. We recommend that you examine these tables as we describe what you can find in them.

Table B.5 lists properties of saturated liquid water and saturated steam at temperatures from 0.01°C (the triple-point temperature) to 102°C. The following properties can be determined for each tabulated temperature (and for intermediate temperatures by interpolation):

- ***Column 2.*** The pressure, P(bar), corresponding to the given temperature on the VLE curve—by definition, the vapor pressure of water at the given temperature. Instead of looking up a given temperature and finding the pressure, you could look up a given pressure in the second column and find the corresponding boiling point temperature in the first column.
- ***Columns 3 and 4.*** The specific volumes, $\hat{V}$(m^3/kg), of liquid water and saturated steam at the given temperature. The inverses of these quantities are the densities (kg/m^3) of liquid water and steam.
- ***Columns 5 and 6.*** The specific internal energies, $\hat{U}$(kJ/kg), of saturated liquid water and saturated steam at the given temperature *relative to a reference state of liquid water at the triple point*. (Remember, we can never know the absolute value of internal energy or enthalpy, but only how these quantities change when the substance goes from one state to another—in this case, from the reference state to the states listed in the table.)
- ***Columns 7–9.*** The specific enthalpies, $\hat{H}$(kJ/kg), of saturated liquid water (Column 7) and saturated steam (Column 9), and the difference between these quantities, known as the *heat of vaporization* (Column 8). The reference point for the tabulated values of $\hat{H}$ is again liquid water at the triple point.

Table B.6 lists the same properties as Table B.5, except that pressure is the first column and temperature the second, and the table covers a much broader range of temperatures and pressures. Tables B.5 and B.6 are commonly referred to as the *saturated steam tables*.

Table B.7—which is referred to as the *superheated steam table*—lists $\hat{V}$, $\hat{U}$, and $\hat{H}$ of water (the latter two properties relative to liquid water at the triple point) at *any* temperature and pressure, not just at points on the VLE curve. If you are given a temperature and a pressure, you can locate the properties of water at the intersection of the column corresponding to the given temperature and the row corresponding to the given pressure. If the intersection falls within the closed region on the table bounded by the vertical line to the left of the 50°C column, the horizontal line below the 221.2 bar row, and the stair-step border, the water is a liquid; outside this region, it is a superheated vapor.

When you look up a pressure in the first column of Table B.7, you will find just below it in parentheses the boiling-point temperature and in Columns 2 and 3 the properties of saturated liquid water and saturated steam at that pressure. If you are at a point in the superheated steam region, you can move all the way to the left to determine the saturation temperature at the same pressure, also known as the *dew point* of the superheated steam.

The next example illustrates the use of these tables to obtain physical property data for water.

Example 7.5-2 The Steam Tables

1. Determine the vapor pressure, specific internal energy, and specific enthalpy of saturated steam at 133.5°C.
2. Show that water at 400°C and 10 bar is superheated steam and determine its specific volume, specific internal energy, and specific enthalpy relative to liquid water at the triple point, and its dew point.
3. Show that $\hat{U}$ and $\hat{H}$ for superheated steam depend strongly on temperature and relatively slightly on pressure.

Solution Verify the results to be given.

1. Table B.5 does not go up to 133.5°C, so we turn to Table B.6. For saturated steam at the given temperature (Column 2),

$$\boxed{p^* = 3.0\,\text{bar},\ \hat{V} = 0.606\,\text{m}^3/\text{kg},\ \hat{U} = 2543.0\,\text{kJ/kg},\ \hat{H} = 2724.7\,\text{kJ/kg}}$$

2. From Table B.7, $[T = 400°\text{C}, P = 10\,\text{bar}]$ falls outside the closed region, showing that water is superheated steam at this temperature and pressure. The table also shows that at this condition,

$$\boxed{\hat{H} = 3264\,\text{kJ/kg},\ \hat{U} = 2958\,\text{kJ/kg},\ \hat{V} = 0.307\,\text{m}^3/\text{kg},\ T_{\text{dp}} = 179.9°\text{C}}$$

3. Look at the properties of water at 400°C and 450°C, both at a pressure of 10 bar. You will see that both $\hat{U}$ and $\hat{H}$ change by about 3% when water goes from the first temperature to the second one (3264 kJ/kg → 3371 kJ/kg for $\hat{H}$, 2958 kJ/kg → 3041 kJ/kg for $\hat{U}$).

   Now consider the properties at 10 bar and 20 bar, both at a temperature of 400°C. Even though the pressure has doubled, the values of $\hat{U}$ and $\hat{H}$ change by much less than 1%. Similar results would be obtained for liquid water. The conclusion is that when you need a value of $\hat{U}$ or $\hat{H}$ for water (or for any other species) at a given T and P, you must look it up at the correct temperature—interpolating if necessary—but you don't have to find it at the exact pressure.

The next example illustrates the use of the steam tables to solve energy balance problems.

Example 7.5-3 Energy Balance on a Steam Turbine

Steam at 10 bar absolute with 190°C of superheat is fed to a turbine at a rate $\dot{m} = 2000$ kg/h. The turbine operation is adiabatic, and the effluent is saturated steam at 1 bar. Calculate the work output of the turbine in kilowatts, neglecting changes in kinetic and potential energy.

Solution The energy balance for this steady-state open system is

$$\dot{W}_s = \Delta\dot{H} = \dot{m}(\hat{H}_{\text{out}} - \hat{H}_{\text{in}})$$

(Why was the heat term dropped?)

Inlet Steam:

Table B.7 indicates that steam at 10 bar is saturated at 180°C (*verify*), so that the inlet steam temperature is 180°C + 190°C = 370°C. Interpolating in the same table,

$$\hat{H}_{\text{in}}(10\,\text{bar}, 370°\text{C}) = 3201\,\text{kJ/kg}$$

Outlet Steam:

From either Table B.6 or B.7, you can find that the enthalpy of saturated steam at 1 bar is

$$\hat{H}_{out}(1\text{ bar, saturated}) = 2675\text{ kJ/kg}$$

Energy Balance:

$$\dot{W}_s = \Delta\dot{H} = \frac{2000\text{ kg}}{\text{h}} \left| \frac{(2675 - 3201)\text{ kJ}}{\text{kg}} \right| \frac{1\text{ h}}{3600\text{ s}}$$

$$= -292\text{ kJ/s} = \boxed{-292\text{ kW}}$$

The turbine thus delivers 292 kW of work to its surroundings.

The superheated steam table, Table B.7, lists values for both liquid water and steam. If you wish to determine $\hat{H}$ for liquid water at a temperature T and pressure P that cannot easily be found in this table, you may calculate it in the following manner: (1) look up $\hat{U}$ and $\hat{V}$ for *saturated* liquid at the specified temperature in Table B.5; (2) assume these values are independent of pressure, and calculate $\hat{H}(P, T) = \hat{U} + P\hat{V}$. Furthermore, if the pressure is not excessive (say, less than 10 bar) or *if it is unknown,* neglect the $P\hat{V}$ correction and use the saturated liquid enthalpy $\hat{H}(T)$ given in Table B.5.

7.6 ENERGY BALANCE PROCEDURES

A properly drawn and labeled flowchart is essential for the efficient solution of energy balance problems. When labeling the flowchart, be sure to include all of the information you will need to determine the specific enthalpy of each stream component, including known temperatures and pressures. In addition, show states (phases) of process materials when they are not obvious: do not simply write H_2O, for example, but rather H_2O(s), H_2O(l), or H_2O(v), according to whether water is present as a solid, a liquid, or a vapor.

In the rest of this chapter, we will consider only species (such as water) for which tabulated internal energies or enthalpies are available. In Chapters 8 and 9 we will show how to choose reference states and calculate the required values of $\hat{U}$ and $\hat{H}$ when tabulated values cannot be found.

Example 7.6-1 Energy Balance on a One-Component Process

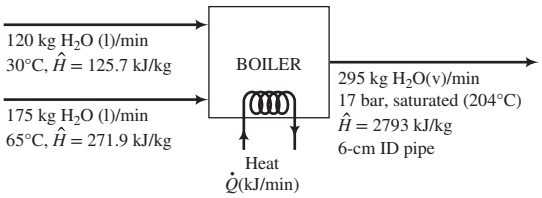
Equipment Encyclopedia
boiler
www.wiley.com/college/felder

Two streams of water are mixed to form the feed to a boiler. Process data are as follows:

Feed stream 1	120 kg/min @ 30°C
Feed stream 2	175 kg/min @ 65°C
Boiler pressure	17 bar (absolute)

Steam emerges from the boiler through a 6-cm ID pipe. Calculate the required heat input to the boiler in kilojoules per minute if the emerging steam is saturated at the boiler pressure. Neglect the kinetic energies of the liquid inlet streams.

Solution



1. ***A first step in solving problems of this sort is to determine (if possible) the flow rates of all stream components using material balances.*** In this case, it is a trivial matter to write and solve a mass balance on water to determine that the flow rate of the emerging steam is 295 kg/min.

2. ***Next, determine the specific enthalpies of each stream component.*** Tables B.5 and B.6 were used to determine $\hat{H}$ for liquid water at 30°C and 65°C and for saturated steam at 17 bar. The latter entry in the table also furnished the temperature of the saturated steam corresponding to this pressure (204°C). Note that the entries for liquid water correspond to pressures that may or may not equal the actual pressures of the inlet streams (which we do not know); we assume, however, that the enthalpy of liquid water is approximately independent of pressure and use the tabulated values.
3. ***The final step is to write the appropriate form of the energy balance and solve it for the desired quantity.*** For this open process system,

$$\begin{aligned}\dot{Q} + \dot{W}_s &= \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p \\ &\Downarrow \quad \dot{W}_s = 0 \quad \text{(no moving parts)} \\ &\Downarrow \quad \Delta\dot{E}_p = 0 \quad \text{(generally assumed unless displacements through large heights are involved)} \\ \dot{Q} &= \Delta\dot{H} + \Delta\dot{E}_k\end{aligned}$$

Evaluate $\Delta\dot{H}$:

From Equation 7.4-14a,

$$\begin{aligned}\Delta\dot{H} &= \sum_{\text{outlet}} \dot{m}_i\hat{H}_i - \sum_{\text{inlet}} \dot{m}_i\hat{H}_i \\ &= \frac{295\ \text{kg}}{\text{min}}\left|\frac{2793\ \text{kJ}}{\text{kg}}\right. - \frac{120\ \text{kg}}{\text{min}}\left|\frac{125.7\ \text{kJ}}{\text{kg}}\right. - \frac{175\ \text{kg}}{\text{min}}\left|\frac{271.9\ \text{kJ}}{\text{kg}}\right. \\ &= 7.61 \times 10^5\ \text{kJ/min}\end{aligned}$$

Evaluate $\Delta\dot{E}_k$:

From Table B.6, the specific volume of saturated steam at 17 bar is 0.1166 m^3/kg, and the cross-sectional area of the 6-cm ID pipe is

$$A = \pi R^2 = \frac{3.1416}{}\left|\frac{(3.00)^2\ \text{cm}^2}{}\right.\left|\frac{1\ \text{m}^2}{10^4\ \text{cm}^2}\right. = 2.83 \times 10^{-3}\ \text{m}^2$$

The steam velocity is

$$\begin{aligned}u(\text{m/s}) &= \dot{V}(\text{m}^3/\text{s})/A(\text{m}^2) \\ &= \frac{295\ \text{kg}}{\text{min}}\left|\frac{1\ \text{min}}{60\ \text{s}}\right.\left|\frac{0.1166\ \text{m}^3}{\text{kg}}\right.\left|\frac{}{2.83 \times 10^{-3}\ \text{m}^2}\right. \\ &= 202\ \text{m/s}\end{aligned}$$

Then, since the kinetic energies of the inlet streams are assumed negligible,

$$\begin{aligned}\Delta\dot{E}_k &\approx (\dot{E}_k)_{\text{outlet stream}} = \dot{m}u^2/2 \\ &= \frac{295\ \text{kg/min}}{2}\left|\frac{(202)^2\ \text{m}^2}{\text{s}^2}\right.\left|\frac{1\ \text{N}}{1\ \text{kg}\cdot\text{m/s}^2}\right.\left|\frac{1\ \text{kJ}}{10^3\ \text{N}\cdot\text{m}}\right. = 6.02 \times 10^3\ \text{kJ/min}\end{aligned}$$

Finally,

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} + \Delta\dot{E}_k \\ &= [7.61 \times 10^5 + 6.02 \times 10^3]\ \text{kJ/min} \\ &= \boxed{7.67 \times 10^5\ \text{kJ/min}}\end{aligned}$$

Observe that the kinetic energy change is only a small fraction—roughly 0.8%—of the total energy requirement for the process. This is a typical result, and it is common to neglect kinetic and potential energy changes (at least as a first approximation) relative to enthalpy changes for processes that involve phase changes, chemical reactions, or large temperature changes.

When process streams contain several components, the specific enthalpies of each component must be determined separately and substituted in the energy balance equation when $\Delta\dot{H}$ is evaluated. *For mixtures of near-ideal gases or of liquids with similar molecular structures* (e.g., mixtures of paraffins), *you may assume that $\hat{H}$ for a mixture component is the same as $\hat{H}$ for the pure substance at the same temperature and pressure*. Procedures to follow for solutions of gases or solids in liquids and for mixtures of dissimilar liquids are outlined in Chapter 8.

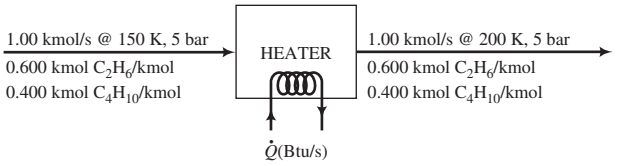
Example 7.6-2 Energy Balance on a Two-Component Process

A liquid stream containing 60.0 mole% ethane and 40.0% *n*-butane is to be heated from 150 K to 200 K at a pressure of 1 MPa. Calculate the required heat input per kmol of the mixture, neglecting potential and kinetic energy changes, using tabulated enthalpy data for C_2H_6 and C_4H_{10}, and assuming that mixture component enthalpies are those of the pure species at the same temperature.

Solution

Basis: 1 kg/s Mixture

The enthalpies of *n*-butane at 150 K and 1 MPa and at 200 K and 1 MPa are given on p. 2-232 of *Perry's Chemical Engineers' Handbook* (see Footnote 2), and those of ethane at the same conditions can be obtained by interpolation of values on p. 2-263 of the *Handbook*. The enthalpy values are shown in the energy balance.



No material balances are necessary since there is only one input stream and one output stream and no chemical reactions, so we may proceed directly to the energy balance:

$$\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$$\Big\Vert \quad \dot{W}_s = 0 \quad \text{(no moving parts)}$$

$$\Big\downarrow \quad \Delta\dot{E}_k = 0, \Delta\dot{E}_p = 0 \quad \text{(by hypothesis)}$$

$$\dot{Q} = \Delta\dot{H}$$

Since the components have similar chemical structures and we can assume the mixture is ideal, we may set the enthalpies of each stream equal to the sums of the individual component enthalpies and write

$$\dot{Q} = \Delta\dot{H} = \sum_{\substack{\text{outlet}\\ \text{components}}} \dot{m}_i\hat{H}_i - \sum_{\substack{\text{inlet}\\ \text{components}}} \dot{m}_i\hat{H}_i$$

$$= \frac{0.600 \text{ kmol } C_2H_6}{\text{s}} \left| \frac{1174 \text{ kJ}}{\text{kmol}} + \frac{0.400 \text{ kmol } C_4H_{10}}{\text{s}} \right| \frac{2446 \text{ kJ}}{\text{kmol}}$$

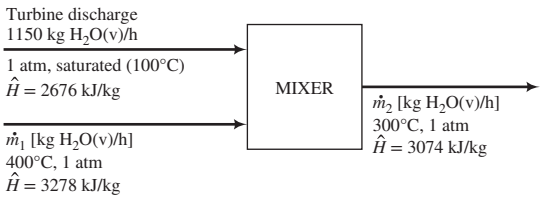
$$- [(0.600)(-2356) + (0.400)(-3418)] \text{ kJ/s} = 4464 \text{ kJ/s} \Longrightarrow \frac{4460 \text{ kJ/s}}{1.00 \text{ kmol/s}} = \boxed{4460 \frac{\text{kJ}}{\text{kmol}}}$$

In the two previous examples, it was possible to complete all material-balance calculations before undertaking the energy balance. In another class of problems one more stream amount or flow rate is unknown than can be determined by material balances alone. To solve problems of this type, you must write and solve material and energy balances simultaneously.

Example 7.6-3 Simultaneous Material and Energy Balances

Superheated steam at 300°C and 1 atm (absolute) is to be fed to a heat exchanger. It is produced by mixing an available stream of saturated steam at 1 atm discharged from a turbine at a rate of 1150 kg/h with a second stream of superheated steam at 400°C and 1 atm. The mixing may be considered adiabatic. Calculate the amount of superheated steam at 300°C produced and the required volumetric flow rate of the 400°C steam.

Solution Specific enthalpies of the two feed streams and the product stream are obtained from the steam tables and are shown below on the flowchart. (*Note:* We have neglected the small difference between 1 atm and 1 bar.)



There are two unknown quantities in this process—$\dot{m}_1$ and $\dot{m}_2$—but only one permissible material balance. (Why?) The material and energy balances must therefore be solved simultaneously to determine the two flow rates.

Mass Balance on Water:
$$1150\ \text{kg/h} + \dot{m}_1 = \dot{m}_2 \tag{1}$$

Energy Balance:
$$\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$\Downarrow$
$\dot{Q} = 0$ (process is adiabatic)
$\dot{W}_s = 0$ (no moving parts)
$\Delta\dot{E}_k \approx 0, \Delta\dot{E}_p \approx 0$ (assumption)

$$\Delta\dot{H} = \sum_{\text{outlet}} \dot{m}_i\hat{H}_i - \sum_{\text{inlet}} \dot{m}_i\hat{H}_i = 0$$

$$\frac{1150\ \text{kg}}{\text{h}}\left|\frac{2676\ \text{kJ}}{\text{kg}}\right. + \dot{m}_1(3278\ \text{kJ/kg}) = \dot{m}_2(3074\ \text{kJ/kg}) \tag{2}$$

Solving Equations 1 and 2 simultaneously yields

$$\dot{m}_1 = 2240\ \text{kg/h}$$

$$\boxed{\dot{m}_2 = 3390\ \text{kg/h}} \quad \text{(product flow rate)}$$

From Table B.7, the specific volume of steam at 400°C and 1 atm (≈1 bar) is 3.11 m^3/kg. The volumetric flow rate of this stream is therefore

$$\frac{2240\ \text{kg}}{\text{h}}\left|\frac{3.11\ \text{m}^3}{\text{kg}}\right. = \boxed{6980\ \text{m}^3/\text{h}}$$

If specific-volume data were not available, the ideal-gas equation of state could be used as an approximation for the last calculation.

7.7 MECHANICAL ENERGY BALANCES

In chemical process units such as reactors, distillation columns, evaporators, and heat exchangers, shaft work and kinetic and potential energy changes tend to be negligible compared with heat

flows and internal energy and enthalpy changes. Energy balances on such units therefore usually omit the former terms and so take the simple form $Q = \Delta U$ (closed system) or $\dot{Q} = \Delta \dot{H}$ (open system).

Another important class of operations is one for which the opposite is true—heat flows and internal energy changes are secondary in importance to kinetic and potential energy changes and shaft work. Most of these operations involve the flow of fluids to, from, and between tanks, reservoirs, wells, and process units. Accounting for energy flows in such processes is most conveniently done with **mechanical energy balances**.

The general form of the mechanical energy balance can be derived starting with the open-system balance and a second equation expressing the law of conservation of momentum, a derivation beyond the scope of this book. This section presents a simplified form for a single incompressible liquid flowing into and out of a process system at steady state.

Consider such a system, letting $\dot{m}$ be the mass flow rate and $\hat{V}$ the specific volume of the liquid. If $\hat{V}$ is replaced by $1/\rho$, where ρ is the liquid density, then the open-system energy balance (Equation 7.4-12) may be written

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z + \left(\Delta \hat{U} - \frac{\dot{Q}}{\dot{m}}\right) = \frac{\dot{W}_s}{\dot{m}} \tag{7.7-1}$$

The shaft work $\dot{W}_s$ is the work done on the fluid by moving elements in the process line.

In many cases only slight amounts of heat are transferred to or from the surroundings, there is little change in temperature from inlet to outlet, and no phase changes or reactions occur. Even under these circumstances, some kinetic or potential energy is always converted to thermal energy as a result of friction due to the movement of the fluid through the system. In consequence, the quantity $(\Delta \hat{U} - \dot{Q}/\dot{m})$ always has a positive component, termed the **friction loss**, and is given the symbol $\hat{F}$. Equation 7.7-1 may therefore be written

$$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z + \hat{F} = \frac{\dot{W}_s}{\dot{m}}} \tag{7.7-2}$$

Equation 7.7-2 is referred to as the **mechanical energy balance**. Once again, it is valid for steady-state flow of an incompressible fluid.

Methods of estimating friction losses for flow through straight pipes, orifices, nozzles, elbows, and so on are given in Section 10 of *Perry's Chemical Engineers' Handbook* (see Footnote 2) and will not be discussed in this text. In the balance of this book we consider only processes in which friction losses are either specified or neglected.

A simplified form of the mechanical energy balance is obtained for frictionless processes ($\hat{F} \approx 0$) in which no shaft work is performed ($\dot{W}_s = 0$):

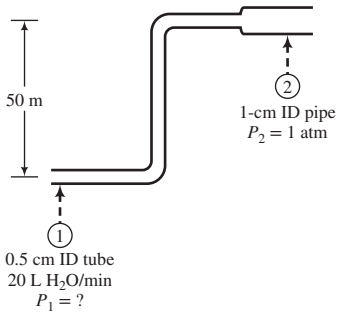
$$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z = 0} \tag{7.7-3}$$

Equation 7.7-3 is called the **Bernoulli equation**.

Example 7.7-1 The Bernoulli Equation

Water flows through the system shown here at a rate of 20 L/min. Estimate the pressure required at point ① if friction losses are negligible.

Solution



All of the terms of the Bernoulli equation, Equation 7.7-3, are known except ΔP, the variable to be determined, and Δu^2, which must be calculated from the known liquid flow rate and the diameters of the inlet and outlet pipes.

Velocities: $$\dot{u}(\text{m/s}) = \dot{V}(\text{m}^3/\text{s})/A(\text{m}^2)$$

The mass flow rates must be the same at points ① and ②, and in this instance the volumetric flow rates also may be taken as identical. (Why?)

$$u_1 = \frac{20\ \text{L}}{\text{min}} \left| \frac{1\ \text{m}^3}{10^3\ \text{L}} \right| \frac{}{\pi(0.25)^2\ \text{cm}^2} \left| \frac{10^4\ \text{cm}^2}{\text{m}^2} \right| \frac{1\ \text{min}}{60\ \text{s}} = 17.0\ \text{m/s}$$

$$u_2 = \frac{20\ \text{L}}{\text{min}} \left| \frac{1\ \text{m}^3}{10^3\ \text{L}} \right| \frac{}{\pi(0.5)^2\ \text{cm}^2} \left| \frac{10^4\ \text{cm}^2}{1\ \text{m}^2} \right| \frac{1\ \text{min}}{60\ \text{s}} = 4.24\ \text{m/s}$$

$$\Downarrow$$

$$\Delta u^2 = (u_2^2 - u_1^2) = (4.24^2 - 17.0^2)\ \text{m}^2/\text{s}^2$$
$$= -271.0\ \text{m}^2/\text{s}^2$$

Bernoulli Equation: (Equation 7.7-3)

$$\frac{\Delta P(\text{N/m}^2)}{\rho(\text{kg/m}^3)} + \frac{\Delta u^2(\text{m}^2/\text{s}^2)}{2 \cdot 1[(\text{kg}\cdot\text{m/s}^2)/\text{N}]} + \frac{g(\text{m/s}^2)\Delta z(\text{m})}{1[(\text{kg}\cdot\text{m/s}^2)/\text{N}]}$$

$$\Downarrow \quad \Delta P = P_2 - P_1,\ \rho = 1000\ \text{kg/m}^3,\ \Delta u^2 = -271.0\ \text{m}^2/\text{s}^2,\ g = 9.81\ \text{m/s}^2,\ \Delta z = z_2 - z_1 = 50\ \text{m}$$

$$\frac{P_2 - P_1}{1000\ \text{kg/m}^3} - 135.5\ \text{N}\cdot\text{m/kg} + 490\ \text{N}\cdot\text{m/kg} = 0$$

$$\Downarrow \quad P_2 = 1\ \text{atm} = 1.01325 \times 10^5\ \text{N/m}^2$$

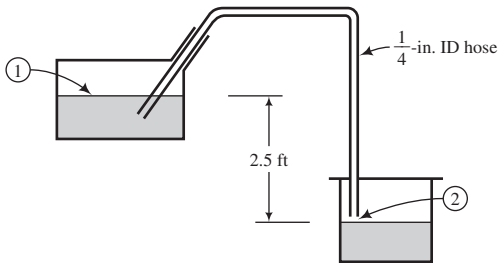
$$P_1 = 4.56 \times 10^5\ \text{N/m}^2$$
$$= 4.56 \times 10^5\ \text{Pa}$$
$$= \boxed{4.56\ \text{bar}}$$

A common type of problem to which the mechanical energy balance is applicable is one that involves drainage or siphoning of a liquid from a container. A suitable choice of the locations of points ① and ② greatly simplifies such problems; it is convenient to choose as point ① a location on the liquid surface in the tank being drained and to take point ② at the discharge stream outlet. If

the container is being drained relatively slowly, the kinetic energy at point ① may be neglected. Example 7.7-2 illustrates the computational procedure for such problems.

Example 7.7-2 Siphoning

Gasoline ($\rho = 50.0\ \text{lb}_\text{m}/\text{ft}^3$) is to be siphoned from a tank. The friction loss in the line is $\hat{F} = 0.80\ \text{ft}\cdot\text{lb}_\text{f}/\text{lb}_\text{m}$. Estimate how long it will take to siphon 5.00 gal, neglecting the change in liquid level in the gasoline tank during this process and assuming that both point ① (at the liquid surface in the gas tank) and point ② (in the tube just prior to the exit) are at 1 atm.



Solution

Point ①: $P_1 = 1$ atm, $u_1 \approx 0$ ft/s, $z_1 = 2.5$ ft

Point ②: $P_2 = 1$ atm, $u_2 = ?$, $z_2 = 0$ ft

Mechanical Energy Balance: (Equation 7.7-2)

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z + \hat{F} = \frac{\dot{W}_\text{s}}{\dot{m}}$$

$\Delta P = 0$
$\Delta u^2 \approx u_2^2$
$g = 32.174\ \text{ft/s}^2$
$\Delta z = -2.5\ \text{ft}$
$\hat{F} = 0.80\ \text{ft}\cdot\text{lb}_\text{f}/\text{lb}_\text{m}$
$\dot{W}_\text{s} = 0$

$$\frac{u_2^2(\text{ft}^2/\text{s}^2)}{2}\left|\frac{1\ \text{lb}_\text{f}}{32.174\ \text{lb}_\text{m}\cdot\text{ft/s}^2}\right. + \left.\frac{32.174\ \text{ft/s}^2}{}\right|\left.\frac{-2.5\ \text{ft}}{}\right|\left.\frac{1\ \text{lb}_\text{f}}{32.174\ \text{lb}_\text{m}\cdot\text{ft/s}^2}\right. + 0.80\ \text{ft}\cdot\text{lb}_\text{f}/\text{lb}_\text{m}$$

$$\Downarrow$$

$$u_2 = 10.5\ \text{ft/s}$$

(Verify that each additive term in the preceding equation has the units $\text{ft}\cdot\text{lb}_\text{f}/\text{lb}_\text{m}$.)

The volumetric flow rate of the fluid in the tube is

$$\dot{V}(\text{ft}^3/\text{s}) = u_2(\text{ft/s}) \times A(\text{ft}^2)$$

$$= \frac{10.5\ \text{ft}}{\text{s}}\left|\frac{\pi(0.125)^2\ \text{in.}^2}{}\right|\left.\frac{1\ \text{ft}^2}{144\ \text{in.}^2}\right. = 3.58 \times 10^{-3}\ \text{ft}^3/\text{s}$$

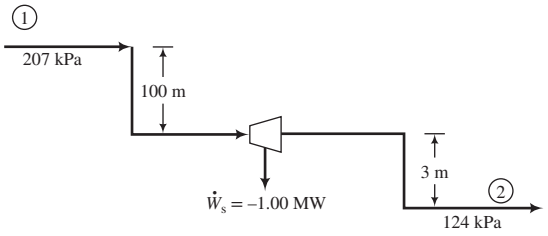
$$t(\text{s}) = \frac{\text{volume to be drained}\ (\text{ft}^3)}{\text{volumetric flow rate}\ (\text{ft}^3/\text{s})}$$

$$= \frac{(5.00\ \text{gal})(0.1337\ \text{ft}^3/\text{gal})}{3.58 \times 10^{-3}\ \text{ft}^3/\text{s}} = \frac{187\ \text{s}}{60\ \text{s/min}} = \boxed{3.1\ \text{min}}$$

The last illustration we will consider is one in which the potential energy lost by falling water is converted to electrical energy by means of a turbine and generator. The work done by the water in rotating the turbine must be included as shaft work in the energy balance.

Example 7.7-3 Hydraulic Power Generation

Water flows from an elevated reservoir through a conduit to a turbine at a lower level and out of the turbine through a similar conduit. At a point 100 m above the turbine the pressure is 207 kPa, and at a point 3 m below the turbine the pressure is 124 kPa. What must the water flow rate be if the turbine output is 1.00 MW?



Solution No data are given for the friction loss so we will set $\hat{F} = 0$, recognizing that doing so introduces an error into the calculation. Since the diameters of the conduits at points (1) and (2) are the same and liquid water may be considered incompressible, $\Delta u^2 = 0$. Equation 7.7-2 then becomes

$$\frac{\Delta P}{\rho} + g\Delta z = \frac{\dot{W}_s}{\dot{m}}$$

$$\Downarrow$$

$$\dot{m} = \frac{\dot{W}_s}{\dfrac{\Delta P}{\rho} + g\Delta z}$$

$$\dot{W}_s = -1.00\ \text{MW} = -1.00 \times 10^6\ \text{N·m/s} \quad \text{(convince yourself)}$$

$$\Delta P = (124 - 207)\ \text{kPa} = -83\ \text{kPa} = -83 \times 10^3\ \text{N/m}^2$$

$$\frac{\Delta P}{\rho} = \frac{-83 \times 10^3\ \text{N/m}^2}{1.00 \times 10^3\ \text{kg/m}^3} = -83\ \text{N·m/kg}$$

$$g = 9.81\ \text{m/s}^2$$

$$\Delta z = -103\ \text{m}$$

$$g\Delta z = \frac{9.81\ \text{m}}{\text{s}^2} \left| \frac{-103\ \text{m}}{} \right| \frac{1\ \text{N}}{1\ \text{kg·m/s}^2} = -1010\ \text{N·m/kg}$$

$$\dot{m} = \frac{-1.00 \times 10^6\ \text{N·m/s}}{(-83 - 1010)\ \text{N·m/kg}} = \boxed{915\ \text{kg/s}}$$

Test Yourself

(Answers, p. 658)

1. Under what conditions is the mechanical energy balance, Equation 7.7-2, applicable? What is the physical significance of the friction loss term, $\hat{F}$, in this equation?
2. Under what conditions is the Bernoulli equation, Equation 7.7-3, applicable?

7.8 SUMMARY

Considerable amounts of energy are required to run most chemical processes. Engineers use **energy balances** to account for the energy that flows into or out of each unit of a process, to determine the net energy requirement for the process, and to design ways to reduce the energy requirement so as to improve process profitability.

- The total energy of a process system has three components: **kinetic energy**—energy due to motion of the system as a whole; **potential energy**—energy due to the position of the system in a potential field (such as the earth's gravitational field); and **internal energy**—energy due to the translation, rotation, vibration, and electromagnetic interactions of the molecules, atoms, and subatomic particles within the system.
- In a **closed system** (no mass is transferred across the system boundaries while the process is taking place), energy may be transferred between the system and its surroundings in two ways: as **heat**—energy that flows due to a temperature difference between the system and its surroundings, and as **work**—energy that flows in response to any other stimulus such as an applied force, a torque, or a voltage. Heat always flows from a higher temperature to a lower temperature. Heat is always defined to be positive if it flows to a system from the surroundings, and in many engineering references (including this one) work is also defined as positive if it flows to the system from the surroundings.
- The **kinetic energy** of a body of mass m moving with velocity u is $E_k = mu^2/2$. The **gravitational potential energy** of the body is $E_p = mgz$, where g is the acceleration of gravity and z is the height of the object above a reference plane at which E_p is arbitrarily defined to be zero. If a stream at height z flows with mass flow rate $\dot{m}$ and velocity u, $\dot{E}_k = \dot{m}u^2/2$ and $\dot{E}_p = \dot{m}gz$ may be thought of as the rates at which the stream is transporting kinetic energy and gravitational potential energy, respectively.[3]
- The **first law of thermodynamics for a closed system** (which we will generally refer to as the *energy balance*) between two instants of time is

$$\boxed{\Delta U + \Delta E_k + \Delta E_p = Q + W} \qquad \textbf{(7.3-4)}$$

where in the context of closed systems, Δ denotes final value minus initial value. This equation states that the total energy transferred to the system in the specified time interval $(Q + W)$ equals the gain in the total energy of the system in the same time interval $(\Delta U + \Delta E_k + \Delta E_p)$. If energy is transferred *away* from the system, both sides of the equation are negative.

- When writing an energy balance for a closed system, first simplify Equation 7.3-4 by dropping negligible terms, then solve the simplified equation for whichever variable cannot be determined independently from other information in the process description.
  - **(a)** If the system is **isothermal** (constant temperature), no phase changes or chemical reactions take place, and pressure changes are no more than a few atmospheres in magnitude, then $\Delta U \approx 0$.
  - **(b)** If the system is not accelerating, then $\Delta E_k = 0$. If the system is not rising or falling, then $\Delta E_p = 0$. (You will almost always be able to drop these terms when writing balances on closed chemical process systems.)
  - **(c)** If the system and its surroundings are at the same temperature or if the system is perfectly insulated, then $Q = 0$. The system is then termed **adiabatic**.
  - **(d)** If energy is not transmitted across the system boundary by a moving part (such as a piston, an impeller, or a rotor), an electric current, or radiation, then $W = 0$.
- In an open system, work must be done to push input streams into the system $[= \sum_{in} P_j \dot{V}_j]$ and work is done by the output streams as they leave the system $[= \sum_{out} P_j \dot{V}_j]$, where P_j is the pressure of input or output stream j and $\dot{V}_j$ is the volumetric flow rate of the stream. The total rate of work done on a system by its surroundings $(\dot{W})$ is customarily divided into **flow work** $(\dot{W}_{fl})$, or work done by the input streams minus work done on the output streams at the system boundary, and **shaft work** $(\dot{W}_s)$, all other work transferred across the system boundary by moving parts or as electricity or radiation. Thus

$$\dot{W} = \dot{W}_s + \dot{W}_{fl} = \dot{W}_s + \sum_{\substack{\text{input}\\ \text{streams}}} P_j \dot{V}_j - \sum_{\substack{\text{output}\\ \text{streams}}} P_j \dot{V}_j$$

- The first law of thermodynamics for an open system at steady state resembles the closed-system balance:

$$\Delta \dot{U} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} + \dot{W}$$

except that each term now has units of (kJ/s) instead of (kJ) and Δ now signifies (output − input) and not (final − initial). The more commonly used form of the first law is derived by (a) substituting for $\dot{W}$ the previously derived expression in terms of flow work and shaft work; (b) expressing the volumetric flow rate of each input and output stream $(\dot{V}_j)$ as $\dot{m}_j \hat{V}_j$, where $\hat{V}_j$ is the **specific volume** (inverse density) of the stream fluid; (c) expressing the rate of transport of internal energy by a stream $(\dot{U}_j)$ as $\dot{m}_j \hat{U}_j$, where $\hat{U}_j$ is the **specific internal energy**

[3] The unit conversion factors $[(1\text{ N})/(1\text{ kg}\cdot\text{m/s}^2)]$ and $[(1\text{ kJ})/(10^3\text{ N}\cdot\text{m})]$ must be applied to the right-hand side of each of these equations to express these quantities in kJ/s (kW).

of the stream fluid; and (d) defining the **specific enthalpy** ($\hat{H}$) of a substance as $\hat{U} + P\hat{V}$. After some algebraic manipulation (Section 7.4c) the balance equation becomes

$$\boxed{\Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p = \dot{Q} + \dot{W}_s} \qquad \textbf{(7.4-15)}$$

where

$$\Delta\dot{H} = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j\hat{H}_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j\hat{H}_j$$

$$\Delta\dot{E}_k = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j u_j^2/2 - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j u_j^2/2$$

$$\Delta\dot{E}_p = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j g z_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j g z_j$$

- When writing an energy balance for an open system at steady state, first simplify Equation 7.4-15 by dropping negligible terms, then solve the simplified equation for whichever variable cannot be determined independently from other information in the process description.
  - **(a)** If no temperature changes, phase changes, or chemical reactions occur in a process and pressure changes from inlet to outlet are no more than a few atmospheres in magnitude, then $\Delta\dot{H} \approx 0$. (Under these circumstances, mechanical energy balances—Section 7.7—tend to be more useful than Equation 7.4-15.)
  - **(b)** If conditions are such that $\Delta\dot{H}$ may not be neglected (i.e., if temperature changes, phase changes, or chemical reactions occur), then $\Delta\dot{E}_k$ and $\Delta\dot{E}_p$ usually may be neglected. In any case, if there are no great vertical distances between the inlets and the outlets of a system, $\Delta\dot{E}_p \approx 0$.
  - **(c)** If the system and its surroundings are at the same temperature or if the system is perfectly insulated, then $\dot{Q} = 0$ and the process is adiabatic.
  - **(d)** If energy is not transmitted across the system boundary by a moving part, an electric current, or radiation, then $\dot{W}_s = 0$.
- The value of $\hat{U}$ for a pure substance in a given state (temperature, pressure, and phase) is the sum of the kinetic and potential energies of the individual molecular, atomic, and subatomic particles in a unit amount of the substance. *It is impossible to determine the absolute value of $\hat{U}$ for a substance, and hence also impossible to determine the absolute value of $\hat{H} = \hat{U} + P\hat{V}$.* However, we can measure the *change* in $\hat{U}$ or $\hat{H}$ corresponding to a specified change of state, which is all we ever need to know for energy balance calculations.
- A common practice is to arbitrarily designate a **reference state** for a substance at which $\hat{U}$ or $\hat{H}$ is declared to equal zero, and then tabulate $\hat{U}$ and/or $\hat{H}$ for the substance relative to the reference state. The statement "The specific enthalpy of CO(g) at 100°C and 1 atm relative to CO(g) at 0°C and 1 atm is 2919 J/mol" therefore has the following meaning:

  $$\text{CO(g, 0°C, 1 atm)} \rightarrow \text{CO(g, 100°C, 1 atm)} : \Delta\hat{H} = 2919\ \text{J/mol}$$

  The statement says nothing about the absolute specific enthalpy of CO at 100°C and 1 atm, which can never be determined.
- Both $\hat{U}$ and $\hat{H}$ are **state properties**, meaning that $\Delta\hat{U}$ and $\Delta\hat{H}$ for a given change in state for a substance are the same regardless of the path the substance follows from the initial state to the final state.
- The **steam tables** (Tables B.5, B.6, and B.7) can be used to estimate $\hat{U}$ and $\hat{H}$ for liquid water and steam (water vapor) at any specified temperature and pressure. The reference state for the tabulated internal energies and enthalpies in the steam tables is liquid water at the triple point—0.01°C and 0.00611 bar.
- At this point, you can perform energy-balance calculations for systems in which ΔU (closed system) or $\Delta\dot{H}$ (open system) can be neglected and for nonreactive systems involving species for which tables of $\hat{U}$ or $\hat{H}$ are available. Energy-balance procedures for other types of systems are presented in Chapters 8 and 9.
- **Mechanical energy balances** are useful for open systems in which heat flows and internal energy (and enthalpy) changes are secondary in importance to kinetic and potential energy changes and shaft work. For a liquid of constant density ρ flowing through such a system, the steady-state mechanical energy balance is

  $$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z + \hat{F} = \frac{\dot{W}_s}{\dot{m}}} \qquad \textbf{(7.7-2)}$$

  where $\hat{F}$(N·m/kg) is the **friction loss**—thermal energy generated by friction between adjacent liquid elements moving at different velocities and between liquid elements and the system walls. The friction loss shows up as a heat loss from the system ($\dot{Q} < 0$) and/or a gain in temperature and hence in internal energy from inlet to outlet ($\Delta\dot{U} > 0$). If $\hat{F}$ and $\dot{W}_s$ can be neglected, the resulting form of Equation 7.7-2 is the **Bernoulli equation**.
- At this point you can solve mechanical energy balances for systems in which the friction loss ($\hat{F}$) is given or negligible or if it is the only unknown quantity in Equation 7.7-2. Texts on fluid mechanics present methods for estimating $\hat{F}$ from information about fluid flow rates and physical properties and various characteristics of the system through which the fluid is flowing.

PROBLEMS

7.1. A certain gasoline engine has an efficiency of 30%; that is, it converts into useful work 30% of the heat generated by burning a fuel.

(a) If the engine consumes 0.80 L/h of a gasoline with a heating value of 3.25×10^4 kJ/L, how much power does it provide? Express the answer both in kW and horsepower.

(b) Suppose the fuel is changed to include 10% ethanol by volume. The heating value of ethanol is approximately 2.34×10^4 kJ/L and volumes of gasoline and ethanol may be assumed additive. At what rate (L/h) does the fuel mixture have to be consumed to produce the same power as gasoline?

7.2. Consider an automobile with a mass of 5500 lb_m braking to a stop from a speed of 55 miles/h.

(a) How much energy (Btu) is dissipated as heat by the friction of the braking process?

(b) Suppose that throughout the United States, 300,000,000 such braking processes occur in the course of a given day. Calculate the average rate (megawatts) at which energy is being dissipated by the resulting friction.

(c) Find a source of information on the average per-capita consumption of electricity (kW) in the United States, France, and India. Roughly how many people in each country would have their electricity needs met if the braking energy calculated in Part (b) could be recovered and used to provide electricity? Show your calculations and identify your information source.

BIOENGINEERING

*__7.3.__ The *food calorie* (also known as *nutritional calorie* and *large calorie*) is a quantity equal to a kilocalorie (kcal). Not surprisingly, the food calorie is used to represent units of energy associated with eating, as in "An average hot dog with ketchup and a bun contains 315 calories."

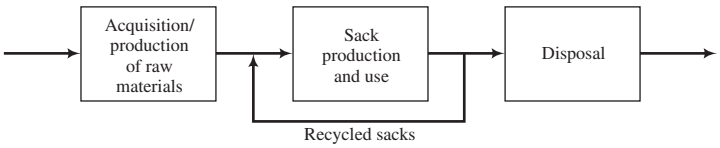
You woke up hungry this morning so you ate a breakfast of hotcakes, eggs, and a large biscuit. An online application indicates that this meal contains 1090 calories (meaning food calories).

(a) How many flights of stairs in a typical office building would you have to climb to burn off the calories you consumed? Make a reasonable assumption about the height of a flight of stairs, and state any other assumptions you make.

(b) The required height of the climb would almost certainly be different from the number calculated in Part (a), even if your assumption about the height of a flight of stairs is correct. Explain why you think it would be more or fewer stairs.

ENVIRONMENTAL

7.4. A simplified version of the life cycle of grocery sacks follows.[4]



In the late 1970s, supermarkets began to replace paper sacks with polyethylene (plastic) sacks. In the 1980s, a movement to go back to paper arose, primarily inspired by environmental considerations. In the 1990s, a countermovement arose, claiming that paper sacks have a greater negative environmental impact than plastic ones.

Following are estimates of the atmospheric emissions and energy consumption associated with the raw materials acquisition and processing (logging, pulping, and papermaking for paper, petroleum production and refining and polymerization for polyethylene) and disposal of sacks, and for the manufacture and use of sacks.

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* Adapted from a problem contributed by Paul Blowers of the University of Arizona.

[4] Problem adapted from D. T. Allen, N. Bakshani, and K. S. Rosselot, *Pollution Prevention: Homework and Design Problems for Engineering Curricula,* American Institute for Pollution Prevention, New York, 1992. The emissions and energy consumption data are from Franklin Associates, Ltd., *Resource and Environmental Profile Analysis of Polyethylene and Unbleached Paper Grocery Sacks*. Report prepared for the Council for Solid Waste Solutions, Prairie Village, KS, June 1990.

Stages	Emissions (oz/sack)		Energy Consumed (Btu/sack)	
	Paper	Plastic	Paper	Plastic
Raw materials production plus product disposal	0.0510	0.0045	724	185
Sack production and use	0.0516	0.0146	905	464

Assume that atmospheric emissions and energy consumption do not depend on whether the new sacks are made from fresh raw materials or recycled sacks, and that it takes roughly twice as many plastic sacks as paper sacks to hold a given quantity of groceries.

(a) Calculate the air emissions (lb_m) and energy consumption (Btu) per 1000 paper sacks used and per 2000 plastic sacks used, assuming that no sacks are recycled.

(b) Repeat the calculations of Part (a) assuming that 60% of the used sacks are recycled. By what percentages are air emissions and energy consumption reduced for each sack material as a consequence of recycling?

(c) Estimate the number of grocery sacks used in a day in the United States (population = 320 million), and calculate the average rate of energy consumption (megawatts, MW) associated with the production, use, and disposal of these sacks, assuming that they are plastic and none are recycled. How many MW would be saved by 60% recycling?

(d) You should have found that both atmospheric emissions and energy consumption are higher when paper is used rather than plastic, although recycling reduces the differences. Nevertheless, deciding to use plastic based entirely on this result could be a serious mistake. List several important factors that were not taken into account in making the decision, including considerations of the potential environmental impact of each type of bag.

Equipment Encyclopedia
pump

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7.5. Liquid ethanol is pumped from a large storage tank through a 1-inch ID pipe at a rate of 3.00 gal/min.

(a) At what rate in (i) $ft \cdot lb_f/s$ and (ii) hp is kinetic energy being transported by the ethanol in the pipe?

(b) The electrical power input to the pump transporting the ethanol must be greater than the amount you calculated in Part (a). What would you guess becomes of the additional energy? (There are several possible answers.)

7.6. Air at 300°C and 130 kPa flows through a horizontal 7-cm ID pipe at a velocity of 42.0 m/s.

(a) Calculate $\dot{E}_k$(W), assuming ideal-gas behavior.

(b) If the air is heated to 400°C at constant pressure, what is $\Delta\dot{E}_k = \dot{E}_k(400°C) - \dot{E}_k(300°C)$?

(c) Why would it be incorrect to say that the rate of transfer of heat to the gas in Part (b) must equal the rate of change of kinetic energy?

7.7. Suppose you pour a gallon of water on a yowling cat 10 ft below your bedroom window.

(a) How much potential energy ($ft \cdot lb_f$) does the water lose?

(b) How fast is the water traveling (ft/s) just before impact?

(c) True or false: Energy must be conserved, therefore the kinetic energy of the water before impact must equal the kinetic energy of the cat after impact. If you decide the answer is false, what happens to most of the kinetic energy that the water possessed just before impact?

*__7.8.__ Most carnivals have a game in which a contestant swings a large hammer and hits a pedal, causing a metal ball to move up a pole. If the pedal is hit hard enough, the ball travels to the top and rings a bell, winning a prize for the contestant. The head of the hammer has a mass of 14 lb_m, the metal ball has a mass of 4.0 lb_m, and the bell is 30.0 ft above the pedal.

(a) How fast must the head of the hammer be traveling at the moment of impact to ring the bell?

(b) To solve Part (a) from the given information, you must have made at least three assumptions—one about the hammer, one about the pedal, and one about the pole. What were they, and what was their probable impact on your solution?

7.9. Methane enters a 3-cm ID pipe at 30°C and 10 bar with an average velocity of 5.00 m/s and emerges at a point 200 m lower than the inlet at 30°C and 9 bar.

* Adapted from a problem contributed by James Newell of Rowan University.

(a) Without doing any calculations, predict the signs (+ or −) of $\Delta\dot{E}_k$ and $\Delta\dot{E}_p$, where Δ signifies (outlet − inlet). Briefly explain your reasoning.
(b) Calculate $\Delta\dot{E}_k$ and $\Delta\dot{E}_p$ (W), assuming that the methane behaves as an ideal gas.
(c) If you determine that $\Delta\dot{E}_k \neq -\Delta\dot{E}_p$, explain how that result is possible.

7.10. You recently purchased a large plot of land in the Amazon jungle at an extremely low cost. You are quite pleased with yourself until you arrive there and find that the nearest source of electricity is 1500 miles away, a fact that your brother-in-law, the real estate agent, somehow forgot to mention. Since the local hardware store does not carry 1500-mile-long extension cords, you decide to build a small hydroelectric generator under a 75-m high waterfall located nearby. The flow rate of the waterfall is 10^5 m^3/h, and you anticipate needing 750 kW·h/wk to run your lights, air conditioner, and television. Calculate the maximum power theoretically available from the waterfall and see if it is sufficient to meet your needs.

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7.11. Write and simplify the closed-system energy balance (Equation 7.3-4) for each of the following processes, and state whether nonzero heat and work terms are positive or negative. Begin by defining the system. The solution of Part (a) is given as an illustration.
(a) The contents of a closed flask are heated from 25°C to 80°C.

Solution. The system is the flask contents.

$$Q + W = \Delta U + \Delta E_k + \Delta E_p$$

$$W = 0 \quad \text{(no moving parts or generated currents)}$$
$$\Delta E_k = 0 \quad \text{(system is stationary)}$$
$$\Delta E_p = 0 \quad \text{(no height change)}$$

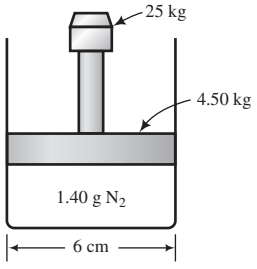
$$\boxed{Q = \Delta U}$$

$$\boxed{Q > 0 \quad \text{(heat is transferred to the system)}}$$

(b) A tray filled with water at 20°C is put into a freezer. The water turns into ice at −5°C. (*Note:* When a substance expands it does work on its surroundings and when it contracts the surroundings do work on it.)
(c) A chemical reaction takes place in a closed adiabatic (perfectly insulated) rigid container.
(d) Repeat Part (c), only suppose that the reactor is isothermal rather than adiabatic and that when the reaction was carried out adiabatically, the temperature in the reactor increased.

7.12. A cylinder with a movable piston contains 5.00 liters of a gas at 30°C and 5.00 bar. The piston is slowly moved to compress the gas to 8.80 bar.
(a) Considering the system to be the gas in the cylinder and neglecting ΔE_p, write and simplify the closed-system energy balance. Do not assume that the process is isothermal in this part.
(b) Suppose now that the process is carried out isothermally, and the compression work done on the gas equals 7.65 L·bar. If the gas is ideal so that $\hat{U}$ is a function only of T, how much heat (in joules) is transferred to or from (state which) the surroundings? (Use the gas-constant table in the back of the book to determine the factor needed to convert L·bar to joules.)
(c) Suppose instead that the process is adiabatic and that $\hat{U}$ increases as T increases. Is the final system temperature greater than, equal to, or less than 30°C? (Briefly state your reasoning.)

7.13. A piston-fitted cylinder with a 6-cm inner diameter contains 1.40 g of nitrogen. The mass of the piston is 4.50 kg, and a 25.00-kg weight rests on the piston. The gas temperature is 30°C, and the pressure outside the cylinder is 2.50 atm.



(a) Prove that the absolute pressure of the gas in the cylinder is 3.55×10^5 Pa. Then calculate the volume occupied by the gas, assuming ideal-gas behavior.

(b) Suppose the weight is abruptly lifted and the piston rises to a new equilibrium position. Further suppose that the process takes place in two steps: a rapid step in which a negligible amount of heat is exchanged with the surroundings, followed by a slow step in which the gas returns to 30°C. Considering the gas as the system, write the energy balances for step 1, step 2, and the overall process. In all cases, neglect ΔE_k and ΔE_p. If $\hat{U}$ varies proportionally with T, does the gas temperature increase or decrease in step 1? Briefly explain your answer.

(c) The work done by the gas equals the restraining force (the weight of the piston plus the force due to atmospheric pressure) times the distance traveled by the piston. Calculate this quantity and use it to determine the heat transferred to or from (state which) the surroundings during the process.

7.14. Oxygen at 150 K and 41.64 atm has a tabulated specific volume of 4.684 cm^3/g and a specific internal energy of 1706 J/mol.

(a) The figure 1706 J/mol is *not* the true internal energy of one g-mole of oxygen gas at 150 K and 41.64 atm. Why not? In a sentence, state the correct physical significance of that figure. (The term "reference state" should appear in your statement.)

(b) Calculate the specific enthalpy of O_2 (J/mol) at 150 K and 41.64 atm, and state the physical significance of this figure. What can you say about the reference state used to calculate it?

7.15. Values of the specific internal energy of bromine at three conditions are listed here.

State	T(K)	P(bar)	$\hat{V}$(L/mol)	$\hat{U}$(kJ/mol)
Liquid	300	0.310	0.0516	−28.24
Vapor	300	0.310	79.94	0.000
Vapor	340	1.33	20.92	1.38

(a) What reference state was used to generate the listed specific internal energies?

(b) Calculate $\Delta\hat{U}$(kJ/mol) for a process in which bromine vapor at 300 K is condensed at constant pressure. Then calculate $\Delta\hat{H}$(kJ/mol) for the same process. (See Example 7.4-1.) Finally, calculate ΔH(kJ) for 5.00 mol of bromine undergoing the process.

(c) Bromine vapor in a 5.00-liter container at 300 K and 0.205 bar is to be heated to 340 K. Calculate the heat (kJ) that must be transferred to the gas to achieve the desired temperature increase, assuming that $\hat{U}$ is independent of pressure.

(d) In reality, more heat than the amount calculated in Part (c) would have to be transferred to the container to raise the gas temperature by 40 K. State two reasons for this.

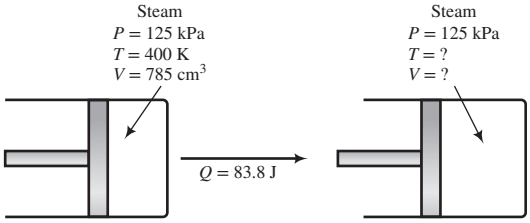
7.16. Prove that for an ideal gas, $\hat{U}$ and $\hat{H}$ are related as $\hat{H} = \hat{U} + RT$, where R is the gas constant. Then:

(a) Taking as given that the specific internal energy of an ideal gas is independent of the gas pressure, justify the claim that $\Delta\hat{H}$ for a process in which an ideal gas goes from (T_1, P_1) to (T_2, P_2) equals $\Delta\hat{H}$ for the same gas going from T_1 to T_2 at a constant pressure of P_1.

(b) Calculate ΔH(cal) for a process in which the temperature of 2.5 mol of an ideal gas is raised by 50°C, resulting in a specific internal energy change $\Delta\hat{U} = 3500$ cal/mol.

7.17. If a system expands in volume by an amount $\Delta V(m^3)$ against a constant restraining pressure $P(N/m^2)$, a quantity $P\Delta V$(J) of energy is transferred as *expansion work* from the system to its surroundings. Suppose that the following four conditions are satisfied for a closed system: (a) the system expands against a constant pressure (so that $\Delta P = 0$); (b) $\Delta E_k = 0$; (c) $\Delta E_p = 0$; and (d) the only work done by or on the system is expansion work. Prove that under these conditions, the energy balance simplifies to $Q = \Delta H$.

7.18. A horizontal cylinder equipped with a frictionless piston contains 785 cm^3 of steam at 400 K and 125 kPa. A total of 83.8 joules of heat is transferred to the steam, causing the steam temperature to rise and the cylinder volume to increase. A constant restraining force is maintained on the piston throughout the expansion, so that the pressure exerted by the piston on the steam remains constant at 125 kPa.



The specific enthalpy of steam at 125 kPa varies with temperature approximately as

$$\hat{H}(\text{J/mol}) = 34{,}980 + 35.5T(\text{K})$$

(a) Taking the steam as the system, convince yourself that $Q = \Delta H$ for this process—that is, the four conditions specified in Part (a) of Problem 7.17 are applicable. Then prove that the final steam temperature is 480 K. Finally, calculate (i) the final cylinder volume, (ii) the expansion work done by the steam, and (iii) ΔU(J).

(b) Which of the specified conditions of Problem 7.17 would have been only an approximation if the cylinder were not horizontal?

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thermocouple
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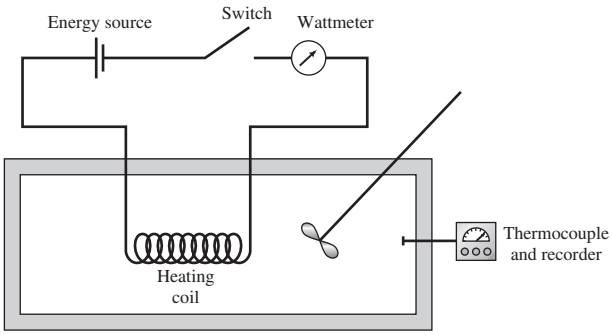
7.19. You are performing an experiment to measure the specific internal energy of a gas relative to a reference state of 25°C and 1 atm (at which conditions $\hat{U}$ is arbitrarily set equal to 0). The gas is placed in a closed insulated 2.10-liter container at 25°C and 1 atm. A switch is alternately closed and opened, causing a current to flow intermittently through an electrical heating coil in the chamber. The gas temperature, which is monitored with a calibrated thermocouple, increases while the circuit is closed and remains constant while it is open. A wattmeter reads 1.4 W when the circuit is closed; 90% of this power is transferred to the gas as heat. The thermocouple calibration curve is a straight line through the points ($T = 0$°C, $E = -0.249$ mV) and ($T = 100$°C, $E = 5.27$ mV), where E is the thermocouple potentiometer reading.



The following data are taken, where t represents the cumulative time during which the circuit was closed:

t(s)	0	30	60	90
E(mV)	1.13	2.23	3.34	4.44

(a) Which given item of information suggests that the chamber may be considered adiabatic? (*Note:* Simply saying the container is insulated does not guarantee that it is adiabatic.)

(b) Write the energy balance for the gas in the chamber and use it to calculate $\hat{U}$(J/mol) at each of the observed temperatures, neglecting the work done on the gas by the stirrer. Express your solution as a table of $\hat{U}$ versus T.

(c) What might be the purpose of the stirrer?

(d) What happens to the 0.14 W of power that does not go to raise the temperature of the gas?

(e) A colleague points out to you that the calculated values of $\hat{U}$ fail to take something into account and so do not precisely correspond to the values at the calculated temperatures and 1 atm. You reply that she is quite correct, but it doesn't matter. Justify her statement and state the basis of your reply. Suggest several ways to provide quantitative validation of your claim.

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7.20. Define a system and simplify the open-system energy balance (Equation 7.4-15) for each of the following cases. State when possible whether nonzero heat and shaft work terms are positive or negative. The solution of Part (a) is given as an illustration.

(a) Steam enters a rotary turbine and turns a shaft connected to a generator. The inlet and outlet steam ports are at the same height. Some energy is transferred to the surroundings as heat.

Solution. The system is the steam flowing from the inlet port to the outlet port:

$$\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$$\Downarrow \quad \Delta\dot{E}_p = 0 \quad \text{(no height change)}$$

$$\boxed{\Delta\dot{H} + \Delta\dot{E}_k = \dot{Q} + \dot{W}_s}$$

$\dot{Q}$ is negative
$\dot{W}_s$ is negative

(b) A liquid stream flows through a heat exchanger in which it is heated from 25°C to 80°C. The inlet and outlet pipes have the same diameter, and there is no change in elevation between these points.

(c) Water passes through the sluice gate of a dam and falls on a turbine rotor, which turns a shaft connected to a generator. The fluid velocity on both sides of the dam is negligible, and the water undergoes insignificant pressure and temperature changes between the inlet and outlet. (See Example 7.4-2.)

(d) Crude oil is pumped through a cross-country pipeline. The pipe inlet is 200 m higher than the outlet, the pipe diameter is constant, and the pump is located near the midpoint of the pipeline. Energy dissipated by friction in the line is transferred as heat through the wall.

(e) A chemical reaction takes place in a continuous reactor that contains no moving parts. Kinetic and potential energy changes from inlet to outlet are negligible.

7.21. Air is heated from 25°C to 140°C prior to entering a combustion furnace. The change in specific enthalpy associated with this transition is 3349 J/mol. The flow rate of air at the heater outlet is 1.65 m^3/min and the air pressure at this point is 122 kPa absolute.

(a) Calculate the heat requirement in kW, assuming ideal-gas behavior and that kinetic and potential energy changes from the heater inlet to the outlet are negligible.

(b) Would the value of $\Delta\dot{E}_k$ [which was neglected in Part (a)] be positive or negative, or would you need more information to be able to tell? If the latter, what additional information would be needed?

7.22. A **Thomas flowmeter** is a device in which heat is transferred at a measured rate from an electric coil to a flowing fluid, and the flow rate of the stream is calculated from the measured increase of the fluid temperature. Suppose a device of this sort is inserted in a stream of nitrogen, the current through the heating coil is adjusted until the wattmeter reads 1.25 kW, and the stream temperature goes from 30°C and 110 kPa before the heater to 34°C and 110 kPa after the heater.

(a) If the specific enthalpy of nitrogen is given by the formula

$$\hat{H}(\text{kJ/kg}) = 1.04[T(^\circ\text{C}) - 25]$$

what is the volumetric flow rate of the gas (L/s) upstream of the heater (i.e., at 30°C and 110 kPa)?

(b) List several assumptions made in the calculation of Part (a) that could lead to errors in the calculated flow rate.

7.23. The specific enthalpy of liquid *n*-hexane at 1 atm varies linearly with temperature and equals 25.8 kJ/kg at 30°C and 129.8 kJ/kg at 50°C.

(a) Determine the equation that relates $\hat{H}$(kJ/kg) to T(°C) and calculate the reference temperature on which the given enthalpies are based. Then derive an equation for $\hat{U}(T)$(kJ/kg) at 1 atm.

(b) Calculate the heat transfer rate required to cool liquid *n*-hexane flowing at a rate of 20 kg/min from 60°C to 25°C at a constant pressure of 1 atm. Estimate the change in specific internal energy (kJ/kg) as the *n*-hexane is cooled at the given conditions.

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nozzle

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7.24. Steam at 260°C and 7.00 bar absolute is expanded through a nozzle to 200°C and 4.00 bar. Negligible heat is transferred from the nozzle to its surroundings. The approach velocity of the steam is negligible. The specific enthalpy of steam is 2974 kJ/kg at 260°C and 7 bar and 2860 kJ/kg at 200°C and 4 bar. Use the open-system energy balance to calculate the exit steam velocity.

BIOENGINEERING

7.25. The heart pumps blood at an average rate of 5 L/min. The gauge pressure on the venous (intake) side is 0 mm Hg and that on the arterial (discharge) side is 100 mm Hg. Energy is supplied to the heart as heat released by the absorption of oxygen in the cardiac muscles: 5 mL (STP) O_2/min is absorbed, and 20.2 J is released per mL of O_2 absorbed. Part of this absorbed energy is converted to flow work (the work done to pump blood through the circulatory system), and the balance is lost as heat transferred to the tissues surrounding the heart.

(a) Simplify Equation 7.4-12 for this system, assuming (among other things) that there is no change in internal energy from inlet to outlet.

(b) What percentage of the heat input to the heart ($\dot{Q}_{in}$) is converted to flow work? (The answer may be thought of as the efficiency of the heart as a pump.)

ALTERNATIVE ENERGY

*7.26. The conversion of the kinetic energy of wind to electricity may be an attractive alternative to the use of fossil fuels. Typically, wind causes the rotor of a turbine to turn, and a generator converts the rotational kinetic energy of the rotor into electricity. Power generated by a wind turbine ($\dot{W}_s$) can be estimated from the density of the air (ρ), wind speed (u), and turbine rotor diameter (D) using the following formula:

$$\dot{W}_s = \frac{1}{2}\dot{m}u^2 \times \eta, \quad \text{where } \dot{m} = \rho A u = \rho \frac{\pi D^2}{4} u$$

The conversion efficiency (η) is a function of many variables, including the electrical and mechanical properties of the turbine, the material of construction, and the blade design.

(a) Develop an equation for the density of air (kg/m^3) as a function of the temperature (K) and relative humidity of the air. Use the Antoine equation for the vapor pressure of water, and assume atmospheric pressure equals 1.0 atm.

(b) A wind turbine with a 30.0-ft diameter and 35.0% conversion efficiency generates electricity on a day when the temperature is 75°F, the relative humidity is 78.0%, and the average wind velocity is 9.50 miles/h. Calculate the generated power in kW.

(c) Seasonal variations can cause significant changes in the power obtained from a wind turbine. Your task is to calculate and analyze these variations over a year for three cities in the United States using historical averages recorded by the National Oceanic and Atmospheric Administration (NOAA). The table below and on the next page gives monthly average relative humidities, mean temperatures, and wind speeds at three different cities, one each from the south, northeast, and western regions of the country. Reproduce the table on a spreadsheet, assume a wind turbine diameter of 30.0 feet and conversion efficiency of 35.0%, and estimate the power generated (kW) for each city and month. (The calculated value for one month is given so you can check your calculations.)

Diameter (ft)	30.0													
Efficiency	35.0%													
City (Pop)		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Yr. Mean
Huntsville, AL (179653)	h_r(%)	80	79	78	81	85	87	89	89	88	86	82	81	
	T(°F)	39.8	44.3	52.3	60.4	68.6	76	79.5	78.6	72.4	61.3	51.2	43.1	
	u(mph)	9	9.4	9.8	9.2	7.9	6.9	6	5.8	6.7	7.3	8.1	9	
	T(K)													
	ρ(kg/m^3)													
	u(m/s)													
	$\dot{W}_s$(kW)	1.004												

* Adapted from a problem contributed by Vinay K. Gupta of the University of South Florida.

(*Continued*)

City (Pop)		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Yr. Mean
Bridgeport, CT (137912)	h_r(%)	69	69	69	68	74	77	77	78	80	78	76	73	
	T(°F)	29.9	31.9	39.5	48.9	59	68	74	73.1	65.7	54.7	45.1	35.1	
	u(mph)	12.5	12.9	13	12.4	11.1	9.9	9.4	9.5	10.5	11.3	12	12.1	
	T(K)													
	ρ(kg/m^3)													
	u(m/s)													
	$\dot{W}_s$(kW)													
Sacramento, CA (1394154)	h_r(%)	90	88	85	82	82	78	77	78	77	79	87	88	
	T(°F)	51.2	54.5	58.9	65.5	71.5	75.4	74.8	71.7	64.4	53.3	45.8	51.2	
	u(mph)	7.3	8.4	8.6	9	9.6	8.9	8.4	7.4	6.4	6	6.4	7.3	
	T(K)													
	ρ(kg/m^3)													
	u(m/s)													
	$\dot{W}_s$(kW)													

(d) Plot the power variation over the course of a year for all three cities. How do the cities compare as locations for wind turbines?

(e) The average electricity consumption in the United States is approximately 12,000 kWh per capita per year. On a wind-turbine farm, a single turbine occupies a space of 1000 m^2. Estimate the number of turbines that would be required to meet the electricity needs of each of the three cities listed in the table if the turbines were operated continuously. Then estimate how many acres and hectares each farm would occupy.

(f) The numbers of turbines actually put in place to meet the power requirements of the three cities would all be greater than the numbers calculated in Part (e). List three reasons for the calculated quantities to be underestimates.

7.27. Saturated steam at 100°C is heated to 350°C. Use the steam tables to determine (a) the required heat input (J/s) if a continuous stream flowing at 100 kg/s undergoes the process at constant pressure and (b) the required heat input (J) if 100 kg undergoes the process in a constant-volume container. What is the physical significance of the difference between the numerical values of these two quantities?

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7.28. A fuel oil is burned with air in a boiler furnace. The combustion produces 813 kW of thermal energy, of which 65% is transferred as heat to boiler tubes that pass through the furnace. The combustion products pass from the furnace to a stack at 550°C. Water enters the boiler tubes as a liquid at 30°C and leaves the tubes as saturated steam at 20 bar absolute.

(a) Calculate the rate (kg/h) at which steam is produced.

(b) Use the steam tables to estimate the volumetric flow rate of the steam produced.

(c) Repeat the calculation of Part (b), only assume ideal-gas behavior instead of using the steam tables. Would you have more confidence in the estimate of Part (b) or Part (c)? Explain.

(d) What happened to the 35% of the thermal energy released by the combustion that did not go to produce the steam?

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7.29. Liquid water is fed to a boiler at 24°C and 10 bar and is converted at constant pressure to saturated steam.

(a) Use the steam tables to calculate $\Delta\hat{H}$(kJ/kg) for this process, and then determine the heat input required to produce 15,800 m^3/h of steam at the exit conditions. Assume the kinetic energy of the entering liquid is negligible and that steam is discharged through a 15-cm ID pipe.

(b) How would the calculated value of the heat input change if you did not neglect the kinetic energy of the inlet water and if the inner diameter of the steam discharge pipe were 13 cm (increase, decrease, stay the same, or no way to tell without more information)?

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*7.30. Energy may be produced from solid waste in two ways: (1) generate methane from anaerobic decomposition of the waste and burn it (landfill-gas-to-energy, or LFGTE) or (2) burn the waste directly (waste-to-energy, or WTE). The heat generated by either method can be used to produce steam, which impinges on a turbine rotor connected to a generator to produce electricity. LFGTE produces about 215 kWh electricity/ton of waste, and WTE produces roughly 600 kWh/ton of waste. The average output of a large power plant is 1 GW, which is enough to supply the annual residential energy consumption of a city of roughly 800,000 people.

(a) The current rate of municipal solid-waste generation in the United States is approximately 413 million tons per year. If all of it were used for energy recovery, how many 1 GW power plants could LFGTE supply? How many if WTE is used?

(b) A municipality trying to decide between LFGTE, WTE, and a natural gas-fired combustion turbine has called you in as a consultant. Use information in the sources cited below to summarize the pros and cons of each choice.

A useful source of information regarding LFGTE is the U.S. EPA Landfill Methane Outreach Program, http://www.epa.gov/lmop/; the Waste-to-Energy Research and Technology Council at Columbia University provides useful information on WTE, http://www.seas.columbia.edu/earth/wtert/; and information on natural gas can be obtained from the U.S. Energy Information Administration, http://www.eia.doe.gov/oil_gas/natural_gas/info_glance/natural_gas.html.

7.31. You have been assigned to collect thermodynamic data for a new liquid product your company is about to begin manufacturing. You decide to use a continuous-flow technique to generate a correlation of $\hat{H}$ versus T. You wrap an electrical heating tape around a pipe, cover the tape with a thick layer of insulation, pump the liquid through the pipe at the rate of 228 g/min, and adjust the power input to the heating tape with a variable resistor. For each resistance setting, you record the power input and the temperature of the liquid at the pipe outlet. You multiply the power input by a correction factor of 0.94 to determine the rate of heat input to the liquid. The entering fluid temperature remains at 25°C throughout the experiment.

The following data are taken:

T_{out}(°C)	Heat Input to the Liquid (W)
25.0	0.0
26.4	17.0
27.8	35.3
29.0	50.9
32.4	94.4

(a) Generate a table of $\hat{H}$(J/g) versus T(°C), taking 25°C and 1 atm as the reference state.

(b) Fit a line to the data (either graphically or by the method of least squares) to determine the coefficient b of an expression of the form $\hat{H} = b(T - 25)$.

(c) Estimate the heat input required to raise 350 kg/min of the liquid from 20°C to 70°C. Why would you be concerned about the accuracy of your estimate?

(d) The correction factor of 0.94 accounts for the fact that the rate of energy input to the heating tape is somewhat greater than the rate of energy input to the liquid. Where does the additional energy go? (There are several answers.)

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heat exchanger
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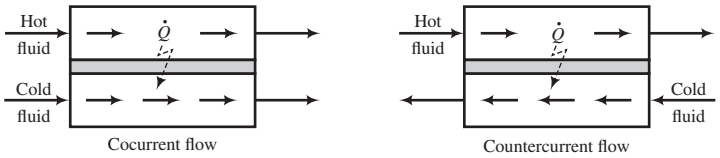
7.32. Saturated steam at a gauge pressure of 2.0 bar is to be used to heat a stream of ethane. The ethane enters a heat exchanger at 16°C and 1.5 bar gauge at a rate of 795 m^3/min and is heated at constant pressure to 93°C. The steam condenses and leaves the exchanger as a liquid at 27°C. The specific enthalpy of ethane at the given pressure is 941 kJ/kg at 16°C and 1073 kJ/kg at 93°C.

(a) How much energy (kW) must be transferred to the ethane to heat it from 16°C to 93°C?

(b) Assuming that all the energy transferred from the steam goes to heat the ethane, at what rate in m^3/s must steam be supplied to the exchanger? If the assumption is incorrect, would the calculated value be too high or too low?

* Adapted from a problem contributed by Joseph DeCarolis of North Carolina State University.

(c) Should the heat exchanger be set up for cocurrent or countercurrent flow (see the following schematic diagram)? Explain. (*Hint:* One of them will not work at all.)



7.33. Superheated steam at 40 bar absolute and 500°C flows at a rate of 250 kg/min to an adiabatic turbine, where it expands to 5 bar. The turbine develops 1500 kW. From the turbine the steam flows to a heater, where it is reheated isobarically to its initial temperature. Neglect kinetic energy changes.

(a) Write an energy balance on the turbine and use it to determine the outlet stream temperature.

(b) Write an energy balance on the heater and use it to determine the required input (kW) to the steam.

(c) Verify that an overall energy balance on the two-unit process is satisfied.

(d) Suppose the turbine inlet and outlet pipes both have diameters of 0.5 meter. Show that it is reasonable to neglect the change in kinetic energy for this unit.

7.34. During a period of relative inactivity, the average rate of transport of enthalpy by the metabolic and digestive waste products leaving the body minus the rate of enthalpy transport by the raw materials ingested and breathed into the body is approximately $\Delta H = -300$ kJ/h. Heat is transferred from the body to its surroundings at a rate given by

$$Q = hA(T_s - T_0)$$

where A is the body surface area (roughly 1.8 m^2 for an adult), T_s is the skin temperature (normally 34.2°C), T_0 is the temperature of the body surroundings, and h is a **heat transfer coefficient**. Typical values of h for the human body are[5]

$$h = 8\ \text{kJ/(m}^2\cdot\text{h}\cdot\text{°C)} \quad \text{(fully clothed, slight breeze blowing)}$$
$$h = 64\ \text{kJ/(m}^2\cdot\text{h}\cdot\text{°C)} \quad \text{(nude, immersed in water)}$$

(a) Consider the human body as a continuous system at steady state. Write an energy balance on the body, making all appropriate simplifications and substitutions.

(b) Calculate the surrounding temperature for which the energy balance is satisfied (i.e., at which a person would feel neither hot nor cold) for a clothed person and for a nude person immersed in water.

(c) At a family party, an elderly relative calls out to you in a loud voice, "Hey, you're an engineer, so you know everything. Explain why I'm comfortable when the room temperature is seventy degrees, but if I get into seventy-degree water in a bathtub, I'm freezing." He stops with a smug expression on his face and along with everyone else within earshot waits for your response. What would it be?

7.35. Liquid water at 30.0°C and liquid water at 90.0°C are combined in a ratio (1 kg cold water/2 kg hot water).

(a) Use a *simple* calculation to estimate the final water temperature. For this part, pretend you never heard of energy balances.

(b) Now assume a basis of calculation and write a closed-system energy balance for the process, assuming that the mixing is adiabatic. Use the balance to calculate the specific internal energy and hence (from the steam tables) the final temperature of the mixture. What is the percentage difference between your answer and that of Part (a)?

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7.36. Steam produced in a boiler is frequently "wet"—that is, it is a mist composed of saturated water vapor and entrained liquid droplets. The **quality** of a wet steam is defined as the fraction of the mixture by mass that is vapor.

A wet steam at a pressure of 5.0 bar with a quality of 0.85 is isothermally "dried" by evaporating the entrained liquid. The flow rate of the dried steam is 52.5 m^3/h.

(a) Use the steam tables to determine the temperature at which this operation occurs, the specific enthalpies of the wet and dry steams, and the total mass flow rate of the process stream.

[5] Data taken from R. C. Seagrave, *Biomedical Applications of Heat and Mass Transfer,* Iowa State University Press, Ames, Iowa, 1971.

(b) Calculate the heat input (kW) required for the evaporation process.
(c) Suppose leaks developed in the feed pipe to the dryer and in the dryer exit pipe. Speculate on what you would see at each location.

7.37. Two hundred kg/min of steam enters a steam turbine at 350°C and 40 bar through a 7.5-cm diameter line and exits at 75°C and 6.5 bar through a 5-cm line. The exiting stream may be vapor, liquid, or "wet steam" (see Problem 7.36).
(a) If the exiting stream were wet steam at 6.5 bar, what would its temperature be?
(b) How much energy is transferred to or from the turbine? (Neglect $\Delta\dot{E}_p$ but not $\Delta\dot{E}_k$.)

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steam trap

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7.38. A **steam trap** is a device to purge steam condensate from a system without venting uncondensed steam. In one of the crudest trap types, the condensate collects and raises a float attached to a drain plug. When the float reaches a certain level, it "pulls the plug," opening the drain valve and allowing the liquid to discharge. The float then drops down to its original position and the valve closes, preventing uncondensed steam from escaping.
(a) Suppose saturated steam at 25 bar is used to heat 100 kg/min of an oil from 135°C to 185°C. Heat must be transferred to the oil at a rate of 1.00×10^4 kJ/min to accomplish this task. The steam condenses on the exterior of a bundle of tubes through which the oil is flowing. Condensate collects in the bottom of the exchanger and exits through a steam trap set to discharge when 1200 g of liquid is collected. How often does the trap discharge?
(b) Especially when periodic maintenance checks are not performed, steam traps often fail to close completely and so leak steam continuously. Suppose a process plant contains 1000 leaking traps (not an unrealistic supposition for some plants) operating at the condition of Part (a), and that on the average 10% additional steam must be fed to the condensers to compensate for the uncondensed steam venting through the leaks. Further suppose that the cost of generating the additional steam is \$7.50 per million Btu, where the denominator refers to the enthalpy of the leaking steam relative to liquid water at 20°C. Estimate the yearly cost of the leaks based on 24 h/day, 360 day/yr operation.

7.39. A turbine discharges 200 kg/h of saturated steam at 10.0 bar absolute. It is desired to generate steam at 250°C and 10.0 bar by mixing the turbine discharge with a second stream of superheated steam of 300°C and 10.0 bar.
(a) If 300 kg/h of the product steam is to be generated, how much heat must be added to the mixer?
(b) If instead the mixing is carried out adiabatically, at what rate is the product steam generated?

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valve

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7.40. Liquid water at 60 bar and 250°C passes through an adiabatic expansion valve, emerging at a pressure P_f and temperature T_f. If P_f is low enough, some of the liquid evaporates.
(a) If $P_f = 1.0$ bar, determine the temperature of the final mixture (T_f) and the fraction of the liquid feed that evaporates (y_v) by writing an energy balance about the valve and neglecting $\Delta\dot{E}_k$.
(b) If you took $\Delta\dot{E}_k$ into account in Part (a), how would the calculated outlet temperature compare with the value you determined? What about the calculated value of y_v? Explain.
(c) What is the value of P_f above which no evaporation would occur?
(d) Sketch the shapes of plots of T_f versus P_f and y_v versus P_f for 1 bar $\leq P_f \leq$ 60 bar. Briefly explain your reasoning.

7.41. A 10.0-m^3 tank contains steam at 275°C and 15.0 bar. The tank and its contents are cooled until the pressure drops to 1.8 bar. Some of the steam condenses in the process.
(a) How much heat was transferred from the tank?
(b) What is the final temperature of the tank contents?
(c) How much steam condensed (kg)?

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valve

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7.42. Jets of high-speed steam are used in spray cleaning. Steam at 15.0 bar with 150°C of superheat is fed to a well-insulated valve at a rate of 1.00 kg/s. As the steam passes through the valve, its pressure drops to 1.0 bar. The outlet stream may be totally vapor or a mixture of vapor and liquid. Kinetic and potential energy changes may be neglected.
(a) Draw and label a flowchart, assuming that both liquid and vapor emerge from the valve.
(b) Write an energy balance and use it to determine the total rate of flow of enthalpy in the outlet stream ($\dot{H}_{out} = \dot{m}_l\hat{H}_l + \dot{m}_v\hat{H}_v$). Then determine whether the outlet stream is in fact a mixture of liquid and vapor or whether it is pure vapor. Explain your reasoning.

(c) What is the temperature of the outlet stream?

(d) Assuming that your answers to Parts (b) and (c) are correct and that the pipes at the inlet and outlet of the valve have the same inner diameter, would $\Delta\dot{E}_k$ across the valve be positive, negative, or zero? Explain your answer. (*Note:* You don't have to calculate the kinetic energies at the inlet and outlet to solve this problem, although you can if you have extra time on your hands.)

Equipment Encyclopedia
refrigeration, condenser, compressor
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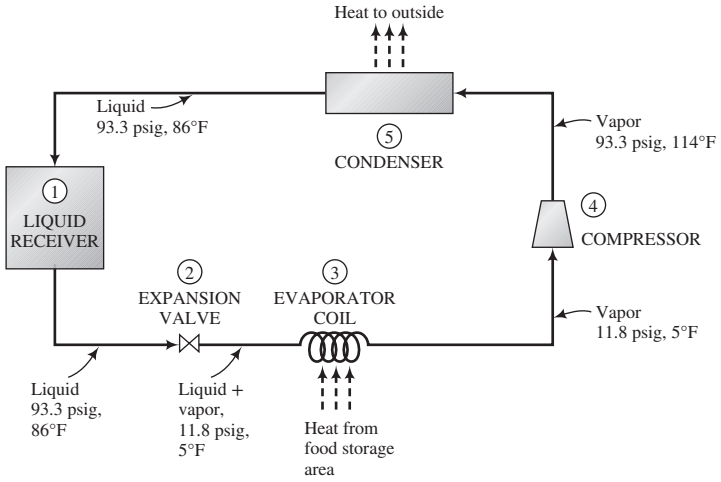
7.43. The following diagram shows a simplified version of how a refrigerator works:



In a **liquid receiver** (1), a liquid refrigerant (any one of a number of halogenated hydrocarbons such as CCl_2F_2) is contained at high pressure and temperature. The liquid passes through an **expansion valve** (2), where it flashes to a low pressure, cooling to its boiling point at this pressure and partially evaporating. The liquid–vapor mixture passes though an **evaporator coil** (3). Air from the food storage area circulates over the coil, and the heat absorbed by the evaporating refrigerant in the coil causes the air to cool. The cold refrigerant vapor emerging from the coil passes to a **compressor** (4), where it is brought back to a high pressure and in the process is raised to a high temperature. The hot vapor then passes through a **condenser** (5), where it is cooled and condensed at constant pressure. The air that absorbs the heat given up by the condensing fluid is discharged outside the refrigerator, and the liquefied refrigerant returns to the liquid receiver.

Suppose Refrigerant R-12 (the standard name for CCl_2F_2) undergoes this cycle at a circulation rate of 40 lb_m/min, with the temperatures and pressures at the different points of the cycle being those shown on the flow diagram. Thermodynamic data for Refrigerant R-12 are as follows:

Saturated Fluid: $T = 5°F, \hat{H}_l = 9.6\ \text{Btu/lb}_m, \hat{H}_v = 77.8\ \text{Btu/lb}_m$

$T = 86°F, \hat{H}_l = 27.8\ \text{Btu/lb}_m, \hat{H}_v = 85.8\ \text{Btu/lb}_m$

Superheated Vapor: $T = 114°F, P = 93.3\ \text{psig}, \hat{H}_v \simeq 90\ \text{Btu/lb}_m$

(a) Suppose the expansion valve operates adiabatically and $\Delta\dot{E}_k$ is negligible. Use an energy balance about the valve to calculate the fraction of the refrigerant that evaporates in this stage of the process.

(b) Calculate the rate in Btu/min at which heat is transferred to the refrigerant that evaporates in the coil. (This is the useful cooling done in the system.)

(c) If the heat loss in the condenser is 2500 Btu/min, how much horsepower must the compressor deliver to the system? (Use an overall energy balance to solve this problem.)

(d) You have just given a "What do engineers do?" talk at a middle-school career day, and one of the students in the audience asks if you can explain how a refrigerator works. Try to do it in terms that a bright 12-year-old student could understand.

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(e) The manufacture of R-12 in the United States was banned as a result of the Montreal Protocol. Why?

7.44. Three hundred L/h of a 20 mole% C_3H_8–80% n-C_4H_{10} gas mixture at 0°C and 1.1 atm and 200 L/h of a 40 mole% C_3H_8–60% n-C_4H_{10} mixture at 25°C and 1.1 atm are mixed and heated to 227°C at constant pressure. Enthalpies of propane and n-butane are listed below. Assume ideal-gas behavior.

T(°C)	Propane $\hat{H}$(J/mol)	Butane $\hat{H}$(J/mol)
0	0	0
25	1772	2394
227	20,685	27,442

(a) Calculate the heat requirement in kJ/h. (See Example 7.6-2.)
(b) Where in your calculations did you use the ideal-gas assumption?

7.45. Air at 38°C and 97% relative humidity is to be cooled to 14°C and fed into a plant area at a rate of 510 m^3/min.
(a) Calculate the rate (kg/min) at which water condenses.
(b) Calculate the cooling requirement in tons (1 ton of cooling = 12,000 Btu/h), assuming that the enthalpy of water vapor is that of saturated steam at the same temperature and the enthalpy of dry air is given by the expression

$$\hat{H}(\text{kJ/mol}) = 0.0291[T(°\text{C}) - 25]$$

Equipment Encyclopedia
distillation column

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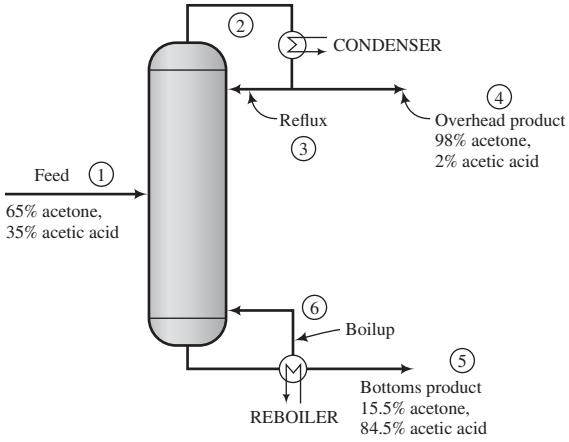
7.46. A mixture containing 65.0 mole% acetone (Ac) and the balance acetic acid (AA) is separated in a continuous distillation column at 1 atm. A flowchart for the operation is as follows:



The stream from the top of the column is a vapor that passes though a condenser. The condensed liquid is divided into two equal streams: one is taken off as the overhead product (distillate) and the other (the *reflux*) is returned to the column. The stream from the bottom of the column is a liquid that is partially vaporized in a reboiler. The liquid stream emerging from the reboiler is taken off as the bottoms product, and the vapor is returned to the column as *boilup*. Negligible heat is lost from the column, so that the only places in the system where external heat transfer takes place are the condenser and the reboiler.

Stream Data

Feed (1)	Liquid, 67.5°C, 65 mole% Ac, 35% AA
Stream (2)	Vapor, 63.0°C, 98 mole% Ac, 2% AA
Reflux (3)	Liquid, 56.8°C, 98 mole% Ac, 2% AA
Distillate (4)	
Bottoms (5)	Liquid, 98.7°C, 15.5 mole% Ac, 84.5% AA
Boilup (6)	Vapor, 98.7°C, 54.4 mole% Ac, 45.6% AA

Thermodynamic Data

	$\hat{H}$(cal/mol)			
	Acetone		*Acetic Acid*	
T(°C)	$\hat{H}_l$	$\hat{H}_v$	$\hat{H}_l$	$\hat{H}_v$
56.8	0	7205	0	5723
63.0	205	7322	194	6807
67.5	354	7403	335	6884
98.7	1385	7946	1312	7420

(a) Taking 100 mol of feed as a basis, calculate the net heat requirement (cal) for the process. (You may neglect heats of mixing, although doing so for dissimilar liquids like acetone and acetic acid may introduce some error.)
(b) For the same basis, calculate the required heat input to the reboiler and the required heat removal from the condenser.
(c) Suppose that instead of the condensed liquid from the top of column being split into two equal streams to form the reflux and the overhead product, it is split into two streams, with the reflux being 3 times the overhead product. As before, take a basis of 100 mol of feed and determine the net heating requirements (cal) for the process and the heat removed in the condenser and added in the reboiler.

7.47. Superheated steam at T_1(°C) and 20.0 bar is blended with saturated steam at T_2(°C) and 10.0 bar in a ratio (1.96 kg of steam at 20 bar)/(1.0 kg of steam at 10 bar). The product stream is at 250°C and 10.0 bar. The process operates at steady state.
(a) Calculate T_1 and T_2, assuming that the blender operates adiabatically.
(b) If in fact heat is being lost from the blender to the surroundings, is your estimate of T_1 too high or too low? Briefly explain.

SAFETY

7.48. A 200.0-liter water tank can withstand pressures up to 20.0 bar absolute before rupturing. At a particular time the tank contains 165.0 kg of liquid water, the fill and exit valves are closed, and the absolute pressure in the vapor head space above the liquid (which may be assumed to contain only water vapor) is 3.0 bar. A plant technician turns on the tank heater, intending to raise the water temperature to 155°C, but is called away and forgets to return and shut off the heater. Let t_1 be the instant the heater is turned on and t_2 the moment before the tank ruptures. Use the steam tables for the following calculations.
(a) Determine the water temperature, the liquid and head-space volumes (L), and the mass of water vapor in the head space (kg) at time t_1.
(b) Determine the water temperature, the liquid and head-space volumes (L), and the mass of water vapor (g) that evaporates between t_1 and t_2. (*Hint:* Make use of the fact that the total mass of water in the tank and the total tank volume both remain constant between t_1 and t_2.)
(c) Calculate the amount of heat (kJ) transferred to the tank contents between t_1 and t_2. Give two reasons why the actual heat input to the tank must have been greater than the calculated value.
(d) List three different factors responsible for the increase in pressure resulting from the transfer of heat to the tank. (*Hint:* One has to do with the effect of temperature on the density of liquid water.)
(e) List ways in which this accident could have been avoided.
(f) One of the suggestions you may have made in Part (e) is to put a relief valve on the top of the tank. Suppose that one had been installed and that it was designed to open when the tank pressure reached 10 bar. The design calls for the opened valve to allow steam to escape into a pipe that vents it to the atmosphere. At what temperature would the valve open? At what rate would the relief valve need to release steam (kg/kJ of added heat) in order to keep the tank pressure from rising above 10 bar?

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steam trap
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7.49. A wet steam at 20 bar with a quality of 0.97 (see Problem 7.36) leaks through a defective steam trap and expands to a pressure of 1 atm. The process can be considered to take place in two stages: a rapid adiabatic expansion to 1 atm accompanied by complete evaporation of the liquid droplets in the wet steam, followed by cooling at 1 atm to ambient temperature. $\Delta\dot{E}_k$ may be neglected in both stages.

(a) Estimate the temperature of the superheated steam immediately following the rapid adiabatic expansion.

(b) Someone looking at the steam trap would see a clear space just outside the leak and a white plume forming a short distance away. (The same phenomenon can be observed outside the spout of a kettle in which water is boiling.) Explain this observation. What would the temperature be at the point where the plume begins?

7.50. Eight fluid ounces (1 qt = 32 oz) of a beverage in a glass at 18.0°C is to be cooled by adding ice and stirring. The properties of the beverage may be taken to be those of liquid water. The enthalpy of the ice relative to liquid water at the triple point is −348 kJ/kg. Estimate the mass of ice (g) that must melt to bring the liquid temperature to 4°C, neglecting energy losses to the surroundings. (*Note:* For this isobaric batch process, the energy balance reduces to $Q = \Delta H$.)

7.51. A 25-g block of iron at 175°C is dropped into a liter of water in an insulated flask at 20°C and 1 atm. The specific enthalpy of iron is given by the expression $\hat{H}(\text{J/g}) = 17.3T(^\circ\text{C})$.

(a) What reference temperature was used as the basis for the enthalpy formula?

(b) Calculate the final temperature of the flask contents, assuming that the process is adiabatic, negligible evaporation of water occurs, negligible heat is transferred to the flask wall, and the specific enthalpy of liquid water at 1 atm and a given temperature is that of the saturated liquid at the same temperature. (*Note:* For this isobaric batch process, the energy balance reduces to $Q = \Delta H$.)

(c) If some of the water in the flask evaporated on contact with the hot iron, would the final temperature in the flask be greater or less than the value you calculated in Part (b)? Explain your answer.

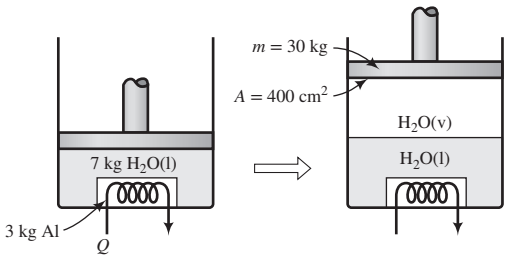
7.52. Horatio Meshuggeneh has his own ideas of how to do things. For instance, when given the task of determining an oven temperature, most people would use a thermometer. Being allergic to doing anything most people would do, however, Meshuggeneh instead performs the following experiment. He puts a copper bar with a mass of 5.0 kg in the oven and puts an identical bar in a well-insulated 20.0-liter vessel containing 5.00 L of liquid water and the remainder saturated steam at 760 mm Hg absolute. He waits long enough for both bars to reach thermal equilibrium with their surroundings, then quickly takes the first bar out of the oven, removes the second bar from the vessel, drops the first bar in its place, covers the vessel tightly, waits for the contents to come to equilibrium, and notes the reading on a pressure gauge built into the vessel. The value he reads is 50.1 mm Hg. He then uses the facts that copper has a specific gravity of 8.92 and a specific internal energy given by the expression $\hat{U}(\text{kJ/kg}) = 0.36T(^\circ\text{C})$ to calculate the oven temperature.

(a) The Meshuggeneh assumption is that the bar can be transferred from the oven to the vessel without any heat being lost. If he makes this assumption, what oven temperature does Meshuggeneh calculate? How many grams of water evaporate in the process? (Neglect the heat transferred to the vessel wall—i.e., assume that the heat lost by the bar is transferred entirely to the water in the vessel. Also, remember that you are dealing with a closed system once the hot bar goes into the vessel.)

(b) In fact, the bar lost 8.3 kJ of heat between the oven and the vessel. What is the true oven temperature?

(c) The experiment just described was actually Meshuggeneh's second attempt. The first time he tried it, the final gauge pressure in the vessel was negative. What had he forgotten to do?

7.53. A perfectly insulated cylinder fitted with a leakproof frictionless piston with a mass of 30.0 kg and a face area of 400.0 cm^2 contains 7.0 kg of liquid water and a 3.0-kg bar of aluminum. The aluminum bar has an electrical coil imbedded in it, so that known amounts of heat can be transferred to it. Aluminum has a specific gravity of 2.70 and a specific internal energy given by the formula $\hat{U}(\text{kJ/kg}) = 0.94T(^\circ\text{C})$. The internal energy of liquid water at any temperature may be taken to be that of the saturated liquid at that temperature. Negligible heat is transferred to the cylinder wall. Atmospheric pressure is 1.00 atm. The cylinder and its contents are initially at 20°C.



Suppose that 3310 kJ is transferred to the bar from the heating coil and the contents of the cylinder are then allowed to equilibrate.

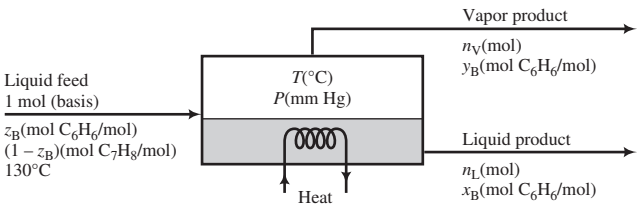
(a) Calculate the pressure of the cylinder contents throughout the process. Then determine whether the amount of heat transferred to the system is sufficient to vaporize any of the water.

(b) Determine the following quantities: (i) the final system temperature; (ii) the volumes (cm^3) of the liquid and vapor phases present at equilibrium; and (iii) the vertical distance traveled by the piston from the beginning to the end of the process. (*Suggestion:* Write an energy balance on the complete process, taking the cylinder contents to be the system. Note that the system is closed and that work is done by the system when it moves the piston through a vertical displacement. The magnitude of this work is $W = P\Delta V$, where P is the constant system pressure and ΔV is the change in system volume from the initial to the final state.)

(c) Calculate an upper limit on the temperature attainable by the aluminum bar during the process, and state the condition that would have to apply for the bar to come close to this temperature.

7.54. A rigid 6.00-liter vessel contains 4.00 L of liquid water in equilibrium with 2.00 L of water vapor at 25°C. Heat is transferred to the water by means of an immersed electrical coil. The volume of the coil is negligible. Use the steam tables to calculate the final temperature and pressure (bar) of the system and the mass of water vaporized (g) if 3915 kJ is added to the water and no heat is transferred from the water to its surroundings. (*Note:* A trial-and-error calculation is required.)

7.55. A liquid mixture of benzene and toluene is to be separated in a continuous single-stage equilibrium flash tank.



The pressure in the unit may be adjusted to any desired value, and the heat input may similarly be adjusted to vary the temperature at which the separation is conducted. The vapor and liquid product streams both emerge at the temperature T(°C) and pressure P(mm Hg) maintained in the vessel.

Assume that the vapor pressures of benzene and toluene are given by the Antoine equation, Table B.4 or APEx; that Raoult's law—Equation 6.4-1—applies; and that the enthalpies of benzene and toluene liquid and vapor are linear functions of temperature. Specific enthalpies at two temperatures are given here for each substance in each phase.

$C_6H_6(l)$	$(T = 0°C, \quad \hat{H} = 0\ kJ/mol)$	$(T = 80°C, \quad \hat{H} = 10.85\ kJ/mol)$
$C_6H_6(v)$	$(T = 80°C, \hat{H} = 41.61\ kJ/mol)$	$(T = 120°C, \hat{H} = 45.79\ kJ/mol)$
$C_7H_8(l)$	$(T = 0°C, \quad \hat{H} = 0\ kJ/mol)$	$(T = 111°C, \hat{H} = 18.58\ kJ/mol)$
$C_7H_8(v)$	$(T = 89°C, \hat{H} = 49.18\ kJ/mol)$	$(T = 111°C, \hat{H} = 52.05\ kJ/mol)$

(a) Suppose the feed is equimolar in benzene and toluene ($z_B = 0.500$). Take a basis of 1 mol of feed and do the degree-of-freedom analysis on the unit to show that if T and P are specified, you can calculate the molar compositions of each phase (x_B and y_B), the moles of the liquid and vapor products (n_L and n_V), and the required heat input (Q). *Don't do any numerical calculations in this part.*

(b) Do the calculations of Part (a) for $T = 90°C$ and $P = 652$ mm Hg. (*Suggestion:* First derive an equation for x_B that can be solved by trial and error from known values of T and P.)

(c) For $z_B = 0.5$ and $T = 90°C$, there is a range of feasible operating pressures for the evaporator, $P_{min} < P < P_{max}$. If the evaporator pressure P fell outside this range, no separation of benzene and toluene would be achieved. Why not? What would emerge from the unit if $P < P_{min}$? What would emerge if $P > P_{max}$? [*Hint:* Look at your solution to Part (b) and think about how it would change if you lowered P.]

(d) Set up a spreadsheet to perform the calculation of Part (b) and then use it to determine P_{max} and P_{min}. The spreadsheet should appear as follows (some solutions are shown):

Problem 7.55—Flash vaporization of benzene and toluene									
zB	T	P	pB*	pT*	xB	yB	nL	nV	Q
0.500	90.0	652	1021				0.5543		8.144
0.500	90.0	714							−6.093
0.500	90.0								

Additional columns may be used to store other calculated variables (e.g., specific enthalpies). Briefly explain why Q is positive when $P = 652$ mm Hg and negative when $P = 714$ mm Hg.

(e) In successive rows, repeat the calculation for the same z_B and T at several pressures between P_{min} and P_{max}. Generate a plot (using the spreadsheet program itself, if possible) of n_V versus P. At approximately what pressure is half of the feed stream vaporized?

7.56. An aqueous solution with a specific gravity of 1.12 flows through a channel with a variable cross section. Data taken at two axial positions in the channel are shown here.

	Point 1	Point 2
P_{gauge}	1.5×10^5 Pa	9.77×10^4 Pa
u	5.00 m/s	?

Point 2 is 6.00 meters higher than point 1.

(a) Neglecting friction, calculate the velocity at point 2. (See Example 7.7-1.)

(b) If the pipe diameter at point 2 is 6.00 cm, what is the diameter at point 1?

*__7.57.__ Your friend has asked you to help move a 60 inch × 78 inch mattress with a mass of 75 lb_m. The two of you position it horizontally in an open flat-bed trailer that you hitch to your car. There is nothing available to tie the mattress to the trailer, but you know there is a risk of the mattress being lifted from the trailer by the air flowing over it and perform the following calculations:

(a) Although the conditions do not exactly match those for which the Bernoulli equation is applicable, use the equation to get a rough estimate of how fast you can drive (miles/h) before the mattress is lifted. Assume the velocity of air above the mattress equals the velocity of the car, the pressure difference between the top and bottom of the mattress equals the weight of the mattress divided by the mattress cross-sectional area, and air has a constant density of 0.075 lb_m/ft^3. What is your result?

(b) You see that your friend also has several boxes of books. Since you would like to drive at 60 miles per hour, what weight of books (lb_f) do you need to put on the mattress to hold it in place?

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differential pressure flowmeters/
venturi tube

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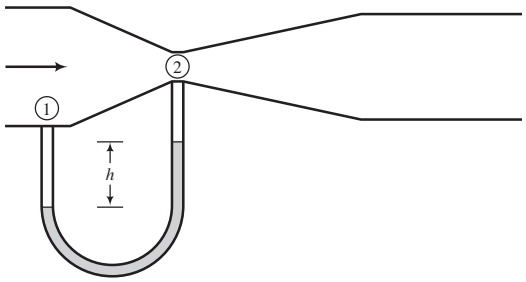
__7.58.__ A **venturi meter** is a device to measure fluid flow rates, which in its operation resembles the orifice meter (Section 3.2b). It consists of a tapered constriction in a line, with pressure taps leading to a differential manometer at points upstream of the constriction and at the point of maximum constriction (the **throat**). The manometer reading is directly related to the flow rate in the line.



* Adapted from a problem contributed by Justin Wood of North Carolina State University.

Suppose the flow rate of an incompressible fluid is to be measured in a venturi meter in which the cross-sectional area at point 1 is four times that at point 2.

(a) Derive the relationship between the velocities u_1 and u_2 at points 1 and 2.

(b) Write the Bernoulli equation for the system between points 1 and 2, and use it to prove that to the extent friction is negligible

$$P_1 - P_2 = \frac{15\,\rho \dot{V}^2}{2A_1^2}$$

where P_1 and P_2 are the pressures at point 1 and 2, ρ and $\dot{V}$ are the density and volumetric flow rate of the flowing fluid, and A_1 is the cross-sectional area of the pipe at point 1.

(c) Suppose this meter is used to measure the flow rate of a stream of acetone, using mercury as the manometer fluid, and a manometer reading $h = 38$ cm is recorded. What is the volumetric flow rate of the acetone if the pipe diameter at point 1 is 15 cm? (Recall the differential manometer equation, Equation 3.4-6.)

7.59. Ethanol is contained in a large tank under a pressure of 3.1 bar absolute. When a valve on the bottom of the tank is opened, the ethanol drains freely though a 1-cm ID tube whose outlet is 7.00 m below the surface of the ethanol. The pressure at the outlet of the discharge pipe is 1 atm.

(a) Use the Bernoulli equation to estimate the ethanol discharge velocity and flow rate in L/min when the discharge valve is fully opened. Neglect the rate of fall of the ethanol level in the tank. (See Example 7.7-2.)

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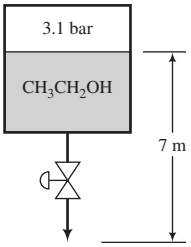
(b) When the discharge valve is partially closed, the flow rate decreases, which means that $\Delta u^2/2$ changes. However, the other two terms in the Bernoulli equation ($\Delta P/\rho$ and $g\Delta z$) remain the same. How do you account for this apparently contradictory result? (*Hint:* Examine the assumptions made in the derivation of the Bernoulli equation.)



7.60. Water is to be pumped from a lake to a ranger station on the side of a mountain (see figure). The length of pipe immersed in the lake is negligible compared to the length from the lake surface to the discharge point. The flow rate is to be 95 gal/min, and the flow channel is a standard 1-inch. Schedule 40 steel pipe (ID = 1.049 inch). A pump capable of delivering 8 hp ($= \dot{W}_s$) is available. The friction loss $\hat{F}$ (ft·lb$_f$/lb$_m$) equals $0.041L$, where L(ft) is the length of the pipe.

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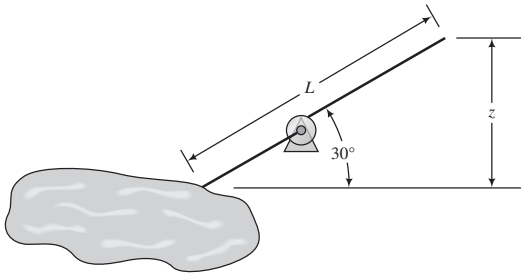
(a) Calculate the maximum elevation, z, of the ranger station above the lake if the pipe rises at an angle of 30°.

(b) Suppose the pipe inlet is immersed to a significantly greater depth below the surface of the lake, but it discharges at the elevation calculated in Part (a). The pressure at the pipe inlet would be greater than it was at the original immersion depth, which means that ΔP from inlet to outlet would be greater, which in turn suggests that a smaller pump would be sufficient to move the water to the same elevation. In fact, however, a larger pump would be needed. Explain (i) why the pressure at the inlet would be greater than in Part (a), and (ii) why a larger pump would be needed.



7.61. Water from a reservoir passes over a dam through a turbine and discharges from a 70-cm ID pipe at a point 55 m below the reservoir surface. The turbine delivers 0.80 MW. Calculate the required flow rate of water in m^3/min if friction is neglected. (See Example 7.7-3.) If friction were included, would a higher or lower flow rate be required? (*Note:* The equation you will solve in this problem has multiple roots. Find a solution less than 2 m^3/s.)

*__7.62.__ Agricultural irrigation uses a significant amount of water, and in some regions it has overwhelmed other water needs. Suppose water is drawn from a reservoir and delivered into an irrigation ditch. For most of the length of the ditch, the delivery is through a 10-cm ID pipe, and in the last few meters the pipe diameter is 7 cm. The exit from the pipe is 300 m lower than the pipe inlet.

(a) Assume that the pipe is smooth (i.e., ignore friction) and that the delivery rate is 4000 kg/h. Estimate the required pressure difference between pipe inlet and outlet. How far below the surface of the reservoir is the pipe inlet?

(b) How would your answer be different if the pipe were not smooth? Explain.

Exploratory Exercise—Research and Discover

ENVIRONMENTAL

(c) What are possible environmental impacts of diverting significant quantities of river water for use in irrigation? Cite at least two sources for your response.

ENVIRONMENTAL

*__7.63.__ Arsenic contamination of aquifers is a major health problem in much of the world and is particularly severe in Bangladesh. One method of removing the arsenic is to pump water from an aquifer to the surface and through a bed packed with granular material containing iron oxide, which binds the arsenic. The purified water is then either used or allowed to seep back through the ground into the aquifer.

In an installation of the type just described, a pump draws 69.1 gallons per minute of contaminated water from an aquifer through a 3-inch ID pipe and then discharges the water through a 2-inch ID pipe to an open overhead tank filled with granular material. The water leaves the end of the discharge line 80 feet above the water in the aquifer. The friction losses in the piping system are 10 $ft \cdot lb_f/lb_m$.

(a) If the pump is 70% efficient (i.e., 30% of the electrical energy delivered to the pump is not used in pumping the water), what is the required pump horsepower?

(b) Even if we assume that the iron oxide binds 100% of the arsenic, what other factors limit the effectiveness of this operation?

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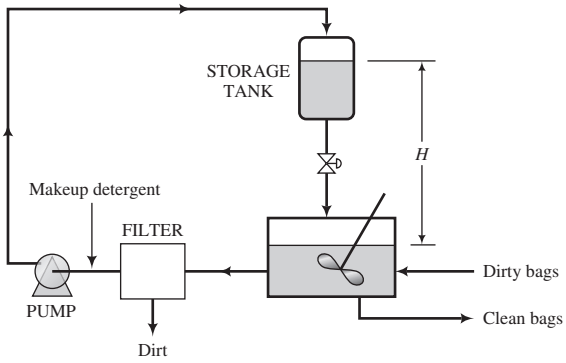
7.64. Cloth bag filters are used to remove particulate matter from the gases passing out through several process and boiler stacks in a large industrial plant. The bags become clogged and must be replaced frequently. Since they are quite expensive, rather than being discarded they are emptied, washed, and reused. In the washing process, a detergent solution with a specific gravity of 0.96 flows from a storage tank to a washing machine. The liquid effluent from the machine is pumped through a filter to remove dirt, and the cleaned detergent is recycled back to the storage tank.

Detergent flows from the storage tank to the washing machine by gravity feed at a rate of 600 L/min. All pipes in the line have 4.0-cm inner diameters. Friction losses are negligible in the line from the tank to the washing machine when the valve is fully opened, and $\hat{F} = 72$ J/kg in the return line, which includes the pump and filter.

(a) Calculate the value of the height H (see figure on the following page) required to provide the desired flow rate of detergent into the washing machine when the valve is fully opened.

(b) Suppose the pump has an efficiency of 75%; that is, it delivers 75% of its rated value as shaft work. What must the rated value (kW) of the pump be to return 600 L/min of detergent to the storage tank?

* Adapted from a problem contributed by James Newell of Rowan University.



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7.65. One thousand liters of a 95 wt% glycerol–5% water solution is to be diluted to 60% glycerol by adding a 35% solution pumped from a large storage tank through a 5-cm ID pipe at a steady rate. The pipe discharges at a point 23 m higher than the liquid surface in the storage tank. The operation is carried out isothermally and takes 13 min to complete. The friction loss ($\hat{F}$ of Equation 7.7-2) is 50 J/kg. Calculate the final solution volume and the shaft work in kW that the pump must deliver, assuming that the surface of the stored solution and the pipe outlet are both at 1 atm.

Data: $\rho_{H_2O} = 1.00$ kg/L, $\rho_{gly} = 1.26$ kg/L. (Use to estimate solution densities.)

CHAPTER 8

Balances on Nonreactive Processes

We have seen that for an open system in which shaft work and kinetic and potential energy changes can be neglected, the energy balance reduces to

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} \\ &= \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i\end{aligned}$$

where the $\hat{H}_i$ values are the specific enthalpies of the inlet and outlet stream components at their respective process conditions (temperatures, pressures, and states of aggregation) relative to those components at some reference conditions. For an integral balance on a closed constant-volume system ($W = 0$), the energy balance is

$$\begin{aligned}Q &= \Delta U \\ &= \sum_{\text{final}} n_i \hat{U}_i - \sum_{\text{initial}} n_i \hat{U}_i\end{aligned}$$

where the $\hat{U}_i$ values are specific internal energies.

In Chapter 7, we dealt only with processes involving species for which specific enthalpies and internal energies at specified conditions could be found in tables. Unfortunately, you cannot count on finding such data for every species with which you work. This chapter presents procedures for evaluating $\Delta\dot{H}$ or ΔU when tables of $\hat{H}$ and $\hat{U}$ are not available for all process species. Once these calculations have been performed, the energy balance may be written and solved as before.

8.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- Define both formally (in terms of internal energies and enthalpies) and in words a high school senior could understand the variables $C_v(T)$ (heat capacity at constant volume), $C_p(T)$ (heat capacity at constant pressure), $\Delta\hat{H}_{\text{m}}$ (heat of fusion or heat of melting), $\Delta\hat{H}_{\text{v}}$ (heat of vaporization), standard heats of fusion and vaporization, and $\Delta\hat{H}_{\text{s}}$ (heat of solution or heat of mixing).
- Calculate $\Delta\hat{U}$ and $\Delta\hat{H}$ for the following changes in state of a species, when possible using enthalpies and internal energies, heat capacities, latent heats, and liquid and solid specific gravities tabulated in this text: (a) isothermal changes in pressure, (b) isobaric (constant-pressure) changes in temperature, (c) isothermal isobaric phase changes, and (d) isothermal isobaric mixing of two or more species. State when the formulas you use for these calculations are exact, good approximations, and poor approximations.
- Given a reference state (phase, temperature, and pressure) and a process state for a species, (a) choose a path from the reference state to the process state consisting of a series of isothermal pressure changes, isobaric temperature changes, and isothermal isobaric phase changes; (b) calculate $\hat{U}$ and $\hat{H}$ for the species at the process state relative to the species at the reference state.
- High school physics and chemistry texts commonly state that the heat (Q) required to raise the temperature of a mass m of a substance by an amount ΔT is $Q = mC_p\Delta T$, where C_p is defined as the heat capacity of the substance. Explain why this formula is only an

approximation. List the assumptions required to obtain it from the closed-system energy balance ($Q + W = \Delta U + \Delta E_k + \Delta E_p$).

- If your class covers Section 8.3e, evaluate

$$\int_{T_1}^{T_2} C_p(T)\, dT$$

using the trapezoidal rule or Simpson's rule (Appendix A.3) from data for C_p at several temperatures between T_1 and T_2.

- Estimate the heat capacity of a liquid or solid species using Kopp's rule. Estimate the heat of fusion and heat of vaporization of a species using correlations in Section 8.4b.
- Given any nonreactive process for which the required heat transfer Q or heat transfer rate $\dot{Q}$ is to be calculated, (a) draw and label the flowchart, including Q or $\dot{Q}$ in the labeling; (b) carry out a degree-of-freedom analysis; (c) write the material and energy balances and other equations you would use to solve for all requested quantities; (d) perform the calculations; and (e) list the assumptions and approximations built into your calculations.
- Given an adiabatic process or any other nonreactive process for which the value of Q (closed system) or $\dot{Q}$ (open system) is specified, write material and energy balances and solve them simultaneously for requested quantities.
- Define the *dry-bulb temperature, wet-bulb temperature,* and *humid volume* of humid air. Given values of any two of the variables plotted on the psychrometric chart (dry-bulb and wet-bulb temperatures, absolute and relative humidity, dew point, humid volume), determine the remaining variable values and the specific enthalpy of the humid air. Use the psychrometric chart to carry out material and energy balance calculations on a heating, cooling, humidification, or dehumidification process involving air and water at 1 atm.
- Explain the meaning of the apparently contradictory term *adiabatic cooling*. Explain how spray cooling and humidification, spray dehumidification, and spray drying work. Explain how it is possible to *de*humidify air by spraying water into it. Use the psychrometric chart to carry out material and energy balance calculations on an adiabatic cooling operation involving air and water at 1 atm.
- Explain to a first-year engineering student why a beaker containing acid gets hot if you add water to it.
- Use the heat of solution data in Table B.11 and solution heat capacity data to (a) calculate the enthalpy of a hydrochloric acid, sulfuric acid, or sodium hydroxide solution of a known composition (solute mole fraction) relative to the pure solute and water at 25°C; (b) calculate the required rate of heat transfer to or from a process in which an aqueous solution of HCl, H_2SO_4, or NaOH is formed, diluted, or combined with another solution of the same species; and (c) calculate the final temperature if an aqueous solution of HCl, H_2SO_4, or NaOH is formed, diluted, or combined with another solution of the same species adiabatically.
- Perform material and energy balance calculations for a process that involves solutions for which enthalpy–concentration charts are available.

8.1 ELEMENTS OF ENERGY BALANCE CALCULATIONS

In this section, we outline a procedure for solving energy balance problems that will be applied to both nonreactive processes (this chapter) and reactive processes (Chapter 9). Section 8.1a reviews the concept of a *reference state* for specific internal energy and enthalpy calculations, and

Section 8.1b reviews the fact that $\hat{U}$ and $\hat{H}$ are state properties, so that the values of ΔU or ΔH (closed system) and $\Delta \dot{H}$ (open system) calculated for a process are independent of the reference states chosen for calculations of $\hat{U}_i$ and $\hat{H}_i$. Section 8.1c outlines a procedure for organizing energy balance calculations and presents an extended illustrative example. The remainder of the chapter presents formulas and methods for calculating ΔU, ΔH, and $\Delta \dot{H}$ for processes that involve heating and cooling, compression and decompression, phase changes, mixing of liquids, and dissolving of gases and solids in liquids.

8.1a Reference States—A Review

Recall that we can never know the absolute values of $\hat{U}$ and $\hat{H}$ for a species at a given state. $\hat{U}$(kJ/mol) is the sum of the energies of motion of all 6.02×10^{23} molecules in one gram-mole of the species plus the intramolecular kinetic and potential energies of all the atoms and subatomic particles, which are quantities we cannot determine. Since $\hat{H} = \hat{U} + P\hat{V}$ and we cannot know the value of $\hat{U}$, we also cannot know the value of $\hat{H}$ at a specified state.

Fortunately, we never need to know the absolute values of $\hat{U}$ or $\hat{H}$ at specified states: we only need to know $\Delta\hat{U}$ and $\Delta\hat{H}$ for specified *changes* of state, and we can determine these quantities experimentally.[1] We may therefore arbitrarily choose a **reference state** for a species and determine $\Delta\hat{U} = \hat{U} - \hat{U}_{\text{ref}}$ for the transition from the reference state to a series of other states. If we set $\hat{U}_{\text{ref}}$ equal to zero, then $\hat{U}(= \Delta\hat{U})$ for a specified state is the *specific internal energy at that state relative to the reference state.* The specific enthalpies at each state can then be calculated from the definition, $\hat{H} = \hat{U} + P\hat{V}$, provided that the specific volume ($\hat{V}$) of the species at the given temperature and pressure is known.

The values of $\hat{U}$ and $\hat{H}$ in the steam tables were generated using this procedure. The reference state was chosen to be liquid water at the triple point [H_2O(l, 0.01°C, 0.00611 bar)], at which point $\hat{U}$ was defined to be zero. According to Table B.7, for water vapor at 400°C and 10.0 bar, $\hat{U} = 2958$ kJ/kg. This does *not* mean that the absolute value of $\hat{U}$ for water in the specified state is 2958 kJ/kg; remember, we cannot know the absolute value of $\hat{U}$. It means that $\hat{U}$ of water vapor at 400°C and 10.0 bar is 2958 kJ/kg *relative to water at the reference state,* or

$$H_2O(\text{l}, 0.01°\text{C}, 0.00611 \text{ bar}) \rightarrow H_2O(\text{v}, 400°\text{C}, 10.0 \text{ bar}), \quad \Delta\hat{U} = 2958 \text{ kJ/kg}$$

Relative to water at the same reference state, the specific enthalpy of water vapor at 400°C and 10.0 bar is

$$\begin{aligned}\hat{H} &= \hat{U} + P\hat{V} \\ &= 2958 \text{ kJ/kg} + \frac{10 \text{ bar}}{} \left| \frac{0.307 \text{ m}^3}{\text{kg}} \right| \frac{10^3 \text{ L}}{1 \text{ m}^3} \left| \frac{8.314 \times 10^{-3} \text{ kJ/(mol·K)}}{0.08314 \text{ L·bar/(mol·K)}} \right. \\ &= 3264 \text{ kJ/kg}\end{aligned}$$

The quantities 8.314×10^{-3} and 0.08314 are values of the gas constant R expressed in different units (see inside back cover).

Test Yourself

(Answers, p. 658)

Suppose water vapor at 300°C and 5 bar is chosen as a reference state at which $\hat{H}$ is defined to be zero. Relative to this state, what is the specific enthalpy of liquid water at 75°C and 1 bar? What is the specific internal energy of liquid water at 75°C and 1 bar? (Use Table B.7.)

[1] The method is to transfer a measured amount of energy, Q, to a known mass of a species, m, in a closed system under conditions such that $W = 0$, $\Delta E_k = 0$, and $\Delta E_p = 0$; measure any changes in temperature, pressure, and phase; and calculate $\Delta\hat{U}$ corresponding to these changes from the energy balance, $Q = m\Delta\hat{U}$.

8.1b Hypothetical Process Paths

In Chapter 7, we observed that $\hat{U}$ and $\hat{H}$ are **state properties** of a species: that is, their values depend only on the state of the species—primarily on its temperature and state of aggregation (solid, liquid, or gas) and, to a lesser extent, on its pressure (and for mixtures of some species, on its mole fraction in the mixture). A state property does not depend on how the species reached its state. Consequently, *when a species passes from one state to another, both* $\Delta\hat{U}$ *and* $\Delta\hat{H}$ *for the process are independent of the path taken from the first state to the second one.*

In most of this chapter and in Chapter 9, you will learn how to calculate internal energy and enthalpy changes associated with certain processes: specifically,

1. ***Changes in P at constant T and state of aggregation*** (Section 8.2).
2. ***Changes in T at constant P and state of aggregation*** (Section 8.3).
3. ***Phase changes at constant T and P***—melting, solidifying, vaporizing, condensing, sublimating (Section 8.4).
4. ***Mixing of two liquids or dissolving of a gas or a solid in a liquid at constant T and P*** (Section 8.5).
5. ***Chemical reaction at constant T and P*** (Chapter 9).

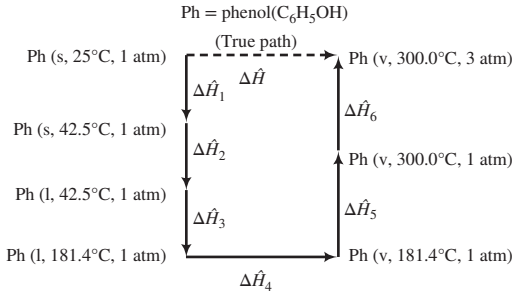
For example, compressing hydrogen gas from 1 atm to 300 atm at 25°C is a Type 1 process; melting ice at 0°C and then heating the liquid water to 30°C, all at 1 atm, is a Type 3 process followed by a Type 2 process; mixing sulfuric acid and water at a constant temperature of 20°C and a constant pressure of 1 atm is a Type 4 process.

Once we know how to calculate $\Delta\hat{U}$ and $\Delta\hat{H}$ for these five types of processes, we can calculate these quantities for *any* process by taking advantage of the fact that $\hat{U}$ and $\hat{H}$ are state properties. The procedure is to construct a hypothetical **process path** from the initial state to the final state consisting of a series of steps of the given five types. Having done this, we calculate $\Delta\hat{H}$ for each of the steps, and then add the $\Delta\hat{H}$'s for the steps to calculate $\Delta\hat{H}$ for the total process. *Since* $\hat{H}$ *is a state property,* $\Delta\hat{H}$ *calculated for the hypothetical process path—which we constructed for convenience—is the same as* $\Delta\hat{H}$ *for the path actually followed by the process.* The same procedure can be followed to calculate $\Delta\hat{U}$ for any process.

Suppose, for example, that we wish to calculate $\Delta\hat{H}$ for a process in which solid phenol at 25°C and 1 atm is converted to phenol vapor at 300°C and 3 atm. If we had a table of enthalpies for phenol, we could simply subtract $\hat{H}$ at the initial state from $\hat{H}$ at the final state, or

$$\Delta\hat{H} = \hat{H}(\text{vapor}, 300°\text{C}, 3\text{ atm}) - \hat{H}(\text{solid}, 25°\text{C}, 1\text{ atm})$$

However, we do not have such a table. Our task is then to construct a hypothetical process path from the solid at 25°C and 1 atm to the vapor at 300°C and 3 atm. To do so, we will look ahead a bit and note that Table B.1 gives enthalpy changes for the melting of phenol at 1 atm and 42.5°C (the normal melting point of phenol) and for the vaporization of phenol at 1 atm and 181.4°C (the normal boiling point of phenol). We therefore choose the following hypothetical process path:



Notice that in this path, the first, third, and fifth steps are Type 2 (change in T at constant P), the second and fourth steps are Type 3 (change in phase at constant T and P), and the sixth step is Type 1 (change in P at constant T). Also notice that the phase changes were made to occur at the conditions for which tabulated enthalpy changes are available.

The next step in the calculation would be to determine the values of $\Delta\hat{H}$ for Steps 1, 3, 5, and 6 using methods to be given in Section 8.2; read the values of $\Delta\hat{H}_2$ and $\Delta\hat{H}_4$ from Table B.1; and then use the fact that enthalpy is a state property to calculate the desired $\Delta\hat{H}$ ($\Delta\hat{H}$ for the upper dashed line in the figure) as

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 + \Delta\hat{H}_4 + \Delta\hat{H}_5 + \Delta\hat{H}_6$$

Test Yourself

(Answers, p. 658)

Construct a process path for each of the following processes consisting of sequential steps of the five types listed in the preceding section. (An illustrative solution is given for the first process.)

1. Nitrogen at 20°C and 200 mm Hg is heated and compressed to 140°C and 40 atm. (One of an infinite number of possible solutions: Heat at 200 mm Hg from 20°C to 140°C, then compress isothermally from 200 mm Hg to 40 atm.)
2. Cyclohexane vapor at 180°C and 5 atm is cooled and condensed to liquid cyclohexane at 25°C and 5 atm. The enthalpy change for the condensation of cyclohexane at 80.7°C and 1 atm is known.
3. Water at 30°C and 1 atm and NaOH at 25°C and 1 atm are mixed to form an aqueous NaOH solution at 50°C and 1 atm. The enthalpy change for the dissolution of NaOH in water at 25°C and 1 atm is known.
4. O_2 at 170°C and 1 atm and CH_4 at 25°C and 1 atm are mixed and react completely to form CO_2 and H_2O at 300°C and 1 atm. The enthalpy change for the reaction occurring at 25°C and 1 atm is known.

8.1c Procedure for Energy Balance Calculations

Most of the problems at the end of this chapter and Chapter 9 look very much like the problems in Chapters 4 to 6: given values of some process variables (feed and product stream temperatures, pressures, phases, amounts or flow rates, and component mole fractions), calculate values of other process variables. Starting in this chapter, you will also be asked to calculate the heat transferred to or from the process system (one additional variable), which will require writing and solving an energy balance (one additional equation).

Here is the procedure to follow for the energy balance calculation.

1. ***Perform all required material balance calculations.***
2. ***Write the appropriate form of the energy balance (closed or open system) and delete any of the terms that are either zero or negligible for the given process system.*** For a stationary closed system, drop ΔE_k and ΔE_p, and neglect W if the system volume is constant, there are no moving parts (such as a mixing impeller in a stirred tank), and no energy is transferred to or from the system by electricity or radiation. For an open system at steady state, drop $\Delta\dot{E}_p$ if there is no appreciable vertical separation between the inlet and outlet ports, and drop $\dot{W}_s$ if there are no moving parts (such as a pump or turbine impeller) and no energy is transferred by electricity or radiation. In addition, if temperature changes of more than a few degrees, phase changes, or chemical reactions occur in the process, $\Delta\dot{E}_k$ usually is negligible compared to $\Delta\dot{U}$ and $\Delta\dot{H}$ and so may be deleted from the equation.
3. ***Choose a reference state—phase, temperature, and pressure—for each species involved in the process.*** If $\hat{H}$ or $\hat{U}$ for a species will be looked up in a table (such as the steam tables for

water), choose the reference state used to generate the table; otherwise, choose one of the inlet or outlet states as the reference state for the species (so that at least one $\hat{H}$ or $\hat{U}$ may be set equal to zero).

4. ***For a closed constant-volume system, construct a table with columns for initial and final amounts of each species (m_i or n_i) and specific internal energies relative to the chosen reference states ($\hat{U}_i$).***[2] ***For an open system, construct a table with columns for inlet and outlet stream component flow rates ($\dot{m}_i$ or $\dot{n}_i$) and specific enthalpies relative to the chosen reference states ($\hat{H}_i$).*** Insert known values of the amounts or flow rates and the specific internal energies and enthalpies, and insert labels for the entries that must be calculated (e.g., $\hat{H}_1, \hat{H}_2, \ldots$). The next example illustrates the construction of such a table.

5. ***Calculate all required values of $\hat{U}_i$ (or $\hat{H}_i$) and insert the values in the appropriate places in the table.*** To perform the calculation for a species in a particular state (inlet or outlet), choose any convenient path from the reference state to the process state and determine $\hat{U}_i$ ($\hat{H}_i$) as $\Delta\hat{U}$ ($\Delta\hat{H}$) for that path. Sections 8.2–8.5 outline these calculations for different types of processes.

6. ***Calculate***

$$\textit{Closed System:} \qquad \Delta U = \sum_{\text{final}} n_i \hat{U}_i - \sum_{\text{initial}} n_i \hat{U}_i \quad \text{or} \quad \sum_{\text{out}} \dot{m}_i \hat{U}_i - \sum_{\text{in}} \dot{m}_i \hat{U}_i$$

$$\textit{Open System:} \qquad \Delta \dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i \quad \text{or} \quad \sum_{\text{out}} \dot{m}_i \hat{H}_i - \sum_{\text{in}} \dot{m}_i \hat{H}_i$$

7. ***Calculate any work, kinetic energy, or potential energy terms that you have not dropped from the energy balance.***

8. ***Solve the energy balance for whichever variable is unknown (often Q or $\dot{Q}$).***

$$\textit{Closed System:} \qquad Q + W = \Delta U + \Delta E_k + \Delta E_p$$

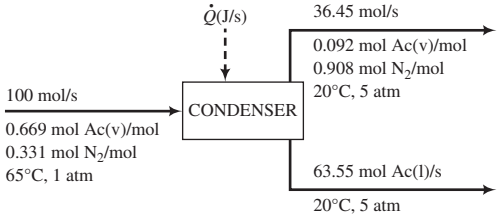
$$\textit{Open System:} \qquad \dot{Q} + \dot{W}_s = \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p$$

The complete procedure for an open system is illustrated in the next example. We encourage you to take the time to follow each step, even though some parts may not be completely clear until you get to material that comes later in the chapter. The better you understand this example, the easier it will be for you to understand the rest of the chapter and to solve the end-of-chapter problems.

Example 8.1-1 Energy Balance on a Condenser

Equipment Encyclopedia
condenser
@
www.wiley.com/college/felder

Acetone (denoted as Ac) is partially condensed out of a gas stream containing 66.9 mole% acetone vapor and the balance nitrogen. Process specifications and material balance calculations lead to the flowchart shown below.



The process operates at steady state. Calculate the required cooling rate.

[2] Use $\hat{H}_i$ instead of $\hat{U}_i$ for a closed constant-pressure system, since $Q = \Delta H$ for such systems.

Solution We will follow the procedure given preceding this example.

1. ***Perform required material balance calculations.*** None are required in this example.
2. ***Write and simplify the energy balance.***

   For this open steady-state system, $\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$. There are no moving parts in the system and no energy is transferred by electricity or radiation, so $\dot{W}_s = 0$. No significant vertical distance separates the inlet and outlet ports, so $\Delta\dot{E}_p \approx 0$. Phase changes and nonnegligible temperature changes occur, so $\Delta\dot{E}_k \approx 0$ (relative to $\Delta\dot{H}$). The energy balance reduces to

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i$$

3. ***Choose reference states for acetone and nitrogen.***

   The reference states may be chosen for computational convenience, since the choice has no effect on the calculated value of $\Delta\dot{H}$. We will arbitrarily choose the inlet stream condition for nitrogen (65°C, 1 atm) as the reference state for this species and one of the two outlet stream conditions for acetone (l, 20°C, 5 atm) as the reference state for acetone, which will enable us to set the corresponding values for $\hat{H}$ in the enthalpy table equal to zero instead of having to calculate them.
4. ***Construct an inlet—outlet enthalpy table.***

   We first write the chosen reference states, then construct the table shown below:

   References: Ac(l, 20°C, 5 atm), N_2(g, 65°C, 1 atm)

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
Ac(v)	66.9	$\hat{H}_1$	3.35	$\hat{H}_2$
Ac(l)	—	—	63.55	0
N_2	33.1	0	33.1	$\hat{H}_3$

   Note the following points about the table:

   - Nitrogen has only one inlet state (gas, 65°C, 1 atm) and one outlet state (gas, 20°C, 5 atm), so we need only one row in the table for N_2. Acetone has one inlet state (vapor, 65°C, 1 atm) but two outlet states (vapor and liquid, each at 20°C and 5 atm), so we need two rows for this species.
   - We mark out (using dashes) the two cells corresponding to $\dot{n}_{in}$ and $\hat{H}_{in}$ for liquid acetone, since no liquid acetone enters the system.
   - The $\dot{n}$ values are obtained from the flowchart. The flow rate of acetone vapor at the inlet, for example, is determined as (100 mol/s)[0.669 mol Ac(v)/mol] = 66.9 mol Ac(v)/s.
   - Since the nitrogen entering the system and the liquid acetone leaving the system area are at their reference states, we set their specific enthalpies equal to zero.
   - Three unknown specific enthalpies have been labeled and must be determined in Step 5.
5. ***Calculate all unknown specific enthalpies.***

   To calculate the three unknown specific enthalpies in the table, we construct hypothetical process paths from the reference states to the states of the species in the process and evaluate $\Delta\hat{H}$ for each path. This is the part of the calculation you have not yet learned to do. We will show you the calculation of $\hat{H}_1$ to illustrate the method, give the results of the other calculations, and go into detail about the required procedures in Sections 8.2–8.5.

$$\begin{aligned}\hat{H}_1 &= \text{specific enthalpy of Ac(v, 65°C, 1 atm) relative to Ac(l, 20°C, 5 atm)}\\ &= \Delta\hat{H} \text{ for Ac(l, 20°C, 5 atm)} \rightarrow \text{Ac(v, 65°C, 1 atm)}\end{aligned}$$

   When choosing a process path for the determination of $\Delta\hat{H}$, it helps to know that formulas and data are given in this chapter for enthalpy changes corresponding to certain types of processes:

   - Section 8.2 gives the formula $\Delta\hat{H} = \hat{V}\,\Delta P$ for a change in pressure (ΔP) undergone by a liquid or solid with constant specific volume $\hat{V}$. The value of $\hat{V}$ for liquid acetone may be determined as 0.0734 L/mol from the specific gravity (0.791) given in Table B.1.

- Section 8.3 shows that $\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT$ for a change from T_1 to T_2 at constant P. Formulas for $C_p(T)$, the *heat capacity at constant pressure,* are given in Table B.2. The formulas for acetone liquid and vapor are as follows:

$$\text{Ac(l):}\quad C_p\left(\frac{\text{kJ}}{\text{mol}\cdot^\circ\text{C}}\right) = 0.123 + 18.6\times10^{-5}T$$

$$\text{Ac(v):}\quad C_p\left(\frac{\text{kJ}}{\text{mol}\cdot^\circ\text{C}}\right) = 0.07196 + 20.10\times10^{-5}T - 12.78\times10^{-8}T^2 + 34.76\times10^{-12}T^3$$

  where T is in °C.

  A time-saving alternative for evaluating the integral by hand is to use the **APEx function** *Enthalpy("species",T1,T2,[temp. units],[state])*, beginning the cell entry with an equal sign. The function integrates the heat capacity formula in Table B.2 for the specified species from temperature *T1* to temperature *T2* and returns $\Delta\hat{H}$ in kJ/mol. If a temperature unit is not specified as "K," "R," or "F," a unit of "C" is assumed. If the state of the species is not specified as "l," "g," or "c" (for solid), the first entry in Table B.2 is assumed.

  For example, the integrals of the heat capacity of acetone liquid and acetone vapor needed in this example would be calculated using the following formulas:

```
=Enthalpy("acetone",20,56)
=Enthalpy("acetone",56,65,,"g")
```

  Notice that internal arguments that go to their default values, like the temperature unit in the first formula, may be left blank but the commas around them must still be supplied. Default values of arguments at the end, such as the temperature unit and state in the second formula, may be omitted.

- Section 8.4 defines the heat of vaporization $\Delta\hat{H}_v(T_b)$ as $\Delta\hat{H}$ for a change from liquid to vapor at the normal boiling point, T_b. Table B.1 lists T_b for acetone as 56.0°C and $\Delta\hat{H}_v(T_b)$ as 30.2 kJ/mol. Normal boiling points in °C and heats of vaporization at the normal boiling point in kJ/mol can also be retrieved using the APEx functions Tb("species") and Hv("species").

The following process path from the reference state [Ac(l), 20°C, 5 atm] to the process state [Ac(v, 65°C, 1 atm)] enables us to use all this information in the determination of $\hat{H}_1$:[3]

$$\text{Ac(l, 20°C, 5 atm)} \xrightarrow{\Delta\hat{H}_{1a}} \text{Ac(l, 20°C, 1 atm)} \xrightarrow{\Delta\hat{H}_{1b}} \text{Ac(l, 56°C, 1 atm)}$$
$$\xrightarrow{\Delta\hat{H}_{1c}} \text{Ac(v, 56°C, 1 atm)} \xrightarrow{\Delta\hat{H}_{1d}} \text{Ac(v, 65°C, 1 atm)}$$
$$\Downarrow$$
$$\hat{H}_1 = \Delta\hat{H}_{\text{path}}$$
$$= \Delta\hat{H}_{1a} + \Delta\hat{H}_{1b} + \Delta\hat{H}_{1c} + \Delta\hat{H}_{1d}$$
$$= \hat{V}_{\text{Ac(l)}}(1\text{ atm} - 5\text{ atm}) + \int_{20^\circ\text{C}}^{56^\circ\text{C}} (C_p)_{\text{Ac(l)}}\,dT + (\Delta\hat{H}_v)_{\text{Ac}} + \int_{56^\circ\text{C}}^{65^\circ\text{C}} (C_p)_{\text{Ac(v)}}\,dT$$

When we substitute the values of $\hat{V}_{\text{Ac(l)}}$ and $\Delta\hat{H}_v$ and the formulas for $C_p(T)$ into the expression for $\hat{H}_1$ and carry out the necessary unit conversions and integrations, we obtain $\hat{H}_1 = (0.0297 + 4.68 + 30.2 + 0.753)$ kJ/mol = 35.7 kJ/mol.

Proceeding in a similar manner, we obtain the values for $\hat{H}_2$ and $\hat{H}_3$ shown in the following revised enthalpy table:

References: Ac(l, 20°C, 5 atm), N_2(g, 65°C, 1 atm)

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
Ac(v)	66.9	35.7	3.35	32.0
Ac(l)	—	—	63.55	0
N_2	33.1	0	33.1	−1.26

[3] To be completely accurate, we would include a step in which the acetone and nitrogen are mixed since the references are the pure species; however, enthalpy changes when gases are mixed are generally negligible (Section 8.5).

6. ***Calculate $\Delta\dot{H}$.***

$$\begin{aligned}\Delta\dot{H} &= \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i \\ &= (3.35\ \text{mol/s})(32.0\ \text{kJ/mol}) + [(63.55)(0) + (33.1)(-1.26) - (66.9)(35.7) - (33.1)(0)]\ \text{kJ/s} \\ &= -2320\ \text{kJ/s}\end{aligned}$$

The factors in the last equation come directly from the inlet–outlet enthalpy table.

7. ***Calculate nonzero work, kinetic energy, and potential energy terms.***

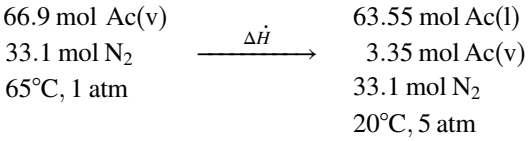
Since there is no shaft work and we are neglecting kinetic and potential energy changes, there is nothing to do in this step.

8. ***Solve the energy balance for $\dot{Q}$.***

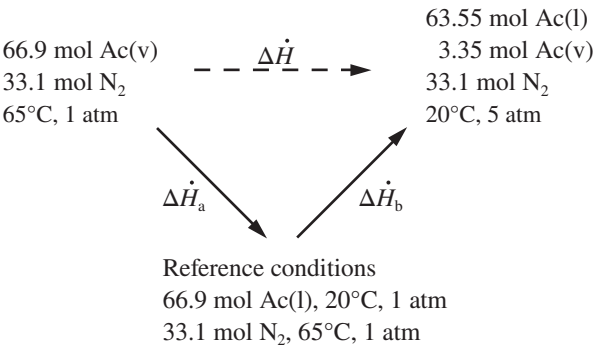
$$\dot{Q} = \Delta\dot{H} = -2320\ \text{kJ/s} = \boxed{-2320\ \text{kW}}$$

Heat must be transferred from the condenser at a rate of 2320 kW to achieve the required cooling and condensation.

Before we leave this section, let us consider what we just did from a different perspective. The process for which we need to calculate $\Delta\dot{H}$ $(= \dot{Q})$ may be depicted as shown below:



To calculate $\Delta\dot{H}$, in effect we constructed the following process path:



The total enthalpy change for the first step, $\Delta\dot{H}_a$, is the negative of $\Delta\dot{H}$ for the process in which acetone and nitrogen go from the reference conditions to the inlet conditions, or

$$\Delta\dot{H}_a = -\sum_{\text{in}} \dot{n}_i\hat{H}_i$$

Similarly, $\Delta\dot{H}_b$ is the enthalpy change for the process in which acetone and nitrogen go from the reference conditions to the outlet conditions, or

$$\Delta\dot{H}_b = \sum_{\text{out}} \dot{n}_i\hat{H}_i$$

Since enthalpy is a state function, the overall enthalpy change for the process must be

$$\Delta\dot{H} = \Delta\dot{H}_a + \Delta\dot{H}_b = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

It remains for us to outline methods for calculating $\Delta\hat{U}$ and $\Delta\hat{H}$ for the different types of processes we have discussed. The methods for the first four (change in P at constant T, change in T at constant P, change in phase at constant T and P, and mixing or dissolving at constant T and P) are outlined in Sections 8.2–8.5 of this chapter, and methods for chemical reactions at constant T and P are given in Chapter 9.

8.2 CHANGES IN PRESSURE AT CONSTANT TEMPERATURE

It has been observed experimentally that internal energy is nearly independent of pressure for solids and liquids at a fixed temperature, as is specific volume. Therefore, *if the pressure of a solid or liquid changes at constant temperature, you may write* $\Delta\hat{U} \approx 0$ *and* $\Delta\hat{H}\ [= \Delta\hat{U} + \Delta(P\hat{V})] \approx \hat{V}\Delta P$.

The specific molar volume ($\hat{V}$) in the formula just given may be calculated from the specific gravity and molecular weight of the solid or liquid species under consideration, but unit conversions typically are needed to make the units of $\hat{V}\Delta P$ consistent with the more common units of terms in energy balances (e.g., kJ/mol). The table for the gas constant on the inside back cover of this text provides useful conversion factors. For example, if you know $\hat{V}$ in L/mol and ΔP in atm, and you want $\hat{V}\Delta P$ in kJ/mol, look for two values of the gas constant with units of L·atm and kJ and use their ratio as a conversion factor. The calculation would look like this:

$$\hat{V}\Delta P\left(\frac{\text{kJ}}{\text{mol}}\right) = \frac{\text{cm}^3 \mid 1\,\text{L} \mid \text{MW(g/mol)} \mid \Delta P\text{(atm)} \mid 8.314\,\text{J/(mol·K)} \mid 1\,\text{kJ}}{\text{SG}\times 1.00\,\text{g} \mid 10^3\,\text{cm}^3 \mid \mid \mid 0.08206\,\text{L·atm/(mol·K)} \mid 10^3\,\text{J}}$$

$$= 1.013\times 10^{-4}\,\frac{(\text{MW})\Delta P}{(\text{SG})} \qquad \textbf{(8.2-1)}$$

Both the specific gravity (SG) and the molecular weight (MW) can be looked up in Table B.1 or retrieved by the APEx functions SG("species") and MW("species").

Both $\hat{U}$ and $\hat{H}$ are independent of pressure for ideal gases. Consequently, *you may generally assume* $\Delta\hat{U} \approx 0$ *and* $\Delta\hat{H} \approx 0$ *for a gas undergoing an isothermal pressure change unless gases at temperatures well below* 0°C *or well above 1 atm are involved.* [If tables of $\hat{U}(T, P)$ or $\hat{H}(T, P)$ *are* available for the gas, there is of course no need to make this assumption.] If gases are far from ideal or if they undergo large pressure changes, you must either use tables of thermodynamic properties (such as the steam tables for water) or thermodynamic correlations beyond the scope of this text to determine $\Delta\hat{U}$ or $\Delta\hat{H}$. A good source for such correlations is Chapter 5 of Poling, Prausnitz, and O'Connell.[4]

In summary, *for changes in pressure at constant temperature*:

$$\begin{aligned} \Delta\hat{U} &= 0 \quad \text{(ideal gases)} \\ &\approx 0 \quad \text{(gases close to ideal, solids and liquids)} \end{aligned} \qquad \textbf{(8.2-2)}$$

$$\begin{aligned} \Delta\hat{H} &= 0 \quad \text{(ideal gases)} \\ &\approx 0 \quad \text{(gases close to ideal)} \\ &\approx \hat{V}\Delta P \quad \text{(solids and liquids)} \end{aligned} \qquad \textbf{(8.2-3)}$$

In the last formula of Equation 8.2-3, $\hat{V}\Delta P$ can be calculated from tabulated specific gravities and molecular weights using Eq. 8.2-1, as long as variables are entered with the appropriate units. Determination of $\Delta\hat{U}$ and $\Delta\hat{H}$ for gases far removed from ideal-gas conditions is beyond the scope of this text.

[4] B. E. Poling, J. H. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th Edition, McGraw-Hill, New York, 2001.

Test Yourself

(Answers, p. 658)

1. Which of the following assumptions appears reasonable for each of the isothermal processes to be described below? (i) $\Delta\hat{U} \approx 0$, $\Delta\hat{H} \approx 0$; (ii) $\Delta\hat{U} \approx 0$, $\Delta\hat{H} \neq 0$; (iii) neither (i) or (ii).
   (a) H_2O (l, 1 atm) $\rightarrow$ H_2O (l, 1200 atm), $T = 25°C$
   (b) N_2 (g, 1 atm) $\rightarrow$ N_2 (g, 1.2 atm), $T = 25°C$
   (c) N_2 (g, 1 atm) $\rightarrow$ N_2 (g, 200 atm), $T = 25°C$
2. Consider the process

$$C_2H_6\,(g, 25°C, 1\text{ atm}) \rightarrow C_2H_6\,(g, 25°C, 30\text{ atm})$$

   How would you use the compressibility charts to determine whether it is reasonable to neglect $\Delta\hat{H}$ for this process?

8.3 CHANGES IN TEMPERATURE

8.3a Sensible Heat and Heat Capacities

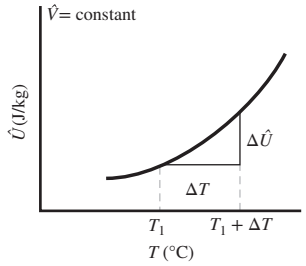
The term **sensible heat** signifies heat that must be transferred to raise or lower the temperature of a substance or mixture of substances. The quantity of heat required to produce a temperature change in a system can be determined from the appropriate form of the first law of thermodynamics:

$$Q = \Delta U \quad \text{(closed system)} \tag{8.3-1}$$

$$\dot{Q} = \Delta\dot{H} \quad \text{(open system)} \tag{8.3-2}$$

(We have neglected kinetic and potential energy changes and work.) To determine the sensible heat requirement for a heating or cooling process, you must therefore be able to determine ΔU or $\Delta\dot{H}$ for the specified temperature change.

The specific internal energy of a substance depends strongly on temperature. If the temperature is raised or lowered in such a way that the system volume remains constant, the specific internal energy might vary as shown in the following plot:



A temperature change ΔT from T_1 leads to a change $\Delta\hat{U}$ in specific internal energy. As $\Delta T \rightarrow 0$, the ratio $\Delta\hat{U}/\Delta T$ approaches a limiting value (i.e., the slope of the curve at T_1), which is by definition the **heat capacity at constant volume** of the substance, denoted by C_v.

$$C_v(T) = \left\{\lim_{\Delta T \rightarrow 0} \frac{\Delta\hat{U}}{\Delta T}\right\} = \left(\frac{\partial\hat{U}}{\partial T}\right)_V \tag{8.3-3}$$

Since the plot of $\hat{U}$ versus T is not generally a straight line, C_v (the slope of the curve) is a function of temperature.

The change in $\hat{U}$ for a temperature rise from T to $T + dT$ at constant volume is from Equation 8.3-3

$$d\hat{U} = C_v(T)\,dT \tag{8.3-4}$$

and the change $\Delta\hat{U} = \hat{U}_2 - \hat{U}_1$ associated with a temperature change from T_1 to T_2 at constant volume is, accordingly,

$$\Delta\hat{U} = \int_{T_1}^{T_2} C_v(T)\,dT \tag{8.3-5}$$

Now, suppose both the temperature and the volume of a substance change. To calculate $\Delta\hat{U}$, you may break the process into two steps—a change in $\hat{V}$ at constant T followed by a change in T at constant $\hat{V}$.

$$A(T_1, \hat{V}_1) \xrightarrow{\Delta\hat{U}_1} A(T_1, \hat{V}_2) \xrightarrow{\Delta\hat{U}_2} A(T_2, \hat{V}_2)$$
$$\downarrow \qquad\qquad\qquad\qquad \uparrow$$
$$\Delta\hat{U}$$

Since $\hat{U}$ is a state property, $\Delta\hat{U}$ (the desired quantity) equals $\Delta\hat{U}_1 + \Delta\hat{U}_2$. But for ideal gases and (to a good approximation) liquids and solids, $\hat{U}$ depends only on T, so that since T is constant in step 1, $\Delta U_1 \approx 0$ for any substance but a nonideal gas. Moreover, since the second step is a change in temperature at constant volume, $\Delta\hat{U}_2$ is given by Equation 8.3-5. In summary, then, for a temperature change from T_1 to T_2

$$\boxed{\Delta\hat{U} \approx \int_{T_1}^{T_2} C_v(T)\,dT}$$

Ideal gas: exact
Solid or liquid: good approximation
Nonideal gas: valid only if V is constant

(8.3-6)

Example 8.3-1 Evaluation of an Internal Energy Change from Tabulated Heat Capacity

Calculate the heat required to raise 200 kg of nitrous oxide from 20°C to 150°C in a constant-volume vessel. The constant-volume heat capacity of N_2O in this temperature range is given by the equation

$$C_v(\text{kJ/kg}\cdot^\circ\text{C}) = 0.855 + 9.42 \times 10^{-4} T$$

where T is in °C.

Solution From Equation 8.3-6,

$$\begin{aligned}\Delta\hat{U}(\text{kJ/kg}) &= \int_{20^\circ\text{C}}^{150^\circ\text{C}} (0.855 + 9.42 \times 10^{-4} T)\left(\frac{\text{kJ}}{\text{kg}\cdot^\circ\text{C}}\right) dT \\ &= 0.855T\Big]_{20^\circ\text{C}}^{150^\circ\text{C}} + \frac{9.42 \times 10^{-4} T^2}{2}\Bigg]_{20^\circ\text{C}}^{150^\circ\text{C}} \\ &= (111 + 10.4)\ \text{kJ/kg} = 121\ \text{kJ/kg}\end{aligned}$$

The energy balance for this closed system neglecting ΔE_k, ΔE_p, and W is

$$Q = \Delta U = m(\text{kg})\,\Delta\hat{U}(\text{kJ/kg}) = (200\ \text{kg})(121\ \text{kJ/kg}) = \boxed{24{,}200\ \text{kJ}}$$

Next, let us suppose that we heat a substance at constant pressure and consider the resulting change in enthalpy. Like internal energy, enthalpy depends strongly on temperature. If $\Delta\hat{H}$ is the change in specific enthalpy resulting from a temperature increase at constant pressure from T to $T + \Delta T$, then as ΔT approaches zero the ratio $\Delta\hat{H}/\Delta T$ approaches a limiting value, defined as the **heat capacity at constant pressure** and denoted by C_p.

$$C_p(T) = \left\{\lim_{\Delta T \to 0} \frac{\Delta\hat{H}}{\Delta T}\right\} = \left(\frac{\partial\hat{H}}{\partial T}\right)_P \tag{8.3-7}$$

Proceeding as before, we observe that the change in $\hat{H}$ for a temperature change at constant pressure from T to $T + dT$ is

$$d\hat{H} = C_p(T)\,dT$$

and so for a change from T_1 to T_2 at constant pressure

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT \tag{8.3-8}$$

For a process $A(T_1, P_1) \rightarrow A(T_2, P_2)$, we may construct a two-step process path

$$\begin{array}{ccccc} A(T_1, P_1) & \xrightarrow{\Delta\hat{H}_1} & A(T_1, P_2) & \xrightarrow{\Delta\hat{H}_2} & A(T_2, P_2) \\ \downarrow & & & & \uparrow \\ & & \Delta\hat{H} & & \end{array}$$

The first step is a change in pressure at constant temperature, the type of process described in Section 8.2. We saw in that section that

$$\begin{aligned} \Delta\hat{H}_1 &= 0 \quad \text{(ideal gas)} \\ &\approx \hat{V}\Delta P \quad \text{(solid or liquid)} \end{aligned} \tag{8.3-9}$$

The second step is a change in temperature at constant pressure, so that $\Delta\hat{H}_2$ is given by Equation 8.3-8. Finally, since $\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2$ (why?), we obtain

$$\boxed{\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT}$$ Ideal gas: exact
Nearly ideal gas: approximate for variable P
Nonideal gas: exact only if P is constant **(8.3-10a)**

$$\boxed{\Delta\hat{H} \approx \hat{V}\Delta P + \int_{T_1}^{T_2} C_p(T)\,dT}$$ Solid or liquid **(8.3-10b)**

For all but large pressure changes and small temperature changes, the first term of Eq. 8.3-10b is usually negligible relative to the second term.

Evaluating $\Delta\hat{H}$ for a nonideal gas undergoing a temperature and pressure change is best done using tabulated enthalpies. If none are available, a thermodynamic relation for variations of $\hat{H}$ with P must be combined with Equation 8.3-8 to determine the enthalpy change; such relations are given by Poling, Prausnitz, and O'Connell (see Footnote 4).

Test Yourself

(Answers, p. 658)

1. By definition, what are C_v and C_p?
2. Suppose the formula

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT$$

is used to calculate the specific enthalpy change for a change in temperature *and pressure* undergone by (a) an ideal gas, (b) a highly nonideal gas, and (c) a liquid. For which of these is the formula exact, and for which is it most likely to lead to significant error?

3. If C_p for an ideal gas is 0.5 cal/(g·°C) (i.e., a constant), what is the enthalpy change in calories corresponding to a change from 10°C to 30°C undergone by five grams of the gas?

CREATIVITY EXERCISE

Your task this time is to estimate the heat capacity of an unknown liquid. You have available a laboratory balance, a very well-insulated container, a sensitive thermometer that can measure liquid temperatures, and a thermocouple that can measure temperatures of solids. The container is a very poor conductor of heat, so that virtually all heat transferred to or from its contents goes entirely into changing the temperature of those contents. If you need anything else (within reason), you can get it. Devise as many ways as you can to estimate C_v, which you may assume is independent of temperature. [*Example:* Mix in the insulated flask a known mass, m_1, of your liquid at temperature T_1, and a known mass, m_2, of hot water at temperature T_2, and measure the final temperature T_f. Since you can calculate the heat lost by water, $Q = m_2 C_{v\mathrm{H_2O}}(T_2 - T_f)$, and you know Q must also equal the heat gained by the other liquid, $m_1 C_v(T_f - T_1)$, you can solve for C_v.]

8.3b Heat Capacity Formulas

The heat capacities C_v and C_p are physical properties of materials and are tabulated in standard references such as *Perry's Chemical Engineers' Handbook*.[5] They may be expressed in any units of energy per unit species amount (mass or moles) per unit temperature interval—for example, J/(mol·K), or Btu/(lb_m·°F). The term **specific heat** is also used for this physical property.

Heat capacities are functions of temperature and are frequently expressed in polynomial form ($C_p = a + bT + cT^2 + dT^3$). Values of the coefficients a, b, c, and d are given in Table B.2 of Appendix B for a number of species at 1 atm, and listings for additional substances are given on pp. 2-156 to 2-180 of *Perry's Chemical Engineers' Handbook*. Heat capacities of solutions and various other substances are given on pp. 2-183 to 2-185.

When reading the coefficients of a heat capacity formula from Table B.2, do not mistake their orders of magnitude: if a value of 72.4 is read from the column labeled $b \cdot 10^5$, then the value of b must be five orders of magnitude *less* than 72.4, or $b = 72.4 \times 10^{-5}$.

Simple relationships exist between C_p and C_v in two cases:

$$\boxed{\textit{Liquids and Solids: } C_p \approx C_v} \qquad \textbf{(8.3-11a)}$$

$$\boxed{\textit{Ideal Gases: } C_p = C_v + R} \qquad \textbf{(8.3-11b)}$$

where R is the gas constant. (Try to prove the second relation.) The relationship between C_p and C_v for nonideal gases is complex and will not be discussed in this text.

You can estimate $\Delta\hat{H}$ or $\Delta\hat{U}$ using Equations 8.2-2, 8.3-10, and 8.3-11 for the heating or cooling of any solid, liquid, or gas (except a gas far from ideal-gas conditions), whether or not the pressure changes. Heat capacity formulas given in Table B.2 may be integrated in these equations, or APEx functions can be used to avoid the integration. The mathematical and APEx formulas are as follows (convince yourself):

Gases:

$$\boxed{\Delta\hat{H}\left(\frac{\mathrm{kJ}}{\mathrm{mol}}\right) \approx \int_{T_1}^{T_2} C_\mathrm{p}(T)\,dT = \text{Enthalpy("Species",T1,T2,"T unit","g")}} \qquad \textbf{(8.3-12a)}$$

$$\boxed{\begin{aligned}\Delta\hat{U}\left(\frac{\mathrm{kJ}}{\mathrm{mol}}\right) &\approx \int_{T_1}^{T_2} C_\mathrm{v}(T)\,dT \approx \int_{T_1}^{T_2} C_\mathrm{p}(T)\,dT - R(T_2 - T_1) \quad \left(R = 8.314 \times 10^{-3}\,\frac{\mathrm{kJ}}{\mathrm{mol \cdot K}}\right) \\ &\approx \text{Enthalpy("Species",T1,T2,"T unit","g") - 8.314e-3*(T2-T1)}\end{aligned}}$$

(8.3-12b)

[5] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008.

Liquids and Solids:

$$\Delta\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right) \approx \hat{V}\Delta P + \int_{T_1}^{T_2} C_{\text{p}}(T)\,dT$$
$$\approx 1.013\text{e-}4^{*}\text{MW}(\text{“species”})^{*}(\text{P2} - \text{P1})/\text{SG}(\text{“species”})$$
$$+ \text{Enthalpy}(\text{“Species”},\text{T1},\text{T2},\text{“T unit”},\text{“state”}) \qquad \textbf{(8.3-12c)}$$

$$\Delta\hat{U}\left(\frac{\text{kJ}}{\text{mol}}\right) \approx \int_{T_1}^{T_2} C_{\text{v}}(T)\,dT \approx \int_{T_1}^{T_2} C_{\text{p}}(T)\,dT$$
$$\approx \text{Enthalpy}(\text{“Species”},\text{T1},\text{T2},\text{“T unit”},\text{“state”}) \qquad \textbf{(8.3-12d)}$$

The APEx formula in Equation 8.3-12c presumes a pressure difference in atmospheres. If pressures are in other units, a pressure conversion factor should be added.

Example 8.3-2 Cooling of an Ideal Gas

Assuming ideal-gas behavior, calculate the heat that must be transferred in each of the following cases.

1. A stream of nitrogen flowing at a rate of 100 mol/min is heated from 20°C to 100°C.
2. Nitrogen contained in a 5-liter flask at an initial pressure of 3 bar is cooled from 90°C to 30°C.

Solution Neglecting kinetic energy changes, the energy balance for the open system of Part 1 is $Q = \Delta H$, and that for the closed system of Part 2 is $Q = \Delta U$. (Show it.) The problem is therefore to evaluate ΔH and ΔU for the two specified processes.

1. From Table B.2, Appendix B, the heat capacity of N_2 at a constant pressure of 1 atm is

$$C_p[\text{kJ/(mol}\cdot\text{°C)}] = 0.02900 + 0.2199\times10^{-5}T + 0.5723\times10^{-8}T^2 - 2.871\times10^{-12}T^3$$

where T is in °C. Since we are assuming ideal-gas behavior, the enthalpy change for the gas is independent of any pressure change that may occur, and hence, from Equation 8.3-10a,

$$\Delta\hat{H} = \int_{20°\text{C}}^{100°\text{C}} C_p(T)\,dT$$
$$\Downarrow$$
$$\Delta\hat{H}(\text{kJ/mol}) = 0.02900T\Big]_{20°\text{C}}^{100°\text{C}} + 0.2199\times10^{-5}\frac{T^2}{2}\Big]_{20°\text{C}}^{100°\text{C}} + 0.5723\times10^{-8}\frac{T^3}{3}\Big]_{20°\text{C}}^{100°\text{C}}$$
$$- 2.871\times10^{-12}\frac{T^4}{4}\Big]_{20°\text{C}}^{100°\text{C}}$$
$$= (2.320 + 0.0106 + 1.9\times10^{-3} - 7\times10^{-5})\ \text{kJ/mol} = 2.332\ \text{kJ/mol}$$

If you were using APEx to perform the preceding calculation, you would simply enter the formula of Equation 8.3-12a

$$=\text{Enthalpy}(\text{“nitrogen”},\ 20,100)\ [\text{or} =\text{Enthalpy}(\text{“nitrogen”},\ 20,100,\text{“C”},\ \text{“g”})]$$

in a spreadsheet cell, and the value 2.332 (in kJ/mol) would be returned. Finally,

$$\dot{Q} = \Delta\dot{H} = \dot{n}\Delta\hat{H}$$
$$= 100\ \frac{\text{mol}}{\text{min}}\left|\ \frac{2.332\ \text{kJ}}{\text{mol}} = \boxed{233\ \text{kJ/min}}\right.$$

2. To evaluate ΔU, we need the number of moles n, which may be calculated using the ideal-gas equation of state, and $\Delta\hat{U}$, which we calculate from Equation 8.3-12b,

$$\Delta\hat{U} \approx \int_{90°C}^{30°C} (C_p)_{N_2} dT - R(30°C - 90°C)$$

Substituting the formula from Table B.2 for the heat capacity and integrating as in Part (1) or entering the APEx formula =Enthalpy("nitrogen",90,30) for the integral, and substituting 8.314×10^{-3} kJ/(mol·K) for R, yields $\Delta\hat{U} = -1.250$ kJ/mol.

Calculate n:
At the initial condition (the only point at which we know P, V, and T)

$$n = PV/RT$$
$$= \frac{(3.00 \text{ bar})(5.00 \text{ L})}{[0.08314 \text{ L·bar/(mol·K)}](363 \text{ K})} = 0.497 \text{ mol}$$

Calculate Q:

$$Q = \Delta U = n\Delta\hat{U}$$
$$= (0.497 \text{ mol})(-1.250 \text{ kJ/mol}) = \boxed{-0.621 \text{ kJ}}$$

When enthalpies must be calculated frequently for a species, it is convenient to prepare a table of $\hat{H}(T)$ for the species (as was done for water in the steam tables) to avoid having to integrate the formula for $C_p(T)$ again and again. Tables B.8 and B.9 in Appendix B list specific enthalpies of species involved in combustion reactions—air, O_2, N_2, H_2 (a fuel), CO, CO_2, and H_2O(v). The values in these tables were generated by integrating $C_p(T)$ from the specified reference state (25°C for Table B.8, 77°F for Table B.9) to the listed temperatures. The next example illustrates the use of these tables.

Example 8.3-3 Evaluation of $\Delta\dot{H}$ Using Heat Capacities and Tabulated Enthalpies

Fifteen kmol/min of air is cooled from 430°C to 100°C. Calculate the required heat removal rate using (1) heat capacity formulas from Table B.2, (2) specific enthalpies from Table B.8, and (3) the Enthalpy function of APEx.

Solution

$$\text{air(g, 430°C)} \rightarrow \text{air(g, 100°C)}$$

With $\Delta\dot{E}_k$, $\Delta\dot{E}_p$, and $\dot{W}_s$ deleted, the energy balance is

$$\dot{Q} = \Delta\dot{H} = \dot{n}_{air}\hat{H}_{air,out} - \dot{n}_{air}\hat{H}_{air,in} = \dot{n}_{air}\Delta\hat{H}$$

Assume ideal-gas behavior, so that pressure changes (if there are any) do not affect $\Delta\hat{H}$.

1. ***The hard way.*** Integrate the heat capacity formula in Table B.2.

$$\Delta\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right) = \int_{430°C}^{100°C} C_p(T)\, dT$$
$$= \int_{430°C}^{100°C} \left[0.02894 + 0.4147 \times 10^{-5}T + 0.3191 \times 10^{-8}T^2 - 1.965 \times 10^{-12}T^3\right] dT$$
$$= \left[0.02894(100 - 430) + \frac{0.4147 \times 10^{-5}}{2}(100^2 - 430^2)\right.$$
$$\left. + \frac{0.3191 \times 10^{-8}}{3}(100^3 - 430^3) - \frac{1.965 \times 10^{-12}}{4}(100^4 - 430^4)\right] \text{ kJ/mol}$$
$$= (-9.5502 - 0.3627 - 0.0835 + 0.0167) \text{ kJ/mol} = -9.98 \text{ kJ/mol}$$

2. ***The easy way.*** Use tabulated enthalpies from Table B.8.

   $\hat{H}$ for air at 100°C can be read directly from Table B.8 and $\hat{H}$ at 430°C can be estimated by linear interpolation from the values at 400°C (11.24 kJ/mol) and 500°C (14.37 kJ/mol).

$$\hat{H}(100°C) = 2.19\ \text{kJ/mol}$$
$$\hat{H}(430°C) = [11.24 + 0.30(14.37 - 11.24)]\ \text{kJ/mol} = 12.17\ \text{kJ/mol}$$
$$\Downarrow$$
$$\Delta\hat{H} = (2.19 - 12.17)\ \text{kJ/mol} = -9.98\ \text{kJ/mol}$$

3. ***The easiest way.*** In a spreadsheet cell, insert =Enthalpy("air",430,100). The value −9.98 (in kJ/mol) will be returned. In using the spreadsheet, it is absolutely essential to keep track of units by adding explicit notation where appropriate; otherwise the probability of getting units wrong increases substantially.

   Whichever way $\Delta\hat{H}$ is determined

$$\dot{Q} = \Delta\dot{H} = \dot{n}\Delta\hat{H} = \frac{15.0\ \text{kmol}}{\text{min}} \left| \frac{10^3\ \text{mol}}{1\ \text{kmol}} \right| \frac{-9.98\ \text{kJ}}{\text{mol}} \left| \frac{1\ \text{min}}{60\ \text{s}} \right| \frac{1\ \text{kW}}{1\ \text{kJ/s}} = \boxed{-2500\ \text{kW}}$$

Reminder: The enthalpies listed in Tables B.8 and B.9 (and for that matter, the heat capacity formulas of Table B.2 and the Enthalpy function of APEx) apply strictly to heating and cooling at a constant pressure of 1 atm. The tabulated enthalpies and heat capacities may also be used for nonisobaric heating and cooling of ideal or nearly ideal gases; however, at pressures high enough (or temperatures low enough) for the gases to be far from ideal, enthalpy tables or more accurate heat capacity formulas should be used.

Test Yourself

(Answers, p. 658)

1. The heat capacity of a species is 28.5 J/(mol·K). Remembering that the temperature unit in the denominator refers to a temperature *interval*, what is the heat capacity of this species in J/(mol·°C)?
2. The gas constant R is approximately equal to 2 cal/(mol·K). If C_p for a vapor is 7 cal/(mol·°C), estimate C_v for the vapor. If C_p for a liquid is 7 cal/(mol·°C), estimate C_v for the liquid.
3. Use Table B.8 or B.9 to calculate the following quantities:
   (a) The specific enthalpy (kJ/mol) of N_2 at 1000°C relative to N_2 at 300°C.
   (b) $\Delta\hat{H}$(kJ/mol) for the process CO_2(g, 800°C, 1 atm) → CO_2(g, 300°C, 1 atm).
   (c) $\Delta\dot{H}$(Btu/h) for 100 lb-mole O_2/h being cooled from 500°F and 1.5 atm to 200°F and 0.75 atm.

8.3c Estimation of Heat Capacities

The polynomial expressions for C_p in Table B.2 are based on experimental data for the listed compounds and provide a basis for reasonably accurate estimations of enthalpy changes. Several rougher approximate methods follow for estimating heat capacities in the absence of tabulated formulas.

Kopp's rule is a simple empirical method for estimating the heat capacity of a solid or liquid at or near 20°C. According to this rule, C_p for a molecular compound is the sum of contributions (given in Table B.10) for each element in the compound. For example, the heat capacity of solid calcium hydroxide, $Ca(OH)_2$, would be estimated from Kopp's rule as

$$(C_p)_{Ca(OH)_2} = (C_{pa})_{Ca} + 2(C_{pa})_O + 2(C_{pa})_H$$
$$= [26 + (2 \times 17) + (2 \times 9.6)]\ \text{J/(mol·°C)} = 79\ \text{J/(mol·°C)}$$

[The true value is 89.5 J/(mol·°C).]

More accurate heat capacity estimation formulas for various types of gases and liquids are given in Chapter 5 of Poling, Prausnitz, and O'Connell (see Footnote 4), and several correlations are presented by Gold and Ogle.[6]

Suppose you wish to calculate the enthalpy change associated with a change in temperature undergone by a mixture of substances. Enthalpies and heat capacities of certain mixtures are tabulated in standard references (e.g., pp. 2-183 and 2-184 of *Perry's Chemical Engineers' Handbook*, Footnote 5). Lacking such data, you may use the following approximation:

Rule 1. *For a mixture of gases or liquids, calculate the total enthalpy change as the sum of the enthalpy changes for the pure mixture components.* You are in effect neglecting enthalpy changes associated with the mixing of the components, which is an excellent approximation for mixtures of gases and for mixtures of similar liquids such as pentane and hexane but a poor one for dissimilar liquids such as nitric acid and water. Enthalpies of mixing for systems of the latter type are discussed in detail in Section 8.5.

Rule 2. *For highly dilute solutions of solids or gases in liquids, neglect the enthalpy change of the solute.* The more dilute the solution, the better this approximation.

The calculation of enthalpy changes for the heating or cooling of a mixture of known composition may often be simplified by calculating a heat capacity for the mixture in the following manner:

$$(C_p)_{\text{mix}}(T) = \sum_{\substack{\text{all} \\ \text{mixture} \\ \text{components}}} y_i C_{pi}(T) \qquad \textbf{(8.3-13)}$$

where

$(C_p)_{\text{mix}}$ = heat capacity of the mixture
y_i = mass or mole fraction of the ith component
C_{pi} = heat capacity of the ith component

If C_{pi} and $(C_p)_{\text{mix}}$ are expressed in molar units, then y_i must be the mole fraction of the ith component, and if the heat capacities are expressed in mass units, then y_i must be the mass fraction of the ith component. Once $(C_p)_{\text{mix}}$ is known, $\Delta\hat{H}$ for a change in temperature from T_1 to T_2 may be calculated as

$$\Delta\hat{H} = \int_{T_1}^{T_2} (C_p)_{\text{mix}}(T)\, dT \qquad \textbf{(8.3-14)}$$

Equation 8.3-14 is valid to the extent that enthalpies of mixing may be neglected.

Example 8.3-4 Heat Capacity of a Mixture

Calculate the heat required to bring 150 mol/h of a stream containing 60% C_2H_6 and 40% C_3H_8 by volume from 0°C to 400°C. Determine a heat capacity for the mixture as part of the problem solution.

Solution Neglecting changes in potential and kinetic energy and recognizing that there is no shaft work involved in the process, the energy balance becomes $\dot{Q} = \Delta\dot{H} = \dot{n}\Delta\hat{H}$ where $\Delta\hat{H} = \int_{0°C}^{400°C} (C_p)_{\text{mix}} dT$. The polynomial expressions for the heat capacity of ethane and propane given in Table B.2 are substituted into Equation 8.3-13 to yield

[6] P. I. Gold and G. J. Ogle, "Estimating Thermochemical Properties of Liquids, Part 7—Heat Capacity," *Chem. Eng.*, Apr. 7, 1969, p. 130.

$$(C_p)_{\text{mix}}[\text{kJ/(mol}\cdot^\circ\text{C)}] = 0.600(0.04937 + 13.92\times10^{-5}T - 5.816\times10^{-8}T^2 + 7.280\times10^{-12}T^3) + 0.400(0.06803 + 22.59\times10^{-5}T - 13.11\times10^{-8}T^2 + 31.71\times10^{-12}T^3)$$

$$= \boxed{0.05683 + 17.39\times10^{-5}T - 8.734\times10^{-8}T^2 + 17.05\times10^{-12}T^3}$$

$$\Delta\hat{H} = \int_{0^\circ\text{C}}^{400^\circ\text{C}} (C_p)_{\text{mix}}\,dT = 34.89\ \text{kJ/mol}$$

If potential and kinetic energy changes and shaft work are neglected, it follows that

$$\dot{Q} = \Delta\dot{H} = \dot{n}\Delta\hat{H} = \frac{150\ \text{mol}}{\text{h}}\left|\frac{34.89\ \text{kJ}}{\text{mol}}\right. = \boxed{5230\ \frac{\text{kJ}}{\text{h}}}$$

As usual, we have assumed that the gases are sufficiently close to ideal for the formulas for C_p at 1 atm to be valid.

Test Yourself

(Answers, p. 658)

1. Estimate the heat capacity of solid calcium carbonate ($CaCO_3$) using Kopp's rule and Table B.10.
2. Two kilograms of liquid *n*-hexane [$C_p = 2.5$ kJ/(kg·°C)] and 1 kg of liquid cyclohexane [$C_p = 1.8$ kJ/(kg·°C)] are mixed and heated from 20°C to 30°C. Use the rule for liquid mixtures (Rule 1) given in this section to show that $\Delta H \approx 68$ kJ for this process. What is $\Delta\hat{H}$(kJ/kg mixture)?
3. A 0.100 wt% aqueous solution of sodium chloride is heated from 25°C to 50°C. Use the rule for solutions (Rule 2) given in this section to estimate $\Delta\hat{H}$(cal/g) for this process. C_p for water is 1 cal/(g·°C).
4. The heat capacity of liquid water is 1 cal/(g·°C), and that of ethanol is 0.54 cal/(g·°C). Estimate the heat capacity of a mixture containing 50% ethanol and 50% water by mass.

8.3d Energy Balances on Single-Phase Systems

We are now in a position to perform energy balances on any processes that do not involve phase changes, mixing steps for which enthalpy changes cannot be neglected, or chemical reactions.

If a process only involves heating or cooling a single species from T_1 to T_2, the procedure is straightforward:

1. Evaluate, $\Delta\hat{U} = \int_{T_1}^{T_2} C_v\,dT$ or $\Delta\hat{H} = \int_{T_1}^{T_2} C_p\,dT$, correcting for pressure changes if necessary.
2. For a closed system at constant volume, calculate $\Delta U = n\Delta\hat{U}$ (where n is the amount of the species being heated or cooled). For a closed system at constant pressure, calculate $\Delta H = n\Delta\hat{H}$. For an open system, calculate $\Delta\dot{H} = \dot{n}\Delta\hat{H}$, where $\dot{n}$ is the species flow rate.
3. Substitute for ΔU, ΔH, or $\Delta\dot{H}$ in the appropriate energy balance equation to determine the required heat transfer, Q, or heat transfer rate, $\dot{Q}$. (See Example 8.3-2.)

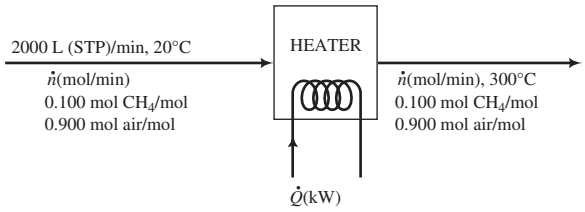
If more than one species is involved or if there are several input or output streams instead of just one of each, the procedure given in Section 8.1 should be followed: choose reference states for each species, prepare and fill in a table of amounts and specific internal energies (closed system) or species flow rates and specific enthalpies (open system), and substitute the calculated values into the energy balance. The next example illustrates the procedure for a continuous heating process.

Example 8.3-5 Energy Balance on a Gas Preheater

A stream containing 10% CH_4 and 90% air by volume is to be heated from 20°C to 300°C. Calculate the required rate of heat input in kilowatts if the flow rate of the gas is 2.00×10^3 liters (STP)/min.

Solution **Basis: Given Flow Rate**

Assume ideal-gas behavior.



Recall that specifying the flow rate in liters (STP)/min does not imply that the feed gas is at standard temperature and pressure; it is simply an alternative way of giving the molar flow rate.

$$\dot{n} = \frac{2000\text{ L (STP)}}{\text{min}} \left| \frac{1\text{ mol}}{22.4\text{ L (STP)}} \right. = 89.3\text{ mol/min}$$

The energy balance with kinetic and potential energy changes and shaft work omitted is $\dot{Q} = \Delta\dot{H}$. The task is to evaluate $\Delta\dot{H} = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$. Since each species has only one inlet condition and one outlet condition in the process, two rows are sufficient for the enthalpy table.

References: CH_4(g, 20°C, 1 atm), air(g, 25°C, 1 atm)

Substance	$\dot{n}_{\text{in}}$ (mol/min)	$\hat{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/min)	$\hat{H}_{\text{out}}$ (kJ/mol)
CH_4	8.93	0	8.93	$\hat{H}_1$
Air	80.4	$\hat{H}_2$	80.4	$\hat{H}_3$

The reference condition for methane was chosen so that $\hat{H}_{\text{in}}$ could be set equal to zero, and that for air was chosen so that $\hat{H}_{\text{in}}$ and $\hat{H}_{\text{out}}$ could be determined directly from Table B.8.

The next step is to evaluate all of the unknown specific enthalpies in the table. $\hat{H}_1$, for example, is the specific enthalpy of methane in the outlet gas mixture at 300°C relative to pure methane at its reference temperature of 20°C. In other words, it is the specific enthalpy change for the process

$$CH_4(\text{g}, 20°\text{C}, 1\text{ atm}) \rightarrow CH_4(\text{g}, 300°\text{C}, P \text{ in outlet mixture})$$

We neglect the effect of pressure on enthalpy (i.e., we assume ideal-gas behavior) and we always neglect heats of mixing of gases, so that the enthalpy change is calculated for the heating of pure methane at 1 atm:

$$\hat{H}_1 = \int_{20°\text{C}}^{300°\text{C}} (C_p)_{CH_4}\, dT$$

$$\Downarrow \text{ Substitute for } C_p \text{ from Table B.2}$$

$$= \int_{20°\text{C}}^{300°\text{C}} (0.03431 + 5.469\times10^{-5}T + 0.3661\times10^{-8}T^2 - 11.0\times10^{-12}T^3)\, dT$$

$$= 12.07\text{ kJ/mol}$$

Alternatively, in APEx enter the formula =Enthalpy("CH4",20,300) into a spreadsheet cell, and the value 12.07 (in kJ/mol) will be returned. The enthalpies of air at the inlet and outlet conditions relative to air at the reference state ($\hat{H}_2$ and $\hat{H}_3$, respectively) are determined from Table B.8 as

$$\hat{H}_2 = -0.15\text{ kJ/mol}, \quad \hat{H}_3 = 8.17\text{ kJ/mol}$$

The energy balance now yields

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i$$
$$= (8.93 \text{ mol/min})(12.09 \text{ kJ/mol}) + [(80.4)(8.17) - (8.93)(0) - (80.4)(-0.15)] \text{ kJ/min}$$
$$\Downarrow$$
$$\dot{Q} = \frac{776 \text{ kJ}}{\text{min}} \left| \frac{1 \text{ min}}{60 \text{ s}} \right| \frac{1 \text{ kW}}{1 \text{ kJ/s}} = \boxed{12.9 \text{ kW}}$$

In the last example the temperatures of all input and output streams were specified, and the only unknown in the energy balance equation was the heat transfer rate required to achieve the specified conditions. You will also encounter problems in which the heat input is known but the temperature of an output stream is not. For these problems, you must evaluate the outlet stream component enthalpies in terms of the unknown T, substitute the resulting expressions in the energy balance equation, and solve for T. Example 8.3-6 illustrates this procedure.

Example 8.3-6 Energy Balance on a Waste-Heat Boiler

ENVIRONMENTAL

Equipment Encyclopedia
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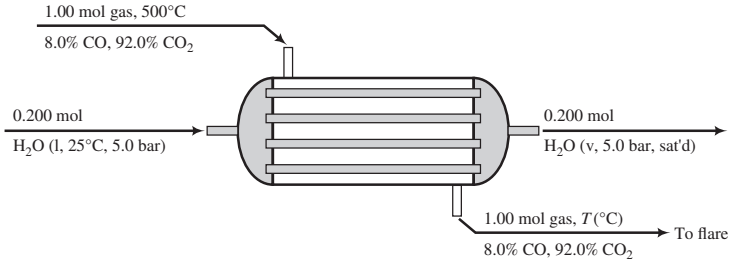
Eliminating discharges of hot streams to the environment has two beneficial effects: the temperature of the receiving entity (e.g., a lake, a river, or the atmosphere) is not raised, which can avoid violating an EPA regulation, and the energy contained in the discharged stream is not wasted by being dissipated in the environment. For example, a gas stream at 500°C containing 8.0 mol% CO and 92.0% CO_2 that was originally going to be sent up a stack is instead sent to a heat exchanger and flows across tubes through which water is flowing. The water enters at 25°C and is fed at a ratio of 0.200 mol water/mol hot gas, is heated to its boiling point, and forms saturated steam at 5.0 bar. The steam may be used for heating or power generation in the plant or as the feed to another process unit. The heat exchanger can be assumed to operate adiabatically—that is, all heat transferred from the hot gas goes to heat the water, as opposed to some of it leaking through the heat exchanger walls to the environment. The flowchart for an assumed basis of 1.00 mol feed gas is shown below. Calculate the temperature of the gas leaving the heat exchanger (a) using data from Tables B.1 and B.2 but not using APEx; (b) using APEx.



Solution Since no material balances are required in this problem, we may proceed directly to the energy balance, which for this adiabatic unit reduces to

$$\Delta H = \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i = 0$$

Note that we do not write $\Delta\dot{H}$ and $\dot{n}_i$ since a quantity (1 mol feed gas) and not a flow rate has been assumed as a basis of calculation.

(*Exercise:* What assumptions have been made in writing the energy balance?)

References: CO(g, 500°C, 1 atm), CO_2(g, 500°C, 1 atm), H_2O(l, triple point)

Substance	n_{in}	$\hat{H}_{\text{in}}$	n_{out}	$\hat{H}_{\text{out}}$
CO	0.080 mol	0 kJ/mol	0.080 mol	$\hat{H}_1$ (kJ/mol)
CO_2	0.920 mol	0 kJ/mol	0.920 mol	$\hat{H}_2$ (kJ/mol)
H_2O	0.00360 kg	$\hat{H}_3$ (kJ/kg)	0.00360 kg	$\hat{H}_4$ (kJ/kg)

The solution strategy will be to calculate $\hat{H}_1(T)$ and $\hat{H}_2(T)$ by integrating the heat capacity formulas of Table B.2 from the reference temperature (500°C) to the unknown T at the gas outlet, look up $\hat{H}_3$ and $\hat{H}_4$ in the steam tables, substitute for $\hat{H}_1$ through $\hat{H}_4$ in the energy balance, and solve the resulting equation for T using a spreadsheet.

Note the following points about the enthalpy table:

- We chose the reference states for CO and CO_2 as the gas inlet temperature and 1 atm. We assume ideal-gas behavior so that deviations of the pressure from 1 atm have no effect on enthalpies, and accordingly set the inlet enthalpies of the gas species equal to zero.
- We will find the enthalpies of the feedwater and product steam in the steam tables. Knowing this, we chose the reference state for the steam tables (liquid water at the triple point) as our reference for water, and knowing that the enthalpies in the steam tables are in kJ/kg, we list the quantity of water in kg ($m = 0.200\ \text{mol}\ H_2O \times 0.0180\ \text{kg/mol} = 0.00360\ \text{kg}$).
- We will integrate the heat capacity formulas of Table B.2 for CO and CO_2 even though enthalpies for those species are listed in Table B.8, since we do not know the temperature at which to look them up.

(a) The specific enthalpies are

$$\hat{H}_1 = \int_{500°C}^{T} (C_p)_{CO}\, dT$$

$$= \int_{500°C}^{T} (0.02895 + 0.4110 \times 10^{-5} T + 0.3548 \times 10^{-8} T^2 - 2.220 \times 10^{-12} T^3)\, dT$$

$$\hat{H}_2 = \int_{500°C}^{T} (C_p)_{CO_2}\, dT$$

$$= \int_{500°C}^{T} (0.03611 + 4.223 \times 10^{-5} T - 2.887 \times 10^{-8} T^2 + 7.464 \times 10^{-12} T^3)\, dT$$

$$\hat{H}_3 = \hat{H}[H_2O(l, 25°C, 5\ \text{bar})] \approx 105\ \text{kJ/kg} \quad \text{(Table B.5: neglect effect of pressure on } \hat{H}\text{)}$$

$$\hat{H}_4 = \hat{H}[H_2O(v, 5\ \text{bar, sat'd})] = 2747.5\ \text{kJ/kg} \quad \text{(Table B.6)}$$

Integrating the expressions for $\hat{H}_1$ and $\hat{H}_2$ and substituting the resulting expressions and the values of $\hat{H}_3$ and $\hat{H}_4$ into the energy balance ($\Delta H = 0$) yields the following equation:

$$1.672 \times 10^{-12} T^4 - 0.8759 \times 10^{-8} T^3 + 1.959 \times 10^{-5} T^2 + 0.03554 T - 12.16 = 0$$

The problem is to find the value of T(°C) that satisfies this equation. The equation can be solved by trial-and-error using any mathematical software program, or using Excel's Solver or Goal Seek. The solution is $\boxed{T = 299°C}$. The heat transferred from the specified quantity of gas as it cools from 500°C to 299°C goes to convert the specified amount of feed water into steam.

(b) Following is a portion of an Excel spreadsheet with the APEx add-on activated. The n values in Columns C and E and the 0s (zeroes) in Column D are entered as numbers, and the T value in Cell C8 is an initial guess at the temperature of the outlet gas. The other values in Columns C through H result from entering the formulas shown on the next page. We strongly recommend that you attempt to replicate the spreadsheet for yourself.

	A	B	C	D	E	F	G	H
1	**Solution to Example 8.3-6b**							
2		**Substance**	**n(in)**	**H(in)**	**n(out)**	**H(out)**	**nH(in)**	**nH(out)**
3		CO	0.08	0	0.08	−12.1852	0	−0.97482
4		CO2	0.92	0	0.92	−18.4467	0	−16.971
5		H2O	0.0036	104.8	0.0036	2547.3	0.37728	9.891
6						Sum->	0.37728	−8.05482
7								
8		T(gas out)	100					
9		Delta H	−8.4321					

Cell Entries

[D5] = SteamSatT(25, "T", "H", "L") [Enthalpy of saturated H_2O(l) at $T = 25°C$]; "T" is the first argument, "H" is the quantity to be provided by the spreadsheet (i.e., enthalpy), "L" is the phase of the water.
[F3] = Enthalpy("CO", 500, C$8) [Integral of $(C_p)_{CO}$ from 500°C to T in Cell C8]
[F4] = Enthalpy("CO2", 500, C$8) [As above for CO_2]
[F5] = SteamSatP(5,"P", "H", "V") [Enthalpy of saturated H_2O(v) at $P = 5$ bar]
[G3] = C3*D3 [H3] = E3*F3
[G4] = C4*D4 [H4] = E4*F4
[G5] = C5*D5 [H5] = E5*F5
[G6] = SUM(G3:G5) [H6] = SUM(H3:H5)
[C9] = H6–G6 [ΔH, which must equal zero when the correct temperature is found]

Once all of the formulas have been entered, open *Solver*; set the target cell to C9 (or $C$9), check "Value of" and enter 0, insert C8 as the cell to be changed, and then click on "Solve." Cell C8 should then contain the solution $\boxed{T = 299°C}$.

8.3e Numerical Integration of Tabulated Heat Capacities

You have now seen two ways to evaluate an expression of the type

$$\int_{T_1}^{T_2} C_p(T)\, dT$$

If a functional relation for $C_p(T)$ is available, such as one of the polynomials of Table B.2, the integration can be carried out analytically; and if tabulated specific enthalpies are available for the substance being heated or cooled, a simple subtraction replaces the integration.

Suppose, however, that the only information you have about C_p is its value at a series of temperatures that span the range from T_1 to T_2. The question is how to estimate the value of the integral from these data.

One way would of course be to plot C_p versus T, draw a curve by visual inspection through the points at which C_p is known, and estimate the integral graphically as the area under the curve from T_1 to T_2. This is a cumbersome procedure, however, even if you have access to a *planimeter*, a device that can calculate the area under a traced-out curve.

A better solution is to use one of the many existing **quadrature formulas**—algebraic expressions that provide estimates of the integrals of tabulated data. Several such formulas are presented and illustrated in Appendix A.3; the use of one of them, **Simpson's rule**, is required for the integration of heat capacity data in several problems at the end of this chapter.

8.4 PHASE-CHANGE OPERATIONS

Consider liquid water and water vapor, each at 100°C and 1 atm. Which would you expect to be greater, $\hat{U}_{\text{liquid}}$ or $\hat{U}_{\text{vapor}}$? (Recall that $\hat{U}$ is related among other things to the energy of motion of the individual molecules at the specified condition.)

If you said $\hat{U}_{\text{vapor}}$, you would be correct. One way to think of it is that the molecules of a vapor, which can move around relatively freely, are much more energetic than the densely packed molecules of a liquid at the same T and P. Also think about the fact that liquid molecules are held in close proximity to each other by attractive forces between the molecules. The energy required to overcome these forces when a liquid is vaporized is reflected in the higher internal energy of the vapor molecules.

Inspection of Table B.5 reveals how dramatic the difference between $\hat{U}_{\text{liquid}}$ and $\hat{U}_{\text{vapor}}$ can be. For water at 100°C and 1 atm, $\hat{U}_{\text{l}} = 419$ kJ/kg and $\hat{U}_{\text{v}} = 2507$ kJ/kg. The difference in specific enthalpy ($= \hat{U} + P\hat{V}$) is even greater, owing to the much greater specific volume of the vapor: at the same temperature and pressure, $\hat{H}_{\text{l}} = 419.1$ kJ/kg and $\hat{H}_{\text{v}} = 2676$ kJ/kg.

Phase changes such as melting and evaporation are usually accompanied by large changes in internal energy and enthalpy, as in the example just given. Heat transfer requirements in phase-change operations consequently tend to be substantial, since $Q \approx \Delta U$ (closed constant-volume system) or $\dot{Q} \approx \Delta \dot{H}$ (open system). The paragraphs that follow outline procedures for setting up and solving energy balances on such operations. The discussion will be limited to phase changes between liquid and vapor (evaporation, condensation) and solid and liquid (melting, freezing); however, the methods may be extended directly to other phase changes, such as sublimation (conversion from solid to vapor) and conversion from one solid phase to another (e.g., amorphous to crystalline).

8.4a Latent Heats

The specific enthalpy change associated with the transition of a substance from one phase to another at constant temperature and pressure is known as the **latent heat** of the phase change (as distinguished from *sensible heat*, which is associated with temperature changes for a single-phase system). For example, the specific enthalpy change $\Delta\hat{H}$ for the transition of liquid water to steam at 100°C and 1 atm, which equals 40.6 kJ/mol, is by definition the **latent heat of vaporization** (or simply the **heat of vaporization**) of water at this temperature and pressure.

Since condensation is the reverse of vaporization and enthalpy is a state property, the heat of condensation must be the negative of the heat of vaporization. Thus, the heat of condensation of water at 100°C and 1 atm must be −40.6 kJ/mol. Similarly, the heat of solidification is the negative of the heat of fusion at the same temperature and pressure.

Latent heats for the two most commonly encountered phase changes are defined as follows:

1. ***Heat of fusion*** (or heat of melting). $\Delta\hat{H}_{\text{m}}(T, P)$ is the specific enthalpy difference between the solid and liquid forms of a species at T and P.[7]
2. ***Heat of vaporization***. $\Delta\hat{H}_{\text{v}}(T, P)$ is the specific enthalpy difference between the liquid and vapor forms of a species at T and P.

Tabulated values of these two latent heats, such as those in Table B.1 and on pp. 2-144 through 2-155 of *Perry's Chemical Engineers' Handbook,* (see Footnote 5) usually apply to a substance at its normal melting or boiling point—that is, at a pressure of 1 atm. These quantities are referred to as *standard* heats of fusion and vaporization.

The standard heats of fusion and vaporization in Table B.1 may be accessed in APEx with the following functions:

$$(\Delta\hat{H}_{\text{m}})_{\text{species}}(T_{\text{m}}, 1\text{ atm}): \text{ =Hm("Species")}, \quad (\Delta\hat{H}_{\text{v}})_{\text{species}}(T_{\text{b}}, 1\text{ atm}): \text{ =Hv("Species")}$$

For example, if you enter =Hv("Acetic acid") in the cell of a spreadsheet with APEx activated, the value 24.39 (in kJ/mol) will be returned, corresponding to the value listed in Table B.1 of the standard heat of vaporization of acetic acid at its normal boiling point of 118°C.

The latent heat of a phase change may vary considerably with the temperature at which the change occurs but hardly varies at all with the pressure at the transition point. For example, the heat of vaporization of water at 25°C is 2442.5 J/g at $P = 23.78$ mm Hg and 2442.3 J/g at $P =$ 760 mm Hg.[8] *When using a tabulated latent heat, you must therefore be sure that the phase*

[7] We call it $\Delta\hat{H}_{\text{m}}$ rather than $\Delta\hat{H}_{\text{f}}$ because the latter symbol is used for the *heat of formation,* a quantity defined in Chapter 9.

[8] In a system containing only pure water at 25°C, evaporation can only occur at $P = p_w^*(25°\text{C}) = 23.78$ mm Hg, but if the system contains several species, evaporation can occur over a range of pressures.

change in question takes place at the temperature for which the tabulated value is reported, but you may ignore moderate variations in pressure.

Example 8.4-1 Heat of Vaporization

At what rate in kilowatts must heat be transferred to a liquid stream of methanol at its normal boiling point to generate 1500 g/min of saturated methanol vapor?

Solution From Table B.1 or using APEx functions Tb and Hv, $\Delta\hat{H}_v = 35.3$ kJ/mol at $T_b = 64.7°C$. The energy balance with potential and kinetic energy changes neglected is

$$\dot{Q} = \Delta\dot{H} = \dot{n}\Delta\hat{H}_v$$

$$\Downarrow$$

$$\dot{Q} = \frac{1500\text{ g CH}_3\text{OH}}{\text{min}} \left| \frac{1\text{ mol}}{32.0\text{ g CH}_3\text{OH}} \right| \frac{35.3\text{ kJ}}{\text{mol}} \left| \frac{1\text{ min}}{60\text{ s}} \right| \frac{1\text{ kW}}{1\text{ kJ/s}} = \boxed{27.6\text{ kW}}$$

Phase changes often occur at temperatures other than the temperature for which the latent heat is tabulated. When faced with this situation, you must select a hypothetical process path that permits the available data to be used.

Suppose, for example, that a substance is to be vaporized isothermally at 130°C, but the only available value of the heat of vaporization is at 80°C. A process path from the liquid at 130°C to the vapor at the same temperature must then be chosen that includes an isothermal vaporization step at 80°C: specifically, cool the liquid from 130°C to 80°C, vaporize the liquid at 80°C, and then heat the vapor back to 130°C. Summing the changes in enthalpy for each of these steps yields the change in enthalpy for the given process. (By definition, the calculated value is the latent heat of vaporization at 130°C.)

Example 8.4-2 Vaporization and Heating

One hundred g-moles per hour of liquid *n*-hexane at 25°C and 7 bar is vaporized and heated to 300°C at constant pressure. Neglecting the effect of pressure on enthalpy, estimate the rate at which heat must be supplied.

Solution An energy balance yields

$$\dot{Q} = \Delta\dot{H} \quad (\dot{W}_s = \Delta\dot{E}_p = 0, \Delta\dot{E}_k \approx 0)$$

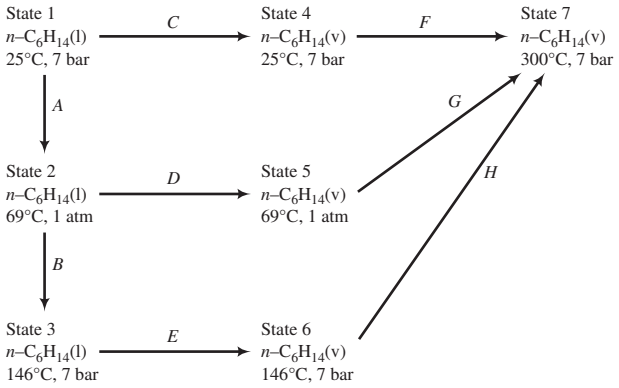
Therefore an evaluation of $\Delta\dot{H}$ will yield the desired value of $\dot{Q}$.

From the Antoine equation (Table B.4) or the APEx function AntoineT ("*n*-hexane," 5250), the temperature at which the vapor pressure of *n*-hexane is 7 bar (5250 mm Hg) is 146°C, and this is therefore the temperature at which the vaporization actually occurs. However, Table B.1 lists a value of $\Delta\hat{H}_v$ at the normal boiling point of *n*-hexane,

$$\Delta\hat{H}_v = 28.85\text{ kJ/mol at } 69°C$$

We must therefore find a path that takes hexane from a liquid to a vapor at 69°C, rather than at the true vaporization temperature of 146°C.

As noted previously, the change in enthalpy associated with a process may be determined from any convenient path as long as the initial and final points of the chosen path correspond to those of the process. The diagram shown on the following page illustrates several possible paths from liquid hexane at 25°C to hexane vapor at 300°C.



If we knew $\Delta\hat{H}_v$ at 146°C, we would follow path *ABEH* (the true process path) to evaluate the overall $\Delta\hat{H}$ for the process, or if we knew $\Delta\hat{H}_v$ at 25°C, we would follow path *CF*, which would require only two calculations. Since we have $\Delta\hat{H}_v$ at 69°C, we must follow path *ADG*, which includes vaporization at that temperature.

$$n\text{-}C_6H_{14}(l, 25°C, 7\text{ bar}) \xrightarrow{\Delta\hat{H}_A} n\text{-}C_6H_{14}(l, 69°C, 1\text{ atm})$$
$$\Big\Downarrow \Delta\hat{H}_D$$
$$n\text{-}C_6H_{14}(v, 69°C, 1\text{ atm}) \xrightarrow{\Delta\hat{H}_G} n\text{-}C_6H_{14}(v, 300°C, 7\text{ bar})$$

$$\Delta\hat{H}_A = \hat{V}\Delta P + \int_{25°C}^{69°C} (C_p)_{C_6H_{14}(l)} dT \quad \text{(from Equation 8.3-10b)}$$

$$\Big\Downarrow \begin{array}{l} \text{Table B.1} \Longrightarrow \text{SG} = 0.659 \Longrightarrow \rho = 0.659\text{ kg/L} \\ \text{Table B.2} \Longrightarrow C_p = 0.2163\text{ kJ/(mol·°C)} \\ 1\text{ atm} = 1.013\text{ bar} \end{array}$$

$$\Delta\hat{H}_A = \frac{1\text{ L}}{0.659\text{ kg}} \left| \frac{(1.013 - 7.0)\text{ bar}}{} \right| \frac{86.17\text{ kg}}{1000\text{ mol}} \left| \frac{0.008314\text{ kJ/(mol·K)}}{0.08314\text{ L·bar/(mol·K)}} \right.$$
$$+ \frac{0.2163\text{ kJ}}{\text{mol·°C}} \left| \frac{(69 - 25)°C}{} \right. = (-0.0782 + 9.517)\text{ kJ/mol} = 9.44\text{ kJ/mol}$$

$$\Delta\hat{H}_D = (\Delta\hat{H}_v)_{C_6H_{14}}(69°C, 1\text{ atm}) = 28.85\text{ kJ/mol}$$

$$\Delta\hat{H}_G = \int_{69°C}^{300°C} (C_p)_{C_6H_{14}(v)}\, dT \quad \text{(from Equation 8.3-10a)}$$

$$\Big\Downarrow C_p[\text{kJ/(mol·°C)}] = 0.13744 + 40.85 \times 10^{-5}T - 23.92 \times 10^{-8}T^2 + 57.66 \times 10^{-12}T^3$$

$$\Delta\hat{H}_G = 47.1\text{ kJ/mol}$$

For the overall process

$$\dot{Q} = \Delta\dot{H} = \dot{n}(\text{mol/h})\Delta\hat{H}(\text{kJ/mol})$$
$$\Big\Downarrow \Delta\hat{H} = \Delta\hat{H}_A + \Delta\hat{H}_D + \Delta\hat{H}_G = 85.5\text{ kJ/mol}$$

$$\dot{Q} = \frac{100\text{ mol}}{\text{h}} \left| \frac{85.5\text{ kJ}}{\text{mol}} \right| \frac{1\text{ h}}{3600\text{ s}} \left| \frac{1\text{ kW}}{1\text{ kJ/s}} \right. = \boxed{2.38\text{ kW}}$$

Notice that the pressure change term in the first step ($\hat{V}\Delta P = -0.0782$ kJ/mol) accounts for less than 0.1% of the overall process enthalpy change. We will generally neglect the effects of pressure changes on $\Delta\hat{H}$ unless ΔP is on the order of 50 atm or more.

If a phase change takes place in a closed system, you must evaluate $\Delta\hat{U} = \Delta\hat{H} - \Delta(P\hat{V})$ for the phase change to substitute into the energy balance equation. For phase changes such as fusion, which involve only liquids and solids, changes in $P\hat{V}$ are generally negligible compared to

changes in $\hat{H}$, so that

$$\Delta\hat{U}_m \approx \Delta\hat{H}_m \tag{8.4-1}$$

For vaporization, $P\hat{V}$ for the vapor (which equals RT if ideal-gas behavior may be assumed) is normally orders of magnitude greater than $P\hat{V}$ for the liquid, so that $\Delta(PV) \approx RT$, and

$$\Delta\hat{U}_v \approx \Delta\hat{H}_v - RT \tag{8.4-2}$$

Test Yourself

(Answers, p. 658)

1. If you are given a value of a heat of vaporization at 100°C and 1 atm, would you be confident about using it to estimate the enthalpy change for a vaporization at 100°C and 2 atm? What about 200°C and 1 atm?
2. The enthalpies of a pure liquid and its vapor at 75°C and 1 atm are 100 J/mol and 1000 J/mol, respectively, both measured relative to the liquid at 0°C.
   (a) What is the enthalpy of the liquid at 0°C?
   (b) What is the heat of vaporization at 75°C?
   (c) Suppose you have heat capacity data for both the liquid and its vapor. What path would you follow to calculate the enthalpy change associated with 100 mol of the vapor at 400°C being cooled and condensed to form a liquid at 25°C?
3. The heat of fusion of zinc chloride at 556 K is $\Delta\hat{H}_m = 5500$ cal/mol, and the heat of vaporization of this substance at 1000 K is $\Delta\hat{H}_v = 28{,}710$ cal/mol. Estimate $\Delta\hat{U}_m(556\text{ K})$ and $\Delta\hat{U}_v(1000\text{ K})$ for $ZnCl_2$. [Say $R = 2$ cal/(mol·K).]

8.4b Estimation and Correlation of Latent Heats

Poling, Prausnitz, and O'Connell (see Footnote 4) review procedures for estimating latent heats of vaporization, fusion, and sublimation. Several of the methods given in this reference are summarized below.

A simple formula for estimating a standard heat of vaporization ($\Delta\hat{H}_v$ at the normal boiling point) is **Trouton's rule**:

$$\Delta\hat{H}_v(\text{kJ/mol}) \begin{cases} \approx 0.088T_b(\text{K}) & \text{(nonpolar liquids)} \\ \approx 0.109T_b(\text{K}) & \text{(water, low molecular weight alcohols)} \end{cases} \tag{8.4-3}$$

where T_b is the normal boiling point of the liquid. Trouton's rule provides an estimate of $\Delta\hat{H}_v$ accurate to within 30%. Another formula that provides roughly 2% accuracy is **Chen's equation**:

$$\Delta\hat{H}_v(\text{kJ/mol}) = \frac{T_b[0.0331(T_b/T_c) - 0.0327 + 0.0297\log_{10}P_c]}{1.07 - (T_b/T_c)} \tag{8.4-4}$$

where T_b and T_c are the normal boiling point and critical temperature in kelvin and P_c is the critical pressure in atmospheres.

A formula for approximating a standard heat of fusion is

$$\Delta\hat{H}_m(\text{kJ/mol}) \begin{cases} \approx 0.0092T_m(\text{K}) & \text{(metallic elements)} \\ \approx 0.0025T_m(\text{K}) & \text{(inorganic compounds)} \\ \approx 0.050T_m(\text{K}) & \text{(organic compounds)} \end{cases} \tag{8.4-5}$$

Latent heats of vaporization may be estimated from vapor pressure data by using the Clausius–Clapeyron equation, which was discussed in Section 6.1b.

$$\ln p^* = -\frac{\Delta\hat{H}_v}{RT} + B \tag{8.4-6}$$

Provided that $\Delta\hat{H}_v$ is constant over the range of temperatures encompassed by the vapor pressure data, the latent heat of vaporization may be determined from a plot of $\ln p^*$ versus $1/T$. (See Example 6.1-1.)

In many cases the latent heat of vaporization varies considerably with temperature, invalidating Equation 8.4-6. It is then necessary to use the **Clapeyron equation**, from which Equation 8.4-6 was derived. From Equation 6.1-2,

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R} \tag{8.4-7}$$

The heat of vaporization at a temperature T may be estimated from vapor pressure data by plotting $\ln p^*$ versus $1/T$, determining $[d(\ln p^*)/d(1/T)]$ at the temperature of interest as the slope of the tangent to the curve, and solving Equation 8.4-7 for $\Delta\hat{H}_v$. The slope may be determined graphically or by any of several numerical differentiation techniques outlined in texts on numerical analysis.

A procedure for calculating the latent heat of vaporization at one temperature from a known value at any other temperature was presented in Section 8.4a. The technique outlined is rigorous but time-consuming, and it requires heat capacity data that might not be available for the substance of interest. A useful approximation for estimating $\Delta\hat{H}_v$ at T_2 from a known value at T_1 is **Watson's correlation**:

$$\Delta\hat{H}_v(T_2) = \Delta\hat{H}_v(T_1)\left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38} \tag{8.4-8}$$

where T_c is the critical temperature of the substance.

Example 8.4-3 Estimation of a Heat of Vaporization

The normal boiling point of methanol is 337.9 K and its critical temperature and pressure are 513.2 K and 78.5 atm. The heat of vaporization at the normal boiling point is 35.3 kJ/mol.

(a) Estimate the heat of vaporization at 337.9 K using Trouton's rule and Chen's equation, and determine the percent error for each estimate.

(b) Using the Watson's correlation estimate: the value of the heat of vaporization of methanol at 200°C using the measured and estimated values at the normal boiling point. Determine the percent error for each estimate if the measured value is 19.8 kJ/mol.

Solution

(a) ***Trouton's Rule:***

$$\Delta\hat{H}_v(337.9\text{ K}) \approx 0.109 \times 337.9 = \boxed{36.8\text{ kJ/mol}}$$

The error associated with this value is +4.4%.

Chen's Equation:

$$\Delta\hat{H}_v(337.9\text{ K}) \approx \frac{337.9\left[0.0331(337.9/513.2) - 0.0327 + 0.0297\log_{10}78.5\right]}{1.07 - (337.9/513.2)} = \boxed{37.2\text{ kJ/mol}}$$

for a +5.6% error.

(b) Using the Watson's correlation estimate:

$$\Delta\hat{H}_v(473\text{ K}) \approx 36.8\frac{\text{kJ}}{\text{mol}}\left(\frac{513.2 - 473}{513.2 - 337.9}\right)^{0.38} = \boxed{21.0\text{ kJ/mol}}$$

for a +6.3% error.

Using the actual value of the heat of vaporization at the normal boiling point:

$$\Delta\hat{H}_v(473\text{ K}) = 35.3\frac{\text{kJ}}{\text{mol}}\left(\frac{513.2 - 473}{513.2 - 337.9}\right)^{0.38} = \boxed{20.2\text{ kJ/mol}}$$

for a +1.8% error.

Test Yourself

(Answers, p. 659)

How would you estimate $\Delta\hat{H}_v$ for a pure hydrocarbon at its normal boiling point under each of the following conditions?

1. You know only the normal boiling point.
2. You know the normal boiling point and the critical constants.
3. You have vapor pressure data over a range that encompasses $p^* = 1$ atm, and a semilog plot of p^* versus $1/T$ is a straight line.
4. Repeat 3, only suppose the plot is curved.
5. You know $\Delta\hat{H}_v$ at a temperature other than T_b and do not know the heat capacities of the substance in its gaseous and liquid forms.
6. Repeat 5, only suppose that you have the heat capacity data.

8.4c Energy Balances on Processes Involving Phase Changes

When writing an energy balance on a process in which a component exists in two phases, you must choose a reference state for that component by specifying both a phase and a temperature and calculate the specific enthalpy of the component in all process streams relative to this state. If the substance is a liquid at its reference state and a vapor in a process stream, $\hat{H}$ may be calculated as outlined in Section 8.4a: that is, bring the liquid from the reference temperature to a point at which $\Delta\hat{H}_v$ is known, vaporize the liquid, bring the vapor to the process stream temperature, and sum the individual enthalpy changes for the three steps.

Example 8.4-4 Partial Vaporization of a Mixture

An equimolar liquid mixture of benzene (B) and toluene (T) at 10°C is fed continuously to a vessel in which the mixture is heated to 50°C. The liquid product is 40.0 mole% B, and the vapor product is 68.4 mole% B. How much heat must be transferred to the mixture per g-mole of feed?

Solution **Basis: 1 mol Feed**

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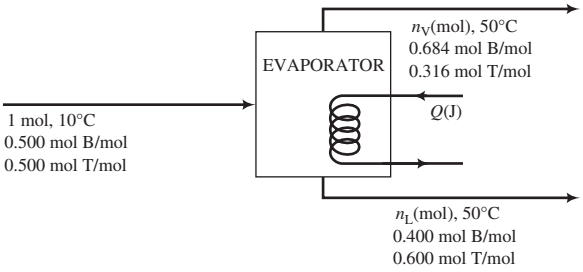

We start with a degree-of-freedom analysis:

$$\begin{aligned} &3 \text{ unknown variables } (n_V, n_L, Q) \\ &-2 \text{ material balances} \\ &-1 \text{ energy balance} \\ &= 0 \text{ degrees of freedom} \end{aligned}$$

We could count each specific enthalpy to be determined as an unknown variable, but then we would also count the equations for each of them in terms of heat capacities and latent heats, leaving the number of degrees of freedom unchanged.

We next determine n_V and n_L from material balances, and then Q from an energy balance.

$$\left.\begin{array}{rr} \textbf{\textit{Total Mass Balance:}} & 1.00\ \text{mol} = n_V + n_L \\ \textbf{\textit{Benzene Balance:}} & 0.500\ \text{mol} = 0.684\, n_V + 0.400\, n_L \end{array}\right\} \Longrightarrow \begin{array}{l} n_V = 0.352\ \text{mol} \\ n_L = 0.648\ \text{mol} \end{array}$$

The energy balance for this process has the form $Q = \Delta H$. An enthalpy table for the process appears as follows:

References: B(l, 10°C, 1 atm), T(l, 10°C, 1 atm)

Substance	n_{in} mol	$\hat{H}_{in}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{out}$ (kJ/mol)
B(l)	0.500	0	0.259	$\hat{H}_1$
T(l)	0.500	0	0.389	$\hat{H}_2$
B(v)	—	—	0.241	$\hat{H}_3$
T(v)	—	—	0.111	$\hat{H}_4$

The values of n_{out} were determined from the known mole fractions of benzene and toluene in the outlet streams and the calculated values of n_V and n_L. We do not know the feed-stream pressure and so we assume that ΔH for the change from 1 atm to P_{feed} is negligible, and since the process is not running at an unusually low temperature or high pressure, we neglect the effects of pressure on enthalpy in the calculations of $\hat{H}_1$ through $\hat{H}_4$. (The pressure can be estimated from the Antoine equation and Raoult's law to be 164 mm Hg.) The heat capacity and latent heat data needed to calculate the outlet enthalpies are obtained from Tables B.1 and B.2.

The formulas (including the APEx formulas) and values of the unknown specific enthalpies are given below. Convince yourself that the formulas represent $\Delta\hat{H}$ for the transitions from the reference states to the process states.

$$\hat{H}_1 = \int_{10°C}^{50°C} (C_p)_{C_6H_6(l)} dT \quad [=\text{Enthalpy("benzene",10,50,"C","l")}] = 5.341\ \text{kJ/mol}$$

$$\hat{H}_2 = \int_{10°C}^{50°C} (C_p)_{C_7H_8(l)} dT \quad [=\text{Enthalpy("toluene",10,50,"C","l")}] = 6.341\ \text{kJ/mol}$$

$$\hat{H}_3 = \int_{10°C}^{80.1°C} (C_p)_{C_6H_6(l)} dT + (\Delta\hat{H}_v)_{C_6H_6}(80.1°C) + \int_{80.1°C}^{50°C} (C_p)_{C_6H_6(v)} dT$$

$$[=\text{Enthalpy("benzene",10,80.1,"C","l")} + \text{Hv("benzene")} + \text{Enthalpy("benzene",80.1,50,"C","g")}] = 37.53\ \text{kJ/mol}$$

$$\hat{H}_4 = \int_{10°C}^{110.62°C} (C_p)_{C_7H_8(l)} dT + (\Delta\hat{H}_v)_{C_7H_8}(110.62°C) + \int_{110.62°C}^{50°C} (C_p)_{C_7H_8(v)} dT$$

$$[=\text{Enthalpy("toluene",10,110.62,"C","l")} + \text{Hv("toluene")} + \text{Enthalpy("toluene",110.62,50,"C","g")}] = 42.94\ \text{kJ/mol}$$

The energy balance is

$$Q = \Delta H = \sum_{out} n_i \hat{H}_i - \sum_{in} n_i \hat{H}_i \Longrightarrow \boxed{Q = 17.7\ \text{kJ}}$$

CREATIVITY EXERCISE

A gas emerges from a stack at 1200°C. Rather than being released directly to the atmosphere, it can be passed through one or several heat exchangers, and the heat it loses can be put to use in a variety of ways. Think of as many uses of this heat as you can. (*Example:* During the winter, pass the gas through a series of radiators, thereby getting free heating.)

8.4d Psychrometric Charts

On a **psychrometric chart** (or **humidity chart**) several properties of a gas–vapor mixture are cross-plotted, providing a concise compilation of a large quantity of physical-property data. The most common of these charts—that for the air-water system at 1 atm—is used extensively in the analysis of humidification, drying, and air-conditioning processes.

A psychrometric chart in SI units for the air–water system at 1 atm is shown in Figure 8.4-1, and a second chart in U.S. customary units is shown in Figure 8.4-2. Charts that cover wider temperature ranges in several formats are given on pp. 12-7 through 12-12 of *Perry's Chemical Engineers' Handbook* (see Footnote 5).

The following paragraphs define and describe the different properties of humid air at 1 atm that appear on the psychrometric chart. Once you know the values of any two of these properties, you can use the chart to determine the values of the others. We will use the abbreviation DA for dry air.

- ***Dry-bulb temperature,*** T—the abscissa of the chart. This is the air temperature as measured by a thermometer, thermocouple, or other conventional temperature-measuring instrument.
- ***Absolute humidity,*** h_a [kg H_2O(v)/kg DA] (called **moisture content** on Figure 8.4-1)—the ordinate of the chart.

  This ratio can easily be calculated from or converted to the mass fraction of water. If, for example, the absolute humidity is 0.0150 kg H_2O/kg DA, then for every kilogram of dry air there is 0.015 kg of water vapor, for a total of 1.015 kg. The mass fraction of water is (0.0150 kg H_2O)/(1.015 kg humid air) = 0.0148 kg H_2O/kg.
- ***Relative humidity***, $h_r = [100 \times p_{H_2O}/p^*_{H_2O}(T)]$.

  Curves on the psychrometric chart correspond to specified values of h_r (100%, 90%, 80%, etc.). The curve that forms the left boundary of the chart corresponds to **100% relative humidity** and is known as the **saturation curve**.
- ***Dew point***, T_{dp}—the temperature at which humid air becomes saturated if it is cooled at constant pressure.

  The dew point of humid air at a given point on the psychrometric chart can easily be determined. For example, locate the point on Figure 8.4-1 corresponding to air at 29°C and 20% relative humidity. Cooling this air at constant pressure (= 1 atm) corresponds to moving horizontally (at constant absolute humidity) to the saturation curve. T_{dp} is the temperature at the intersection, or 4°C. (Verify this statement.)
- ***Humid volume,*** $\hat{V}_H$ (m^3/kg DA).

  The humid volume is the volume occupied by 1 kg of dry air plus the water vapor that accompanies it. Lines of constant humid volume on the psychrometric chart are steep and have negative slopes. On Figure 8.4-1, humid-volume lines are shown corresponding to 0.75, 0.80, 0.85, and 0.90 m^3/kg dry air.

  To determine the volume of a given mass of wet air using the psychrometric chart, you must first determine the corresponding mass of dry air from the absolute humidity, then multiply this mass by $\hat{V}_H$. Suppose, for example, you wish to know the volume occupied by 150 kg of humid air at T = 30°C and h_r = 30%. From Figure 8.4-1, h_a = 0.0080 kg H_2O(v)/kg DA and $\hat{V}_H \approx 0.87$ m^3/kg DA. The volume may then be calculated as

$$V = \frac{150 \text{ kg humid air}}{} \left| \begin{array}{l|l} \dfrac{1.00 \text{ kg DA}}{1.008 \text{ kg humid air}} & \dfrac{0.87 \text{ m}^3}{\text{kg DA}} \end{array} \right. = 129 \text{ m}^3$$

  (In this calculation, we used the fact that if the absolute humidity is 0.008 kg H_2O/kg DA, then 1 kg DA is accompanied by 0.008 kg water for a total of 1.008 kg humid air.)

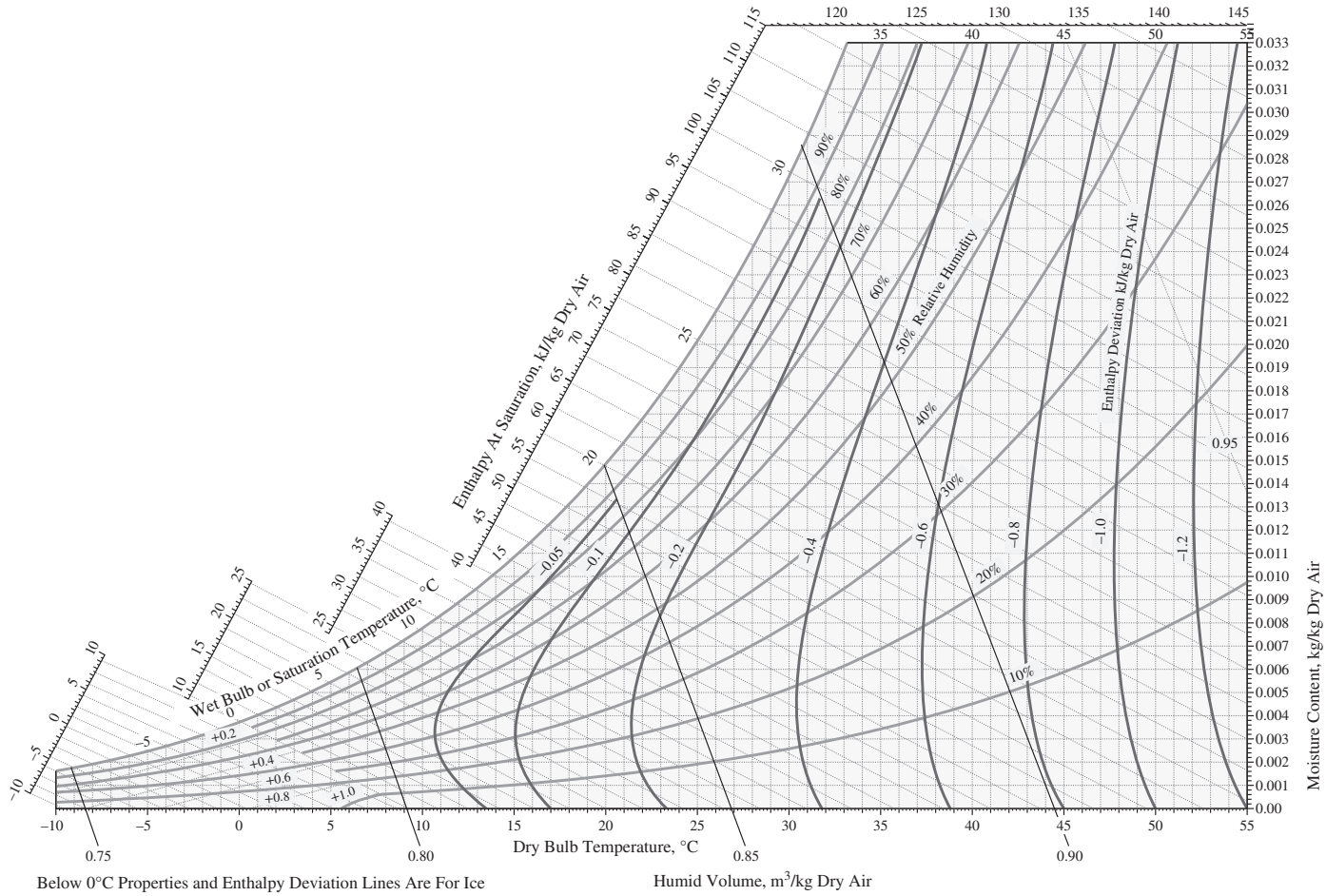

FIGURE 8.4-1 Psychrometric chart—SI units. Reference states: H_2O (liquid, 0°C, 1 atm), dry air (0°C, 1 atm). (Data obtained from Carrier Corporation.)

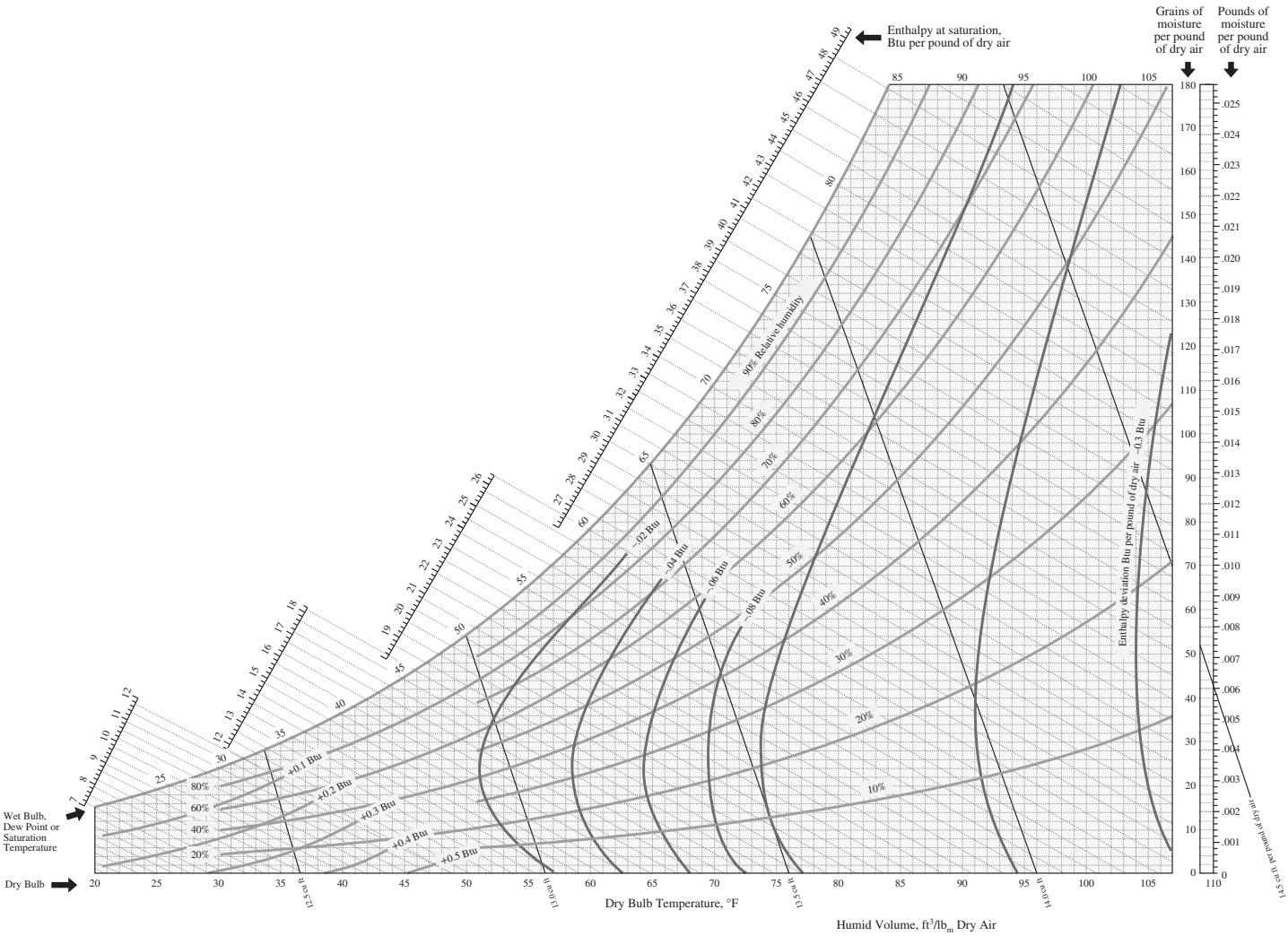

FIGURE 8.4-2 Psychrometric chart—U.S. customary units. Reference states: H_2O (liquid, 32°F, 1 atm), dry air (0°F, 1 atm). (Data obtained from Carrier Corporation.)

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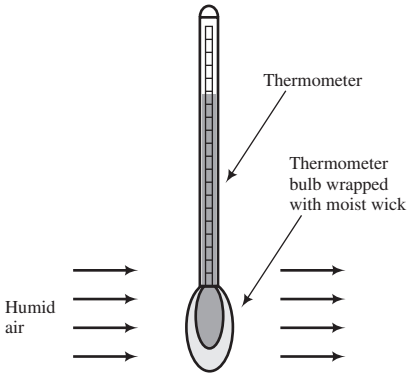
- ***Wet-bulb temperature***, T_{wb}.

  This quantity is best defined in terms of how it is measured. A porous material such as cloth or cotton is soaked in water and wrapped around the bulb of a thermometer to form a *wick*, and the thermometer is placed in a stream of flowing air, as in the figure shown below.[9] Evaporation of water from the wick into the flowing air is accompanied by a transfer of heat from the bulb, which in turn causes a drop in the bulb temperature and hence in the thermometer reading.[10] Provided that the wick remains moist, the bulb temperature falls to a certain value and remains there. The final temperature reading is the wet-bulb temperature of the air flowing past the wick.



  The wet-bulb temperature of humid air depends on both the dry-bulb temperature and the moisture content of the air. If the air is saturated (100% relative humidity), no water evaporates from the wick, and the wet-bulb and dry-bulb temperatures are the same. The lower the humidity, the greater the difference between the two temperatures.

  The humid air conditions that correspond to a given wet-bulb temperature fall on a straight line on the psychrometric chart, called a **constant wet-bulb temperature line**. The constant wet-bulb temperature lines for air–water at 1 atm appear on Figures 8.4-1 and 8.4-2 as lines with negative slopes extending beyond the saturation curve that are less steep than the lines of constant humid volume. The value of T_{wb} corresponding to a given line can be read at the intersection of the line with the saturation curve.

  For example, suppose you wish to determine the wet-bulb temperature of air at 30°C (dry bulb) with a relative humidity of 30%. Locate the point on Figure 8.4-1 at the intersection of the vertical line corresponding to $T = 30°C$ and the curve corresponding to $h_r = 30\%$. The diagonal line through the point is the constant wet-bulb temperature line for air at the given condition. Follow that line upward to the left until you reach the saturation curve. The temperature value you read on the curve (or vertically down from it on the abscissa) is the wet-bulb temperature of the air. You should get a value of 18°C. This means that if you wrap a wet wick around a thermometer bulb and blow air with $T = 30°C$ and $h_r = 30\%$ past the bulb, the thermometer reading will drop and eventually stabilize at 18°C.

- ***Specific enthalpy of saturated air***

  The diagonal scale above the saturation curve on the psychrometric chart shows the enthalpy of a unit mass (1 kg or 1 lb_m) of dry air plus the water vapor it contains at saturation. The reference states are liquid water at 1 atm and 0°C (32°F) and dry air at 1 atm and 0°C (Figure 8.4-1) or 0°F (Figure 8.4-2). To determine the enthalpy from the chart, follow the constant wet-bulb temperature line from the saturation curve at the desired temperature up to the enthalpy scale.

[9] Alternatively, the thermometer may be mounted in a *sling psychrometer* and whirled around in stationary air.

[10] Think about what happens when you step out of a shower or swimming pool. Water evaporates, your skin temperature drops, and you feel cold, even if you felt perfectly comfortable when you were dry.

For example, saturated air at 25°C and 1 atm—which has an absolute humidity h_a = 0.0202 kg H_2O/kg DA—has a specific enthalpy of 76.5 kJ/kg DA. (Verify these values of both h_a and $\hat{H}$ on Figure 8.4-1.) The enthalpy is the sum of the enthalpy changes for 1.00 kg dry air and 0.0202 kg water going from their reference conditions to 25°C. The following calculation uses heat capacity data from Table B.2 for air and data from the steam tables (Table B.5) for water.

$$1.00\text{ kg DA}(0°\text{C}) \rightarrow 1\text{ kg DA}(25°\text{C})$$

$$\Downarrow$$

$$\Delta H_{air} = (1.00\text{ kg DA})\left(\frac{1\text{ kmol}}{29.0\text{ kg}}\right)\left[\int_0^{25} C_{p,air}(T)dT\right]\left(\frac{\text{kJ}}{\text{kmol}}\right) = 25.1\text{ kJ}$$

$$0.0202\text{ kg } H_2O(l, 0°\text{C}) \rightarrow 0.0202\text{ kg } H_2O(v, 25°\text{C})$$

$$\Downarrow$$

$$\Delta H_{water} = (0.0202\text{ kg})\left[\hat{H}_{H_2O(v,25°C)} - \hat{H}_{H_2O(l,0°C)}\right]\left(\frac{\text{kJ}}{\text{kg}}\right) = 51.4\text{ kJ}$$

$$\hat{H} = \frac{(\Delta H_{air} + \Delta H_{water})(\text{kJ})}{1.00\text{ kg DA}} = \frac{(25.1 + 51.4)\text{ kJ}}{1.00\text{ kg DA}} = 76.5\text{ kJ/kg DA}$$

- ***Enthalpy deviation***

  The remaining curves on the psychrometric chart are almost vertical and convex to the left, with labeled values (on Figure 8.4-1) of −0.05, −0.1, −0.2, and so on. (The units of these numbers are kJ/kg DA). These curves are used to determine the enthalpy of humid air that is not saturated. The procedure is as follows: (a) locate the point on the chart corresponding to air at its specified condition; (b) interpolate to estimate the enthalpy deviation at this point; (c) follow the constant wet-bulb temperature line to the enthalpy scale above the saturation curve, read the value on that scale, and add the enthalpy deviation to it.

  For example, air at 35°C and 10% relative humidity has an enthalpy deviation of about −0.52 kJ/kg DA. The specific enthalpy of saturated air at the same wet-bulb temperature is 45.0 kJ/kg DA. (Verify both of these numbers.) The specific enthalpy of the humid air at the given condition is therefore (45.0 − 0.52) kJ/kg DA = 44.5 kJ/kg DA.

The basis for the construction of the psychrometric chart is the Gibbs phase rule (Section 6.3a), which states that specifying a certain number of the intensive variables (temperature, pressure, specific volume, specific enthalpy, component mass or mole fractions, etc.) of a system automatically fixes the value of the remaining intensive variables. Humid air contains one phase and two components,[11] so that from Equation 6.2-1 the number of degrees of freedom is

$$F = 2 + 2 - 1 = 3$$

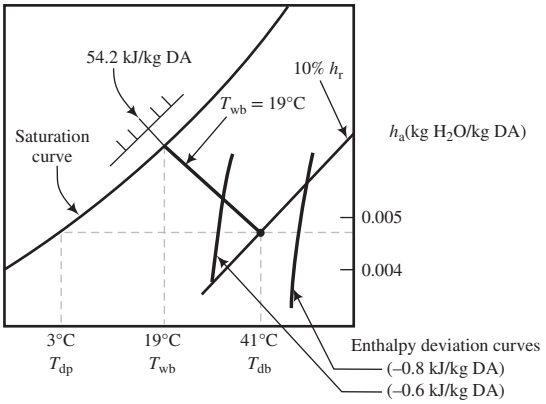
Specifying three intensive variables therefore fixes all other system properties. If the system pressure is fixed at 1 atm, then all other properties may be plotted on a two-dimensional plot, such as those shown in Figures 8.4-1 and 8.4-2.

Example 8.4-5 The Psychrometric Chart

Use the psychrometric chart to estimate (1) the absolute humidity, wet-bulb temperature, humid volume, dew point, and specific enthalpy of humid air at 41°C and 10% relative humidity, and (2) the amount of water in 150 m^3 of air at these conditions.

[11] Since the components of dry air do not condense and are present in fixed proportion, dry air may be considered a single species (designated DA) in humidity calculations.

Solution Following is a sketch of the psychrometric chart (Figure 8.4-1) showing the given state of the air:



1. Reading from the chart,

$$\begin{aligned} &h_a \approx 0.0048 \text{ kg } H_2O/\text{kg DA} \\ &T_{wb} = 19°C \\ &\hat{V}(\text{m}^3/\text{kg DA}) \approx 0.897 \text{ (curve not shown)} \end{aligned}$$

The dew point is the temperature at which the air with the given water content would be saturated at the same total pressure (1 atm) and is therefore located at the intersection of the horizontal constant absolute humidity line ($h_a \equiv 0.0048$) and the saturation curve, or

$$\boxed{T_{dp} = 3°C}$$

The specific enthalpy of saturated air at $T_{wb} = 19°C$ is 54.2 kJ/kg DA. Since the point corresponding to 41°C and 10% relative humidity falls roughly midway between the enthalpy deviation curves corresponding to −0.6 kJ/kg and −0.8 kJ/kg, we may calculate $\hat{H}$ as

$$\hat{H} = (54.2 - 0.7) \text{ kJ/kg DA}$$
$$\Downarrow$$
$$\boxed{\hat{H} = 53.5 \text{ kJ/kg DA}}$$

2. ***Moles of humid air.*** From Figure 8.4-1, the humid volume of the air is 0.897 m^3/kg DA. We therefore calculate

$$150 \text{ m}^3 \left| \frac{1.00 \text{ kg DA}}{0.897 \text{ m}^3} \right| \frac{0.0048 \text{ kg } H_2O}{1.00 \text{ kg DA}} = \boxed{0.803 \text{ kg } H_2O}$$

The psychrometric chart can be used to simplify the solution of material and energy balance problems for constant-pressure air–water systems, at the expense of some precision. Note the following points:

1. Heating or cooling humid air at temperatures above the dew point corresponds to horizontal movement on the psychrometric chart. The ordinate on the chart is the ratio kg H_2O/kg dry air, which does not change as long as no condensation occurs.

2. If superheated humid air is cooled at 1 atm, the system follows a horizontal path to the left on the chart until the saturation curve (dew point) is reached; thereafter, the gas phase follows the saturation curve.

3. Since the psychrometric chart plots the mass ratio kg H_2O/kg dry air rather than the mass fraction of water, it is usually convenient to assume a quantity of dry air in a feed or product stream as a basis of calculation if the chart is to be used in the solution.

Example 8.4-6 Material and Energy Balances on an Air Conditioner

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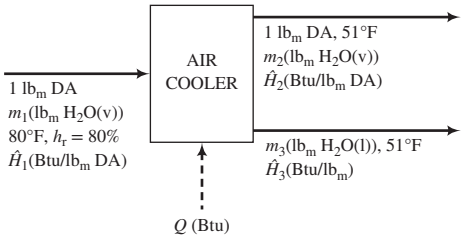
Air at 80°F and 80% relative humidity is cooled to 51°F at a constant pressure of 1 atm. Use the psychrometric chart to calculate the fraction of the water that condenses and the rate at which heat must be removed to deliver 1000 ft^3/min of humid air at the final condition.

Solution

Basis: 1 lb_m Dry Air[12]

A flowchart for the process is shown below. By convention we show heat transfer (Q) into the process unit, but since the air is being cooled we know that Q will be negative.



Note: In labeling the outlet gas stream, we have implicitly written a balance on dry air.

Degree-of-Freedom Analysis:

7 unknowns ($m_1, m_2, m_3, \hat{H}_1, \hat{H}_2, \hat{H}_3, Q$)
−1 material balance (H_2O—dry air is already balanced on the chart)
−2 absolute humidities from psychrometric chart (for inlet and outlet air)
−2 enthalpies from psychrometric chart (for inlet and outlet air)
−1 enthalpy of condensate (from known heat capacity of liquid water)
−1 energy balance
= 0 degrees of freedom

Point 1:

$$\left.\begin{array}{r}80°\text{F}\\ 80\%\ \text{RH}\end{array}\right\} \xrightarrow{\text{Figure 8.4-2}} \begin{array}{l} h_a = 0.018\ \text{lb}_\text{m}\ \text{H}_2\text{O/lb}_\text{m}\ \text{DA}\\ \hat{H}_1 = 38.8\ \text{Btu/lb}_\text{m}\ \text{DA}\end{array}$$

$$m_1 = \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{} \left| \frac{0.018\ \text{lb}_\text{m}\ \text{H}_2\text{O}}{\text{lb}_\text{m}\ \text{DA}} \right. = 0.018\ \text{lb}_\text{m}\ \text{H}_2\text{O}$$

Point 2:

$$\left.\begin{array}{r}51°\text{F}\\ \text{Saturated}\end{array}\right\} \xrightarrow{\text{Figure 8.4-2}} \begin{array}{l} h_a = 0.0079\ \text{lb}_\text{m}\ \text{H}_2\text{O/lb}_\text{m}\ \text{DA}\\ \hat{H}_2 = 20.9\ \text{Btu/lb}_\text{m}\ \text{DA}\end{array}$$

$$m_2 = \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{} \left| \frac{0.0079\ \text{lb}_\text{m}\ \text{H}_2\text{O}}{\text{lb}_\text{m}\ \text{DA}} \right. = 0.0079\ \text{lb}_\text{m}\ \text{H}_2\text{O}$$

Balance on H_2O:

$$m_1 = m_2 + m_3$$
$$\Downarrow\ m_1 = 0.018\ \text{lb}_\text{m},\ m_2 = 0.0079\ \text{lb}_\text{m}$$
$$m_3 = 0.010\ \text{lb}_\text{m}\text{H}_2\text{O condensed}$$

Fraction H_2O Condensed:

$$\frac{0.010\ \text{lb}_\text{m}\ \text{condensed}}{0.018\ \text{lb}_\text{m}\ \text{fed}} = \boxed{0.555}$$

[12] In assuming this basis, we are temporarily ignoring the specification of the volumetric flow rate at the outlet. After the process is balanced for the assumed basis, we will scale up to an outlet flow rate of 1000 ft^3/min.

Enthalpy of Condensate:

Since the reference condition for water on Figure 8.4-2 is liquid water at 32°F, we must use the same condition to calculate $\hat{H}_3$.

$$H_2O(l, 32°F) \rightarrow H_2O(l, 51°F)$$

$$\Delta\hat{H} = \hat{H}_3 = 1.0\frac{\text{Btu}}{\text{lb}_\text{m}\cdot°\text{F}}(51°\text{F} - 32°\text{F}) = 19.0\ \text{Btu/lb}_\text{m}\ H_2O$$

Energy Balance:

The open-system energy balance with W_s, ΔE_k, and ΔE_p set equal to zero is

$$Q = \Delta H = \sum_{\text{out}} m_i\hat{H}_i - \sum_{\text{in}} m_i\hat{H}_i$$

(There are no dots over the extensive variables in this equation because the basis of calculation is an amount, not a flow rate.) The enthalpy table for the process is shown below. Since (1) the enthalpies ($\hat{H}_i$) of the humid air streams are obtained from the psychrometric chart in Btu/lb$_\text{m}$ dry air, and (2) the mass units of m_i and $\hat{H}_i$ must cancel when the two are multiplied in the energy balance, the tabulated values of m_i for these streams must be in lb$_\text{m}$ dry air.

References: Dry air (DA) (g, 0°F, 1 atm), H_2O (l, 32°F, 1 atm)

Substance	m_{in}	$\hat{H}_{in}$	m_{out}	$\hat{H}_{out}$
Humid air	1.0 lb$_\text{m}$ DA	38.8 Btu/lb$_\text{m}$ DA	1.0 lb$_\text{m}$ DA	20.9 Btu/lb$_\text{m}$ DA
H_2O(l)	—	—	0.010 lb$_\text{m}$	19 Btu/lb$_\text{m}$

The references were of necessity chosen to be the ones used to generate the psychrometric chart. Substituting the values in the table into the energy balance yields

$$Q = \Delta H = \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{}\left|\frac{20.9\ \text{Btu}}{\text{lb}_\text{m}\ \text{DA}}\right. + \frac{0.010\ \text{lb}_\text{m}\ H_2O(l)}{}\left|\frac{19\ \text{Btu}}{\text{lb}_\text{m}\ H_2O}\right. - \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{}\left|\frac{38.8\ \text{Btu}}{\text{lb}_\text{m}\ \text{DA}}\right.$$

$$= -17.7\ \text{Btu}$$

To calculate the cooling requirement for 1000 ft^3/min of delivered air, we must first determine the volume of delivered air corresponding to our assumed basis and scale the calculated value of Q by the ratio (1000 ft^3/min)/(V_{basis}). From the psychrometric chart, for humid air saturated at 51°F

$$\hat{V}_H = 13.0\ \text{ft}^3/\text{lb}_\text{m}\ \text{DA}$$

$$\Downarrow$$

$$V_{basis} = \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{}\left|\frac{13.0\ \text{ft}^3}{\text{lb}_\text{m}\ \text{DA}}\right. = 13.0\ \text{ft}^3$$

$$\Downarrow$$

$$\dot{Q} = \frac{-17.7\ \text{Btu}}{}\left|\frac{1000\ \text{ft}^3/\text{min}}{13.0\ \text{ft}^3}\right. = \boxed{-1360\ \text{Btu/min}}$$

Test Yourself

(Answers, p. 659)

Air at 25°C and 1 atm has a relative humidity of 20%. Use the psychrometric chart to estimate the absolute humidity, wet-bulb temperature, dew point, humid volume, and specific enthalpy of the air.

CREATIVITY EXERCISE

In home air-conditioning systems, the controlling thermostat is set to the desired room temperature T_1, and the AC unit typically cools air passing through it to a temperature T_2 significantly lower than T_1. Give at least two reasons why.

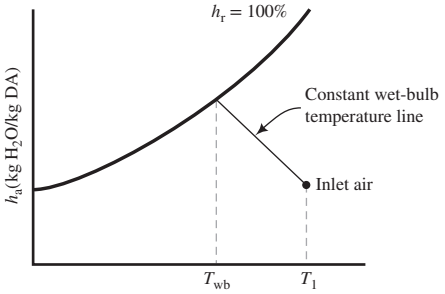
8.4e Adiabatic Cooling

Equipment Encyclopedia
humidifier, dryer, spray dryer
www.wiley.com/college/felder

In **adiabatic cooling**, a warm gas is brought into contact with a cold liquid, causing the gas to cool and some of the liquid to evaporate. Heat is transferred from the gas to the liquid but no heat is transferred between the gas–liquid system and its surroundings (hence "adiabatic" cooling). Some common processes of this type are described below.

- ***Spray cooling, spray humidification.*** Liquid water is sprayed into a relatively dry warm stream of air. Some of the water evaporates, and the temperature of the air and of the unevaporated liquid both decrease. If the object is to cool the water or the air, the operation is called spray cooling; if the point is to increase the moisture content of the air, the operation is spray humidification.[13]
- ***Spray dehumidification.*** Warm humid air is *de*humidified by spraying cold water into it. Provided that the liquid temperature is low enough, the air is cooled below its dew point, causing some of the water vapor in it to condense.
- ***Drying.*** Hot air is blown over wet solids—for example, over a wet cake deposited in a filter or centrifuge. The water evaporates, leaving a dry solid product. Drying is the last step in the production of most crystalline products and powders, including many pharmaceuticals and food products.
- ***Spray drying.*** A suspension of small solid particles in water is sprayed as a fine mist into a stream of hot air. The water evaporates, larger solid particles settle out of the air and are removed by a conveyor, and fine suspended particles are separated from the air by a bag filter or cyclone separator. Dried milk is produced in this manner.

Writing material and energy balances on an adiabatic cooling operation is a straightforward but cumbersome procedure. It can be shown, however, that if certain well-justified assumptions are made (we will state them later), *air undergoing adiabatic cooling through contact with liquid water moves along a constant wet-bulb temperature line on the psychrometric chart from its initial condition to the 100% relative humidity curve*. Further cooling of the air below its saturation temperature leads to condensation and hence dehumidification.



This result (which is not at all obvious) allows us to perform adiabatic cooling calculations with relative ease using the psychrometric chart. First locate the initial state of the air on the

[13] Spraying the water into the air rather than simply blowing air over a water surface provides a large liquid surface-to-volume ratio, greatly increasing the evaporation rate.

chart; then locate the final state on the constant wet-bulb temperature line that passes through the initial state (or on the 100% humidity curve if cooling below the *adiabatic saturation temperature* (T_{as}) takes place); and finally perform whatever material and energy balance calculations are required. Example 8.4-7 illustrates such a calculation for an adiabatic humidification operation.

Example 8.4-7 Adiabatic Humidification

Equipment Encyclopedia
humidifer–water spray
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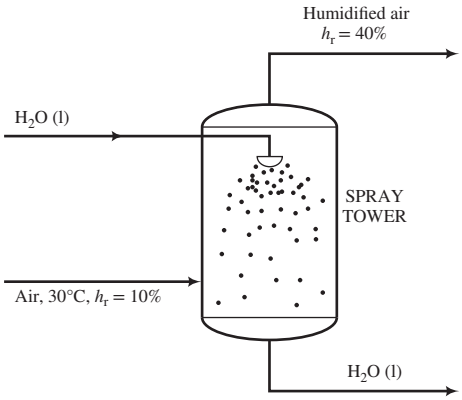
A stream of air at 30°C and 10% relative humidity is humidified in an adiabatic spray tower operating at $P \approx 1$ atm. The emerging air is to have a relative humidity of 40%.



1. Determine the absolute humidity and the adiabatic saturation temperature of the entering air.
2. Use the psychrometric chart to calculate (i) the rate at which water must be added to humidify 1000 kg/h of the entering air, and (ii) the temperature of the exiting air.

Solution We assume that the heat required to raise the temperature of the liquid in the spray tower is negligible compared with the heat of vaporization of water, so that the air follows an adiabatic saturation curve (constant wet-bulb temperature line) on the psychrometric chart.

1. Air at 30°C, 10% relative humidity

   ⇓ Figure 8.4-1

   $h_a = 0.0026$ kg H_2O/kg DA

   $T_{wb} = T_{as} = 13.2$°C

2. The state of the outlet air must lie on the $T_{wb} = 13.2$°C line. From the intersection of this line with the curve for $h_r = 40\%$, the absolute humidity of the exit gas is determined to be 0.0063 kg H_2O/kg DA. The inlet (and outlet) flow rate of dry air, $\dot{m}_{DA}$, is

   $$\dot{m}_{DA} = (1000 \text{ kg air/h})(1 \text{ kg DA}/1.0026 \text{ kg air}) = 997.4 \text{ kg DA/h}$$

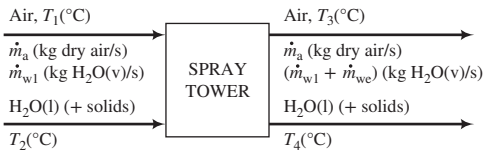
   The amount of water that must be evaporated, $\dot{m}_{H_2O}$, may be calculated as the difference between the outlet and inlet water flow rates in the air stream.

   $$\dot{m}_{H_2O} = (997.4 \text{ kg DA/h})(0.0063 - 0.0026)\frac{\text{kg } H_2O}{\text{kg DA}}$$

   $$= \boxed{3.7 \text{ kg } H_2O/\text{h}}$$

   From Figure 8.4-1 the temperature of the exiting air is $\boxed{21.2°\text{C}}$.

A complete justification of the procedure given above is beyond the scope of this text,[14] but we can at least offer a partial explanation. A flowchart of an adiabatic cooling operation is shown below. A stream of warm air and either a stream of liquid water (spray cooling or spray humidification), a wet solid (drying), or a solid suspension (spray drying) are brought into contact. The air enters at T_1 and leaves at T_3, the water and any solids enter at T_2 and leave at T_4, and entering liquid water evaporates at a rate $\dot{m}_{we}$(kg/s).



We assume:

1. $(C_p)_{air}$, $(C_p)_{H_2O}$, and $(\Delta\hat{H}_v)_{H_2O}$ are independent of temperature at the process conditions.
2. The enthalpy changes undergone by the unevaporated liquid water and the solid (if there is one) in going from T_2 to T_4 are negligible compared to the changes undergone by the entering wet air and the evaporated water.
3. The heat required to raise liquid water from T_2 to T_3 is negligible compared to the heat of vaporization of water.

If the energy balance equation ($\Delta\dot{H} = 0$) is written for this process and these three assumptions are made, the simplified equation becomes

$$\dot{m}_a(C_p)_{air}(T_3 - T_1) + \dot{m}_{w1}(C_p)_{H_2O(v)}(T_3 - T_1) + \dot{m}_{we}(\Delta\hat{H}_v)_{H_2O} = 0$$

$$\Downarrow$$

$$\frac{\dot{m}_{we}}{\dot{m}_a} = \frac{1}{(\Delta\hat{H}_v)_{H_2O}}\left[(C_p)_{air} + \frac{\dot{m}_{w1}}{\dot{m}_a}(C_p)_{H_2O(v)}\right](T_1 - T_3) \qquad \textbf{(8.4-9)}$$

Suppose now that the temperature T_1 and absolute humidity $\dot{m}_{w1}/\dot{m}_a$ of the inlet air are specified, so that the state of the inlet air is fixed on the psychrometric chart. If we specify in addition the outlet air temperature $T_3 (< T_1)$, then $\dot{m}_{we}/\dot{m}_a$ may be calculated from Equation 8.4-9, and it may in turn be used to calculate the absolute humidity of the outlet air, $(\dot{m}_{we} + \dot{m}_{w1})/\dot{m}_a$.

The outlet temperature and humidity determined in this manner are represented by a point on the psychrometric chart. If a lower value of T_3 is assumed, a higher outlet humidity would be calculated, yielding another point on the chart. The set of all such points for a specified T_1 and $\dot{m}_{w1}/\dot{m}_a$ defines a curve on the chart, known as the **adiabatic saturation curve**. *If the three stated assumptions are valid, the final state of air undergoing an adiabatic humidification must lie on the adiabatic saturation curve that passes through the inlet state on the psychrometric chart.*

If the outlet temperature T_3 is low enough, the air leaves saturated with water. The temperature corresponding to this condition is the adiabatic saturation temperature and is found at the intersection of the adiabatic saturation curve with the 100% relative humidity curve.

[14] One can be found in W. L. McCabe, J. C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering,* 7th Edition, McGraw-Hill, New York, 2004, Chap. 19.

The psychrometric chart for most gas–liquid systems would show a family of adiabatic saturation curves in addition to the families of curves shown on Figures 8.4-1 and 8.4-2. However, *for the air–water system at 1 atm, the adiabatic saturation curve through a given state coincides with the constant wet-bulb temperature line through that state, so that* $T_{as} = T_{wb}$. The simple material and energy balance procedure for adiabatic cooling outlined in this section is possible only because of this coincidence.

Test Yourself

(Answers, p. 659)

1. **(a)** Under what conditions do the temperature and humidity of a gas undergoing adiabatic cooling follow a unique curve on the psychrometric chart, regardless of the entering liquid temperature?
   (b) Does this curve coincide with a constant wet-bulb temperature line if the gas is air and the liquid is water?
   (c) What if they were nitrogen and acetone?
2. Air at 26°C with a relative humidity of 10% undergoes an adiabatic humidification. Use Figure 8.4-1 to estimate the adiabatic saturation temperature of the air. If the exiting air has a dry-bulb temperature of 14°C, determine its absolute humidity, relative humidity, and specific enthalpy.

8.5 MIXING AND SOLUTION

You may have carried out an experiment in a chemistry laboratory in which you mixed two liquids (such as concentrated sulfuric acid and water) or dissolved a solid in a liquid (such as sodium hydroxide in water) and observed that the mixture or solution became quite hot. The question is: Why?

When two different liquids are mixed or when a gas or solid is dissolved in a liquid, bonds are broken between neighboring molecules—and possibly between atoms—of the feed materials, and new bonds are formed between neighboring molecules or ions in the product solution. If less energy is required to break the bonds in the feed materials than is released when the solution bonds form, a net release of energy results. Unless this energy is transferred from the solution to its surroundings as heat, it goes into raising the solution temperature, which is what happened in the experiments described in the first paragraph.

Suppose you mix 1 mol of pure liquid sulfuric acid with water at a specified temperature and pressure and then cool the mixture at constant pressure to bring it back to the initial temperature. The energy balance for this constant-pressure process is

$$Q = \Delta H = H_{H_2SO_4(aq)} - (H_{H_2SO_4(l)} + H_{H_2O})$$

where ΔH—the difference between the enthalpy of the solution at the specified temperature and pressure and the total enthalpy of the pure solute and solvent at the same T and P—is the *heat of solution* at that temperature and pressure. For the sulfuric acid dilution, we know $Q < 0$ (the container must be cooled to keep the solution temperature from rising) and so it follows that ΔH—the heat of solution—is negative for this process.

An **ideal mixture** is one for which the heat of mixing or solution is negligible and so $H_{mixture} \approx \sum n_i \hat{H}_i$, where n_i is the amount of mixture component i and $\hat{H}_i$ is the specific enthalpy of the pure component at the temperature and pressure of the mixture. Up to now in this text, we have assumed ideal-mixture behavior for all mixtures and solutions. This assumption works well for nearly all gas mixtures and for liquid mixtures of similar compounds (such as mixtures of paraffins or of aromatics), but for other mixtures and solutions—such as aqueous solutions of strong acids or bases or certain gases (such as hydrogen chloride) or solids (such as sodium hydroxide)—heats of solution should be included in energy balance calculations. This section outlines the required procedures.

8.5a Heats of Solution and Mixing

The **heat of solution** $\Delta\hat{H}_s(T, r)$ is defined as the change in enthalpy for a process in which 1 mole of a solute (gas or solid) is dissolved in r moles of a liquid solvent at a constant temperature T. As r becomes large, $\Delta\hat{H}_s$ approaches a limiting value known as the **heat of solution at infinite dilution**. The **heat of mixing** has the same meaning as the heat of solution when the process involves mixing two fluids rather than dissolving a gas or solid in a liquid.

Perry's Chemical Engineers' Handbook (see Footnote 5) on pp. 2-203 through 2-206 gives heats of solution of various substances in water at either 18°C or "room temperature," which is roughly 25°C. *Caution:* The values given in the *Handbook* are evolved heats and thus negatives of the heats of solution $(-\Delta\hat{H}_s)$.

As an illustration of how to use these data, suppose you wish to calculate ΔH for a process in which 2 mol of potassium cyanide (KCN) is dissolved in 400 mol of water at 18°C. First, calculate the moles of solvent per mole of solute:

$$r = 400/2 = 200 \text{ mol } H_2O/\text{mol KCN}$$

The value of $-\Delta H_s$ (18°C, $r = 200$) is listed as -3.0 kcal/mol (meaning per mol of KCN dissolved). The total enthalpy change is therefore

$$\Delta H = n\Delta\hat{H}_s = \frac{2.0 \text{ mol KCN}}{\text{mol KCN}} \left| \frac{3.0 \text{ kcal}}{\text{mol KCN}} \right. = +6.0 \text{ kcal}$$

Table B.11 lists values of the heats of solution at 25°C of HCl(g) and NaOH(s) in water, and the heat of mixing at 25°C of H_2SO_4(l) and water. Heats of solution such as those given in Table B.11 may be used to determine directly the specific enthalpies of solutions at 25°C relative to the pure solute and solvent at this temperature. Another common choice of reference conditions, however, is the pure solvent and an infinitely dilute solution at 25°C.

Consider, for example, a hydrochloric acid solution for which $r = 10$ moles H_2O/mole HCl. From Table B.11, the specific enthalpy of this solution relative to pure HCl(g) and H_2O(l) at 25°C is $\Delta\hat{H}_s(r = 10) = -69.49$ kJ/mol HCl. Now, the enthalpy of the solution relative to H_2O(l) and a highly dilute solution of HCl (say, $r = 10^6$ moles H_2O/mole HCl) is the enthalpy change for the isothermal process

$$\left\{ \begin{matrix} 1 \text{ mol HCl} \\ 10^6 \text{ mol } H_2O \end{matrix} \right\} \xrightarrow{25°C} \left\{ \begin{matrix} 1 \text{ mol HCl} \\ 10 \text{ mol } H_2O \end{matrix} \right\} + (10^6 - 10) \text{ mol } H_2O(l)$$

We may evaluate this enthalpy change using any convenient reference state—in particular, taking pure HCl(g) and H_2O(l) at 25°C as references. In view of the latter choice, $\hat{H}$ for the $(10^6 - 10)$ moles of pure water equals zero, and the enthalpy change for the process is therefore

$$\begin{aligned} \Delta\hat{H} &= \Delta\hat{H}_s(r = 10) - \Delta\hat{H}_s(r = \infty) \\ &= (-69.49 + 75.14) \text{ kJ/mol HCl} = 5.65 \text{ kJ/mol HCl} \end{aligned}$$

In general, the enthalpy of a solution containing r moles H_2O/mole solute is for reference states of pure solute and solvent at 25°C and 1 atm

$$\boxed{\hat{H} = \Delta\hat{H}_s(r)} \qquad \textbf{(8.5-1)}$$

and for reference states of pure solvent and an infinitely dilute solution at 25°C and 1 atm

$$\boxed{\hat{H} = \Delta\hat{H}_s(r) - \Delta\hat{H}_s(\infty)} \qquad \textbf{(8.5-2)}$$

Note again that these enthalpies are expressed per mole of *solute*, not per mole of solution.

Test Yourself

(Answers, p. 659)

The heat of solution of a solute A in water at 25°C is −40 kJ/mol A for $r = 10$ mol H_2O/mol A and −60 kJ/mol A for infinite dilution.

1. What is the specific enthalpy (kJ/mol A) of an aqueous solution of A for which $r = 10$ mol H_2O/mol A relative to
   (a) pure H_2O and A at 25°C?
   (b) pure H_2O and an infinitely dilute aqueous solution of A?
2. If 5 mol of A is dissolved in 50 mol of H_2O at 25°C, how much heat is evolved or absorbed? (State which, observing that $Q = \Delta H$ for this process.)
3. How much heat is evolved or absorbed if the solution prepared in question 2 is poured into a large tank of water at 25°C?

8.5b Balances on Dissolution and Mixing Processes

When setting up an energy balance on a process that involves forming, concentrating, or diluting a solution for which the heat of solution or mixing cannot be neglected, prepare an inlet–outlet enthalpy table considering the solution as a single substance and the pure components at 25°C as reference states. To calculate the enthalpy of the solution at a temperature $T \neq 25$°C, first calculate its enthalpy at 25°C from tabulated heat of solution data, then add the enthalpy change for the heating or cooling of the solution from 25°C to T. The enthalpy change for the latter step should be calculated from tabulated solution heat capacities if they are available [e.g., if they are listed on pp. 2-183 and 2-184 of *Perry's Chemical Engineers' Handbook* (see Footnote 5)]; otherwise, use the average heat capacity determined using Equation 8.3-13 for liquid mixtures or the heat capacity of the pure solvent for dilute solutions.

Example 8.5-1 Production of Hydrochloric Acid

Equipment Encyclopedia
absorber
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www.wiley.com/college/felder

Hydrochloric acid is produced by absorbing gaseous HCl (hydrogen chloride) in water. Calculate the heat that must be transferred to or from an absorption unit if HCl(g) at 100°C and H_2O(l) at 25°C are fed to produce 1000 kg/h of 20.0 wt% HCl(aq) at 40°C.

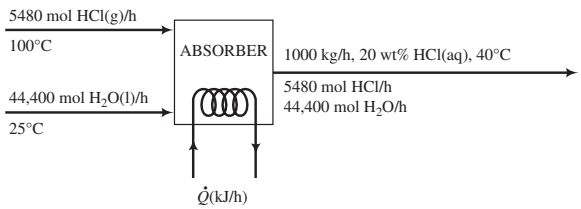
Solution

It is advisable to determine the molar amounts or flow rates of the components of all feed and product solutions before drawing and labeling the flowchart. In this case

1000 kg/h of 20.0 wt% HCl(aq)

$$\dot{n}_{HCl} = \frac{1000\ \text{kg}}{\text{h}} \left| \frac{0.200\ \text{kg HCl}}{\text{kg}} \right| \frac{10^3\ \text{mol}}{36.5\ \text{kg HCl}} = 5480\ \text{mol HCl/h}$$

$$\dot{n}_{H_2O} = \frac{1000\ \text{kg}}{\text{h}} \left| \frac{0.800\ \text{kg } H_2O}{\text{kg}} \right| \frac{10^3\ \text{mol}}{18.0\ \text{kg } H_2O} = 44{,}400\ \text{mol } H_2O/\text{h}$$



The enthalpy table for the process is shown below. As usual, physical property data valid at $P = 1$ atm are used and the effects on enthalpy of any pressure differences that may occur in the process are neglected.

Note that the value of $\dot{n}$ for the product solution is the molar flow rate of the *solute* (HCl) rather than the solution, since the enthalpy will be determined in kJ/mol solute.

References: HCl(g), H_2O(l) at 25°C and 1 atm

Substance	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
HCl(g)	5480 mol HCl	$\hat{H}_1$ (kJ/mol HCl)	—	—
H_2O(l)	44,400 mol H_2O	0	—	—
HCl(aq)	—	—	5480 mol HCl	$\hat{H}_2$ (kJ/mol HCl)

Calculate $\hat{H}_1$ and $\hat{H}_2$:

$$\text{HCl}(g, 25°C) \rightarrow \text{HCl}(g, 100°C)$$

$$\hat{H}_1 = \Delta\hat{H} = \int_{25°C}^{100°C} C_p\, dT$$

$$\Downarrow C_p \text{ for HCl(g) from Table B.2}$$

$$\hat{H}_1 = 2.178 \text{ kJ/mol}$$

For the product solution,

$$r = (44{,}400 \text{ mol } H_2O)/(5480 \text{ mol HCl}) = 8.10$$

$$\text{HCl}(g, 25°C) + 8.10\, H_2O(1, 25°C) \xrightarrow{\Delta\hat{H}_a} \text{HCl}(aq, 25°C) \xrightarrow{\Delta\hat{H}_b} \text{HCl}(aq, 40°C)$$

$$\Delta\hat{H}_a = \Delta\hat{H}_s(25°C, r = 8.1) \xrightarrow{\text{Table B.11}} -67.4 \text{ kJ/mol HCl}$$

The heat capacities of aqueous hydrochloric acid solutions are listed on p. 2-183 of *Perry's Chemical Engineers' Handbook* (see Footnote 5) as a function of the mole fraction of HCl in the solution, which in our problem is

$$\frac{5480 \text{ mol HCl/h}}{(5480 + 44{,}400) \text{ mol/h}} = 0.110 \text{ mol HCl/mol}$$

$$\Downarrow$$

$$C_p = \frac{0.73 \text{ kcal}}{\text{kg} \cdot °C} \left| \frac{1000 \text{ kg solution}}{5480 \text{ mol HCl}} \right| \frac{4.184 \text{ kJ}}{\text{kcal}} = 0.557 \frac{\text{kJ}}{\text{mol HCl} \cdot °C}$$

$$\Delta\hat{H}_b = \int_{25°C}^{40°C} C_p\, dT = 8.36 \text{ kJ/mol HCl}$$

$$\Downarrow$$

$$\hat{H}_2 = \Delta\hat{H}_a + \Delta\hat{H}_b = (-67.4 + 8.36) \text{ kJ/mol HCl} = -59.0 \text{ kJ/mol HCl}$$

Energy Balance:

$$\dot{Q} = \Delta\dot{H} = \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$$

$$= (5480 \text{ mol HCl/h})(-59.0 \text{ kJ/mol HCl}) - (5480 \text{ mol HCl/h})(2.178 \text{ kJ/mol HCl})$$

$$= \boxed{-3.35 \times 10^5 \text{ kJ/h}}$$

Heat must be transferred out of the absorber at a rate of 335,000 kJ/h to keep the product temperature from rising above 40°C.

8.5c Enthalpy–Concentration Charts—Single Liquid Phase

Energy balance calculations on liquid-phase systems involving mixtures can be cumbersome when heats of mixing are significant. The calculations can be simplified for binary (two-component) systems by using an **enthalpy–concentration chart**, a plot of specific enthalpy versus mole fraction (or mole percent) or mass fraction (or weight percent) of one component. An $\hat{H}$-x chart for aqueous solutions of sulfuric acid at several temperatures is shown in Figure 8.5-1. The reference conditions for the plotted enthalpies are pure liquid H_2SO_4 at 77°F and liquid water at 32°F.

The points on the isotherms of Figure 8.5-1 were determined using the procedure outlined in the last section. Suppose, for example, you wish to calculate the specific enthalpy (Btu/lb_m) of a 40 wt% sulfuric acid solution at 120°F. If you know the heat of mixing of sulfuric acid at 77°F, the process path you would follow would be to bring pure liquid water from its reference temperature of 32°F to 77°F (the sulfuric acid starts at 77°F and so does not require this step), mix the two liquids at 77°F, bring the product solution to 120°F, and calculate and add the enthalpy changes for each of these steps.

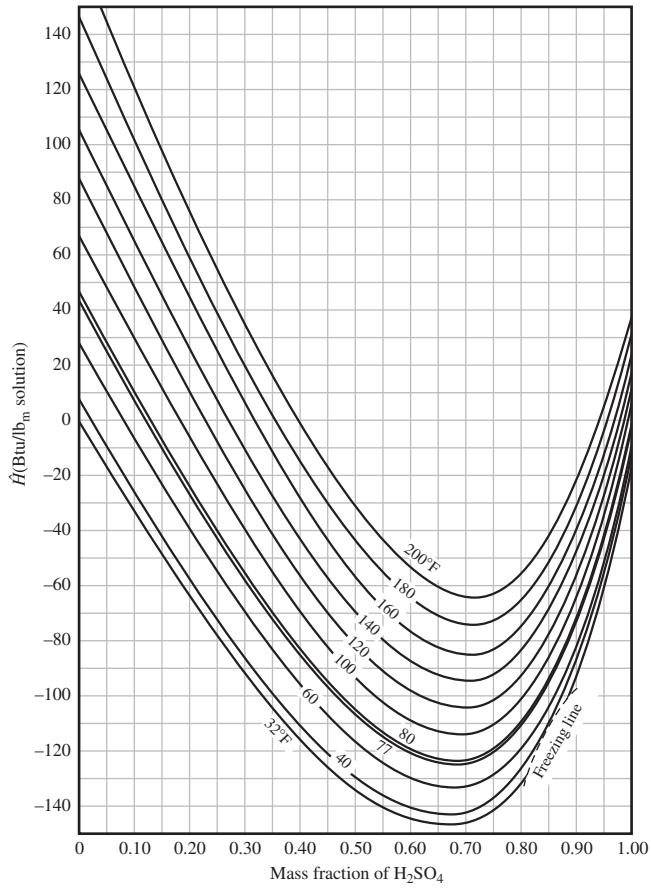


FIGURE 8.5-1 Enthalpy–concentration chart for H_2SO_4–H_2O. (Redrawn from the data of W. D. Ross, *Chem. Eng. Progr.*, **43**:314, 1952.)

Basis: 1 lb_m solution ($\Longrightarrow$ 0.40 lb_m H_2SO_4 = 4.08×10^{-3} lb-mole, 0.60 lb_m H_2O = 3.33×10^{-2} lb-mole)

- 0.60 lb_m H_2O(l, 32°F) → 0.60 lb_m H_2O (l,77°F)

$$\Delta H_1(\text{Btu}) = (0.60\ \text{lb}_\text{m}\ \text{H}_2\text{O})\left[\int_{32°\text{F}}^{77°\text{F}} (C_p)_{\text{H}_2\text{O}}\, dT\right]\left(\frac{\text{Btu}}{\text{lb}_\text{m}}\right)$$

The heat capacity of liquid water is approximately 1 Btu/(lb_m·°F).

- 0.40 lb_m H_2SO_4(77°F) + 0.60 lb_m H_2O (77°F) → 1.0 lb_m H_2SO_4 solution (aq, 77°F)

$$\Delta H_2(\text{Btu}) = (0.40\ \text{lb}_\text{m}\ \text{H}_2\text{SO}_4)\left[\Delta\hat{H}_s\left(77°\text{F}, r = 8.2\frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole H}_2\text{SO}_4}\right)\left(\frac{\text{Btu}}{\text{lb}_\text{m}\ \text{H}_2\text{SO}_4}\right)\right]$$

The heat of mixing can be determined from the data in Table B.11 to be −279 Btu/lb_m H_2SO_4.

- 1.0 lb_m H_2SO_4 solution (aq, 77°F) → 1.0 lb_m H_2SO_4 solution (aq, 120°F)

$$\Delta H_3(\text{Btu}) = (1.0\ \text{lb}_\text{m})\int_{77°\text{F}}^{120°\text{F}} (C_p)_{40\%\ \text{H}_2\text{SO}_4(\text{aq})}\, dT$$

The heat capacity of the 40% sulfuric acid solution is roughly 0.67 Btu/(lb_m·°F).[15]

- $\hat{H}(40\%\ \text{H}_2\text{SO}_4, 120°\text{F}) = \dfrac{(\Delta H_1 + \Delta H_2 + \Delta H_3)(\text{Btu})}{1.0\ \text{lb}_\text{m}\ \text{solution}} \approx \boxed{-56\ \text{Btu/lb}_\text{m}}$

(Verify that this is the value shown in Figure 8.5-1.)

If any reference temperature but 77°F had been chosen for sulfuric acid, another step would have been included in which H_2SO_4 was brought from T_{ref} to 77°F prior to mixing.

Once someone has gone to the trouble of preparing an enthalpy-concentration chart like that of Figure 8.5-1, energy balance calculations become relatively simple, as shown in Example 8.5-2.

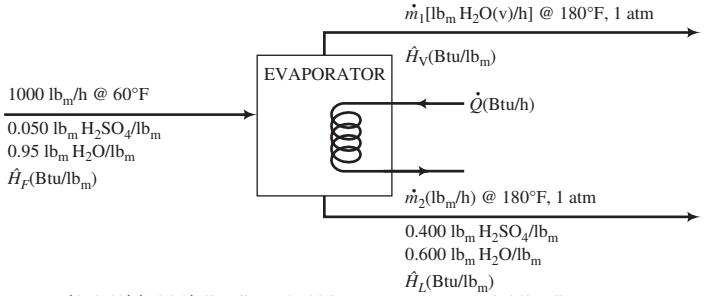
Example 8.5-2 Concentration of an Aqueous H_2SO_4 Solution

A 5.0 wt% H_2SO_4 solution at 60°F is to be concentrated to 40.0 wt% by evaporation of water. The concentrated solution and water vapor emerge from the evaporator at 180°F and 1 atm. Calculate the rate at which heat must be transferred to the evaporator to process 1000 lb_m/h of the feed solution.

Solution

Basis: Given Feed Rate of 5%

Equipment Encyclopedia
evaporator
@
www.wiley.com/college/felder



H_2SO_4 Balance: $(0.050)(1000)\ \text{lb}_\text{m}/\text{h} = 0.400\dot{m}_2 \Longrightarrow \dot{m}_2 = 125\ \text{lb}_\text{m}/\text{h}$

Total Mass Balance: $1000\ \text{lb}_\text{m}/\text{h} = \dot{m}_1 + \dot{m}_2 \xrightarrow{\dot{m}_2 = 125\ \text{lb}_\text{m}/\text{h}} \dot{m}_1 = 875\ \text{lb}_\text{m}/\text{h}$

Reference States for Energy Balance: H_2O(l, 32°F), H_2SO_4(l, 77°F)

[15] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008, p. 2-184.

From Figure 8.5-1:

$$\hat{H}_F = 10 \text{ Btu/lb}_\text{m} \quad (5\% \text{ H}_2\text{SO}_4 \text{ at } 60^\circ\text{F})$$
$$\hat{H}_L = -17 \text{ Btu/lb}_\text{m} \quad (40\% \text{ H}_2\text{SO}_4 \text{ at } 180^\circ\text{F})$$

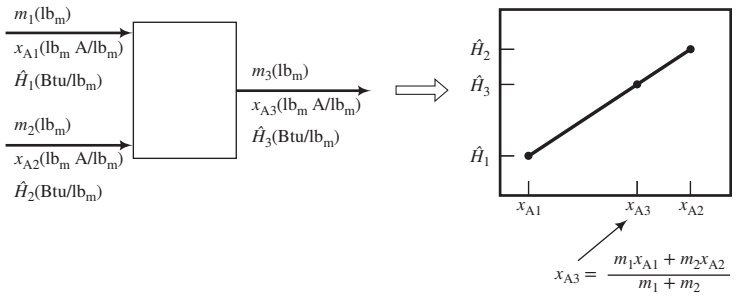
The enthalpy of water vapor at 180°F and 1 atm relative to liquid water at 32°F may be obtained from the steam tables in *Perry's Chemical Engineers' Handbook* (see Footnote 5) as

$$\hat{H}_\text{V} = 1138 \text{ Btu/lb}_\text{m}$$

Energy Balance:
$$\dot{Q} = \Delta\dot{H} = \dot{m}_1\hat{H}_V + \dot{m}_2\hat{H}_L - (1000 \text{ lb}_\text{m}/\text{h})\hat{H}_F$$
$$= [(875)(1138) + (125)(-17) - (1000)(10)] \text{ Btu/h}$$
$$= \boxed{984{,}000 \text{ Btu/h}}$$

Compare the ease of this computation with that of Example 8.5-1. Having the enthalpy–concentration chart eliminates the need for all of the hypothetical heating, cooling, and isothermal mixing steps that would normally be required to evaluate the total enthalpy change for the process.

Processes involving *adiabatic mixing* are particularly simple to analyze when an $\hat{H}$-x chart is available. Suppose x_A is the mass fraction of A in a mixture of two species, A and B, and that a mass m_1 of Solution 1 $(x_{\text{A}1}, \hat{H}_1)$ is mixed adiabatically with a mass m_2 of Solution 2 $(x_{\text{A}2}, \hat{H}_2)$. We will show that the condition of the product mixture, $(x_{\text{A}3}, \hat{H}_3)$, is on a straight line on the $\hat{H}$-x chart between the points corresponding to the feed stream conditions.



To prove this result, we write a total mass balance, a material balance on species A, and an energy balance ($\Delta H = 0$ for this constant-pressure batch process):

Total Mass Balance:
$$m_1 + m_2 = m_3 \tag{a}$$

A Balance:
$$m_1x_{\text{A}1} + m_2x_{\text{A}2} = m_3x_{\text{A}3} \tag{b}$$
$$\Downarrow \text{Substitute for } m_3 \text{ from (a), rearrange}$$
$$m_1(x_{\text{A}3} - x_{\text{A}1}) = m_2(x_{\text{A}2} - x_{\text{A}3}) \tag{c}$$

Energy Balance:
$$\Delta H = m_3\hat{H}_3 - m_1\hat{H}_1 - m_2\hat{H}_2 = 0$$
$$\Downarrow \text{Substitute for } m_3 \text{ from (a), rearrange}$$
$$m_1(\hat{H}_3 - \hat{H}_1) = m_2(\hat{H}_2 - \hat{H}_3) \tag{d}$$

Dividing (d) by (c) yields

$$\frac{\hat{H}_3 - \hat{H}_1}{x_{\text{A}3} - x_{\text{A}1}} = \frac{\hat{H}_2 - \hat{H}_3}{x_{\text{A}2} - x_{\text{A}3}} \tag{e}$$

Since the slope of the line segment from $(x_{\text{A}1}, \hat{H}_1)$ to $(x_{\text{A}3}, \hat{H}_3)$ (the left-hand side of this equation) equals the slope of the segment from $(x_{\text{A}3}, \hat{H}_3)$ to $(x_{\text{A}2}, \hat{H}_2)$ (the right-hand side) and the segments

have a point in common, the three points must lie on a straight line. The value of x_{A3} can be calculated from Equations a and b:

$$x_{A3} = \frac{m_1 x_{A1} + m_2 x_{A2}}{m_1 + m_2} \tag{8.5-3}$$

It follows that if two feed solutions of known masses and compositions (m_i, x_i, $i = 1, 2$) are mixed adiabatically and you have an $\hat{H}$-x chart, you may (i) calculate x_3 for the product mixture from Equation 8.5-3, (ii) draw a line connecting the points on the chart corresponding to the two feeds, and (iii) read the enthalpy and temperature of the product mixture from the point on the connecting line for which $x = x_3$.

Example 8.5-3 Adiabatic Mixing

Pure water at 60°F is mixed with 100 g of an aqueous 80 wt% H_2SO_4 solution, also at 60°F. The mixing vessel is insulated well enough to be considered adiabatic.

1. If 250 g H_2O is mixed with the acid, what will the final solution temperature be?
2. What is the maximum attainable solution temperature and how much water must be added to achieve it?

Solution

1. From Equation 8.5-3, the mass fraction of H_2SO_4 in the product solution is

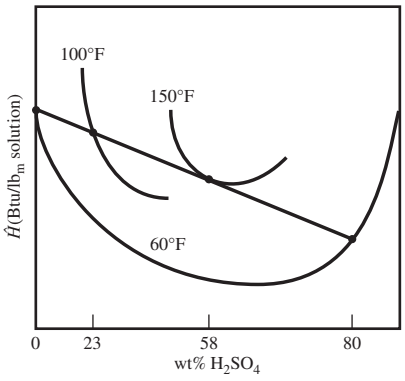
$$x_p = \frac{[(100)(0.80) + (250)(0)]\ \text{g } H_2SO_4}{(100 + 250)\ \text{g}} = 0.23\ \text{g } H_2SO_4/\text{g}$$

A straight line on Figure 8.5-1 between points at ($x = 0$, $T = 60$°F) and ($x = 0.80$, $T = 60$°F) goes through the point ($x = 0.23$, $\boxed{T \approx 100\text{°F}}$). (Verify this result.)

2. The line between ($x = 0$, $T = 60$°F) and ($x = 0.80$, $T = 60$°F) passes through a temperature maximum at roughly ($x \approx 0.58$, $\boxed{T \approx 150\text{°F}}$). (*Verify.*) From Equation 8.5-3,

$$0.58 = \frac{(100)(0.80)\ \text{g} + (m_w)(0)}{100\ \text{g} + m_w} \Longrightarrow \boxed{m_w = 38\ \text{g } H_2O}$$

The graphical construction of these solutions is illustrated below.



Test Yourself

(Answers, p. 659)

Use Figure 8.5-1 to answer the following questions.

1. What is the specific enthalpy of 80 wt% H_2SO_4(aq, 110°F) relative to pure H_2SO_4 at 77°F and pure water at 32°F?
2. The 100 wt% intercepts of the isotherms on Figure 8.5-1 are difficult to read. Which isotherm must have an intercept of 0 Btu/lb$_m$? (Your answer should be a temperature.)

3. Pure water at 32°F is used to dilute a 90 wt% H_2SO_4 solution (aq, 32°F). Estimate the maximum temperature the product solution can achieve and the concentration of sulfuric acid (wt%) in this solution.

4. Estimate (a) the specific enthalpy of a 30 wt% H_2SO_4 solution (aq, 77°F) and (b) the specific enthalpy of a 30 wt% solution obtained by mixing pure water at 77°F and pure sulfuric acid at 77°F adiabatically. What is the physical significance of the difference between these two enthalpies?

8.5d Using Enthalpy–Concentration Charts for Vapor–Liquid Equilibrium Calculations

Enthalpy–concentration charts are particularly useful for two-component systems in which vapor and liquid phases are in equilibrium. The Gibbs phase rule (Equation 6.2-1) specifies that such a system has $(2 + 2 - 2) = 2$ degrees of freedom. If as before we fix the system pressure, then specifying only one more intensive variable—the system temperature, or the mass or mole fraction of either component in either phase—fixes the values of all other intensive variables in both phases. An $\hat{H}$-x diagram for the ammonia–water system at 1 atm is shown in Figure 8.5-2. The specific enthalpies of aqueous solutions and gaseous mixtures of ammonia and water in equilibrium with each other are shown on the two curves on this figure. Each phase is said to be *saturated*.

Suppose the mass fraction of ammonia in a saturated liquid solution of NH_3 and H_2O at 1 atm is specified to be 0.25. According to the phase rule, the system temperature and the mass fraction of NH_3 in the vapor phase are uniquely determined by these specifications. (*Verify.*) A **tie line** may therefore be drawn on the enthalpy–concentration chart from $x = 0.25$ on the liquid-phase curve to the corresponding point on the vapor-phase curve, which experimental data have shown to be at

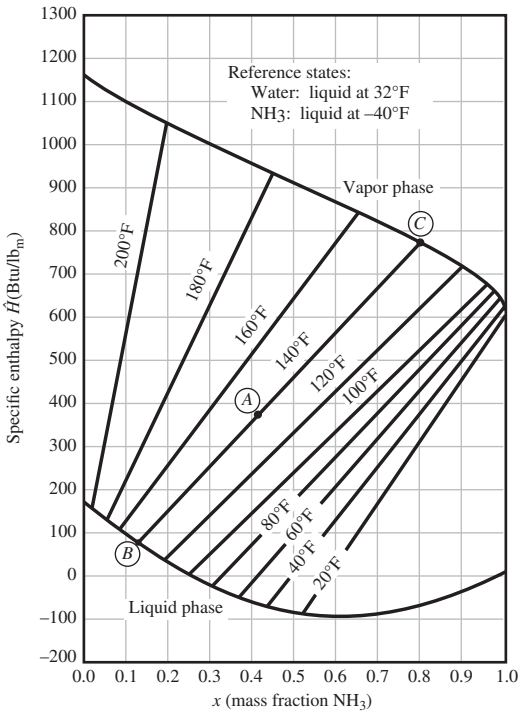


FIGURE 8.5-2 Enthalpy–concentration diagram for the ammonia–water system at 1 atm. (From G. G. Brown et al., *Unit Operations*, ©1950, Figure 551. Reprinted by permission of John Wiley & Sons.)

$y = 0.95$; the tie line may be labeled with the corresponding temperature, 100°F. Several tie lines constructed in this manner are shown in Figure 8.5-2; once drawn, the lines may be used to determine the equilibrium composition and the specific enthalpy of each phase at a specified temperature.

Example 8.5-4 Use of the Enthalpy–Concentration Chart for a Two-Phase System

An aqueous ammonia solution is in equilibrium with a vapor phase in a closed system at 160°F and 1 atm. The liquid phase accounts for 95% of the total mass of the system contents. Use Figure 8.5-2 to determine the weight percent of NH_3 in each phase and the enthalpy of the system per unit mass of the system contents.

Solution The mass fractions of ammonia and specific enthalpies of each phase may be read from the intersections of the 160°F tie line with the vapor and liquid equilibrium curves on Figure 8.5-2.

Liquid Phase: $\boxed{8\%\ NH_3, 92\%\ H_2O}$ $\quad \hat{H}_L = 110\ \text{Btu/lb}_\text{m}$

Vapor Phase: $\boxed{64\%\ NH_3, 36\%\ H_2O}$ $\quad \hat{H}_V = 855\ \text{Btu/lb}_\text{m}$

Basis: $1\ \text{lb}_\text{m}\ \text{total mass} \Longrightarrow 0.95\ \text{lb}_\text{m}\ \text{liquid}, 0.05\ \text{lb}_\text{m}\ \text{vapor}$

$$\hat{H}(\text{Btu/lb}_\text{m}) = \frac{0.95\ \text{lb}_\text{m}\ \text{liquid}}{\text{lb}_\text{m}} \left| \frac{110\ \text{Btu}}{\text{lb}_\text{m}} + \frac{0.05\ \text{lb}_\text{m}\ \text{vapor}}{\text{lb}_\text{m}} \right| \frac{855\ \text{Btu}}{\text{lb}_\text{m}}$$

$$= \boxed{147\ \text{Btu/lb}_\text{m}}$$

If the overall composition of a two-phase two-component system at a given temperature and pressure is known, the fraction of the system that is liquid or vapor may easily be determined from the enthalpy–concentration chart.

Suppose, for example, that a mixture of ammonia and water that is 40% NH_3 by mass is contained in a closed vessel at 140°F and 1 atm. Point *A* on Figure 8.5-2 corresponds to this condition. Since this point lies between the vapor and liquid equilibrium curves, the mixture separates into two phases whose compositions are found at the extremities of the 140°F tie line (points *B* and *C*).

In general, if *F*, *L*, and *V* are the total mass of the mixture, the mass of the liquid phase and the mass of the vapor phase, respectively, and x_F, x_L, and x_V are the corresponding mass fractions of NH_3, then

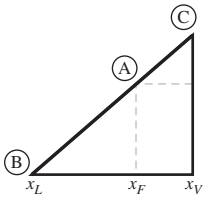
Total balance: $$F = L + V \tag{8.5-4}$$

NH_3 balance: $$x_F F = x_L L + x_V V \tag{8.5-5}$$

Substituting the expression of Equation 8.5-4 for *F* into Equation 8.5-5 and rearranging the result yields

$$\frac{L}{V} = \frac{x_V - x_F}{x_F - x_L} \tag{8.5-6}$$

The tie line in question appears as shown below:



From the properties of similar triangles, the right side of Equation 8.5-6 equals the ratio of distances $\overline{AC}/\overline{AB}$. We have thus proved the following general rule: if A, B, and C are the points on a tie line corresponding to the total mixture, the liquid phase, and the vapor phase, respectively, and if F, L, and V are the corresponding masses, then the liquid-to-vapor mass ratio is

$$\frac{L}{V} = \frac{x_V - x_F}{x_F - x_L} = \frac{\overline{AC}}{\overline{AB}} \tag{8.5-7}$$

This is the *lever rule*. It is also not difficult to prove that the mass fractions of the liquid and vapor phases are

$$\frac{L}{F} = \frac{x_V - x_F}{x_V - x_L} = \frac{\overline{AC}}{\overline{BC}} \tag{8.5-8}$$

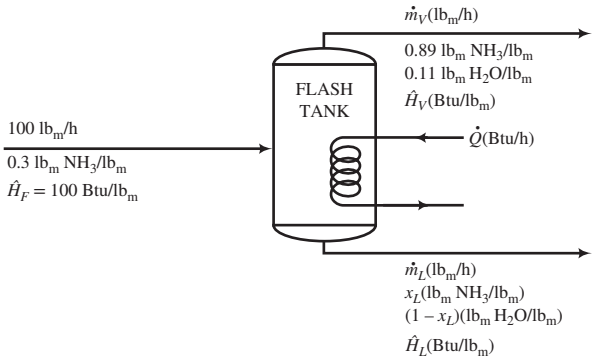
$$\frac{V}{F} = \frac{x_F - x_L}{x_V - x_L} = \frac{\overline{AB}}{\overline{BC}} \tag{8.5-9}$$

Once you have located the total mixture on the chart from a specified set of feed conditions, it becomes a simple matter to determine the compositions, enthalpies, and relative proportions of each phase, calculations that would take much more time in the absence of the chart.

Example 8.5-5 Equilibrium Flash Vaporization

A 30 wt% NH_3 solution at 100 psia is fed at a rate of 100 lb_m/h to a tank in which the pressure is 1 atm. The enthalpy of the feed solution relative to the reference conditions used to construct Figure 8.5-2 is 100 Btu/lb_m. The vapor composition is to be 89 wt% NH_3. Determine the temperature of the stream leaving the tank, the mass fraction of NH_3 in the liquid product, the flow rates of the liquid and vapor product streams, and the rate at which heat must be transferred to the vaporizer.

Solution Basis: 100 lb_m/h Feed



From Figure 8.5-2,

$$x_V = 0.89 \text{ lb}_m \text{ NH}_3/\text{lb}_m$$

$$\boxed{T = 120°\text{F}}$$

$$\boxed{x_L = 0.185 \text{ lb}_m \text{ NH}_3/\text{lb}_m}$$

$$\hat{H}_V = 728 \text{ Btu/lb}_m$$

$$\hat{H}_L = 45 \text{ Btu/lb}_m$$

From Equation 8.5-8

$$\frac{\dot{m}_L}{100\ \text{lb}_\text{m}/\text{h}} = \frac{x_V - x_F}{x_V - x_L}$$

$$\Downarrow$$

$$\dot{m}_L = (100\ \text{lb}_\text{m}/\text{h})\frac{0.89 - 0.30}{0.89 - 0.185} = \boxed{84\ \text{lb}_\text{m}/\text{h liquid product}}$$

$$\dot{m}_V = (100 - 84)\ \text{lb}_\text{m}/\text{h} = \boxed{16\ \text{lb}_\text{m}/\text{h vapor product}}$$

Energy Balance: $\dot{Q} = \Delta\dot{H} = \dot{m}_V\hat{H}_V + \dot{m}_L\hat{H}_L - 100\hat{H}_F$

$$= [(16)(728) + (84)(45) - (100)(100)]\ \text{Btu/h} = \boxed{5400\ \text{Btu/h}}$$

Test Yourself (Answers, p. 659)

Use Figure 8.5-2 for the following calculations.

1. Estimate (a) the temperature at which the mass fraction of NH_3 in the vapor phase of a two-phase system equals 0.85, and (b) the corresponding liquid-phase NH_3 mass fraction.
2. What is the heat of vaporization of NH_3 at its normal boiling point?
3. If an NH_3–H_2O mixture whose overall composition is 50% NH_3–50% H_2O is in equilibrium at 120°F, what fraction of the mixture is a vapor?

8.6 SUMMARY

An integral energy balance (the first law of thermodynamics) for a closed constant-volume system with no kinetic or potential energy changes ($\Delta E_\text{k} = 0$, $\Delta E_\text{p} = 0$) and no energy transferred in or out as work ($W = 0$) is

$$Q = \Delta U = \sum_{\text{final}} n_i\hat{U}_i - \sum_{\text{initial}} n_i\hat{U}_i$$

For a closed system expanding or contracting against a constant external pressure, the balance is

$$Q = \Delta H = \sum_{\text{final}} n_i\hat{H}_i - \sum_{\text{initial}} n_i\hat{H}_i$$

For an open system at steady state with negligible kinetic and potential energy changes from inlet to outlet and no energy transfer as shaft work, the balance is

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{outlet}} \dot{n}_i\hat{H}_i - \sum_{\text{inlet}} \dot{n}_i\hat{H}_i$$

In these equations n is the amount (mass or moles) of a species in one of its initial or final states in the process, $\dot{n}$ is the flow rate (mass or molar) of a species in a continuous stream entering or leaving the process, and $\hat{U}$ and $\hat{H}$ are respectively the specific internal energy and specific enthalpy of a species in a process state relative to a specified reference state for the same species.

This chapter presents formulas and methods for evaluating $\hat{U}$ and $\hat{H}$ (and hence ΔU, ΔH, and $\Delta\dot{H}$) when tables of internal energies and enthalpies are not readily available. Here is the general procedure:

1. Choose a reference state (phase, temperature, and pressure) for each species involved in a process.
2. Choose a path from the reference state to each initial and final (or inlet and outlet) process state for each species, and evaluate $\hat{U}_i$ (or $\hat{H}_i$) as $\Delta\hat{U}$ (or $\Delta\hat{H}$) for the transition from the reference state to the process state.
3. Once all of the $\hat{U}_i$ (or all $\hat{H}_i$) values are determined in this manner and all of the n_i (or all $\dot{n}_i$) values are determined from material balances, densities or equations of state, and phase equilibrium relations, calculate ΔU, ΔH, or $\Delta\dot{H}$ and substitute the result in the energy balance to determine whichever variable is unknown (usually the heat, Q, or heat transfer rate, $\dot{Q}$).

Following are points regarding the implementation of this procedure for various types of processes. Each step can be conveniently carried out on a spreadsheet.

- Energy balance calculations for a system (a process unit or combination of units) are conveniently organized through the construction of an *inlet–outlet internal energy table* (or *enthalpy table*). The table lists n (or $\dot{n}$) and $\hat{U}$ (*or* $\hat{H}$) for each species at each state (phase, temperature, pressure) in which the species is found in process streams. Once all of these variable values have been determined and inserted in the table, the subsequent evaluation of ΔU, ΔH, or $\Delta\dot{H}$ is straightforward.
- The fact that internal energy and enthalpy are *state properties* means that any convenient process path from a reference state to a process state may be chosen, even if the actual process

proceeds by a different path. As a rule, you would choose a path that allows you to make use of heat capacities, phase transition temperatures, and latent heats tabulated in an available reference (such as this text).

- *Changes in pressure at constant temperature.* For a species undergoing an isothermal pressure change, ΔP,

  $\Delta\hat{U} \approx 0$ for solids, liquids, and nearly ideal gases. For ideal gases, $\Delta\hat{U} = 0$.

  $\Delta\hat{H} \approx \hat{V}\Delta P$ for solids and liquids, where $\hat{V}$ is the (presumably constant) specific volume of the solid or liquid.

  $\Delta\hat{H} \approx 0$ for nearly ideal gases or for moderately small pressure changes (on the order of a few atmospheres). For ideal gases, $\Delta\hat{H} = 0$.

  If gases are at conditions at which they are far from ideal or if they undergo large pressure changes, you must either use tables of thermodynamic properties (such as the steam tables for water) or thermodynamic correlations beyond the scope of this text to determine $\Delta\hat{U}$ or $\Delta\hat{H}$.

- *Changes in temperature.* The specific internal energy of a species increases with increasing temperature. If a species is heated at constant volume and $\hat{U}$ is plotted versus T, the slope of the resulting curve is the *heat capacity at constant volume* of the species, $C_v(T)$, or $C_v = (\partial\hat{U}/\partial T)_{\text{constant }\hat{V}}$. If a species undergoes a change in temperature from T_1 to T_2 without changing phase,

$$\Delta\hat{U} \approx \int_{T_1}^{T_2} C_v(T)\,dT$$

  This equation is

  (a) exact for an ideal gas, even if $\hat{V}$ changes during the heating or cooling process. (For an ideal gas, $\hat{U}$ does not depend on $\hat{V}$.)

  (b) a good approximation for a solid or liquid.

  (c) valid for a nonideal gas only if $\hat{V}$ is constant.

- The specific enthalpy of a species ($\hat{H} = \hat{U} + P\hat{V}$) also increases with increasing temperature. If a species is heated at constant pressure and $\hat{H}$ is plotted versus T, the slope of the resulting curve is the *heat capacity at constant pressure* of the species, $C_p(T)$, or $C_p = (\partial\hat{H}/\partial T)_{\text{constant }P}$. It follows that if a *gas* undergoes a change in temperature from T_1 to T_2, with or without a concurrent change in pressure,

$$\Delta\hat{H} \approx \int_{T_1}^{T_2} C_p(T)\,dT$$

  This equation is

  (a) exact for an ideal gas, even if P changes during the heating or cooling process. (For an ideal gas, $\hat{H}$ does not depend on P.)

  (b) valid for a nonideal gas only if P is constant.

  If a liquid or solid undergoes a temperature change from T_1 to T_2 and a simultaneous pressure change, ΔP, then

$$\Delta\hat{H} \approx \hat{V}\Delta P + \int_{T_1}^{T_2} C_p(T)\,dT$$

- Table B.2 lists coefficients of polynomial expressions for $C_p(T)$[kJ/(mol·°C)] at $P = 1$ atm. The expressions should be accurate for solids, liquids, and ideal gases at any pressure and for nonideal gases only at 1 atm.

- To determine an expression or value for $C_v(T)$ from a known expression or value for $C_p(T)$, use one of the following relationships:

  Liquids and Solids: $C_v \approx C_p$

  Ideal Gases: $C_v = C_p - R$

  where R is the gas constant. Since the degree unit in the denominator of the heat capacity is a temperature interval, R can be subtracted directly from the expressions for C_p in Table B.2.

- The heat capacity of a solid or liquid can be estimated in the absence of tabulated data using *Kopp's rule* (Section 8.3c).

- If only tabulated values of C_p or C_v at discrete temperatures are available, the integrals in the expressions for $\Delta\hat{U}$ and $\Delta\hat{H}$ must be evaluated by *numerical integration*, using formulas such as those given in Appendix A.3.

- *Phase changes at constant temperature and pressure. Latent heats* are changes in specific enthalpy associated with phase changes at constant T and P. For example, the *latent heat of fusion* (more commonly, the *heat of fusion*), $\Delta\hat{H}_m(T, P)$, is the enthalpy change for the process in which a solid at temperature T and pressure P becomes a liquid at the same temperature and pressure, and the *heat of vaporization*, $\Delta\hat{H}_v(T, P)$, is $\Delta\hat{H}$ for the process in which a liquid at T and P becomes a vapor at the same T and P.

- Table B.1 lists *standard heats of fusion and vaporization* for a number of species, or $\Delta\hat{H}_m$ and $\Delta\hat{H}_v$ at the normal melting and boiling point temperatures ($P = 1$ atm), which are also listed in Table B.1. If latent heat data are not available for a species, $\Delta\hat{H}_m$ and $\Delta\hat{H}_v$ may be estimated using formulas given in Section 8.4b.

- You can use the formulas given above to determine the specific enthalpy of any species in one state relative to that species in any other state. For example, to calculate $\hat{H}$ for benzene vapor at temperature 300°C and 15 atm relative to solid benzene at a reference state of −20°C and 1 atm, you would carry out the following steps.

  1. Heat the solid from the reference temperature (−20°C) to its normal melting point T_m, which from Table B.1 is 5.53°C.

$$\Delta\hat{H}_1 = \int_{0°C}^{5.53°C} (C_p)_{\text{solid}}\,dT$$

  $(C_p)_{\text{solid}}$ is not listed in Table B.2, so it must either be found elsewhere or estimated using Kopp's rule. The latter provides a crude approximation but a very reasonable one to make in this case, considering how little this step will contribute to the overall enthalpy change.

  2. Melt the solid at T_m. $\Delta\hat{H}_2 = \Delta\hat{H}_m(5.53°C)$, which from Table B.1 is 9.837 kJ/mol.

3. Heat the liquid from T_m to the normal boiling point, T_b, which from Table B.1 is 80.10°C.

$$\Delta\hat{H}_3 = \int_{5.53°C}^{80.1°C} (C_p)_{\text{liquid}}\, dT$$

A polynomial formula for $(C_p)_{\text{liquid}}$ is given in Table B.2. Since it applies to T expressed in kelvins, the limits of the integral should be changed to their kelvin equivalents.

4. Vaporize the liquid at T_b. $\Delta\hat{H}_4 = \Delta\hat{H}_v(80.1°C)$, which from Table B.1 is 30.765 kJ/mol.
5. Heat the vapor from T_b to 300°C.

$$\Delta\hat{H}_5 = \int_{80.1°C}^{300°C} (C_p)_{\text{vapor}}\, dT$$

A formula for $(C_p)_{\text{vapor}}$ is given in Table B.2.

6. Bring the vapor from 1 atm to 15 atm at 300°C. $\Delta\hat{H}_6 \approx 0$ as long as the vapor behaves like an ideal gas, which it would at this high temperature.
7. Add the enthalpy changes for each of the preceding steps to calculate the desired specific enthalpy.

- The *psychrometric chart* (or *humidity chart*) contains values of a number of process variables for air–water vapor systems at 1 atm. The values listed on the chart include *dry-bulb temperature* (the temperature measured by common temperature-measurement instruments), *moisture content* or *absolute humidity* (mass ratio of water vapor to dry air), *relative humidity, humid volume* (volume per mass of dry air), *wet-bulb temperature* (the equilibrium temperature reading on a thermometer with a water-saturated wick around the bulb immersed in a flowing stream of humid air), and *enthalpy per mass of dry air.* If you know the values of any two of these variables for humid air at or near 1 atm, you can use the chart to determine the values of the other four, which can greatly simplify material and energy balance calculations.
- In *adiabatic cooling* operations, a stream of warm gas is brought into contact with a stream of cold liquid, causing the gas to cool and some liquid to evaporate. If (a) the gas is dry or humid air, the liquid is water, and the process takes place at about 1 atm, (b) the process is adiabatic, (c) the heat capacities of liquid water, water vapor, and air can be considered constant over the temperature range of the process, and (d) enthalpy changes associated with temperature changes of the liquid may be neglected, then the final state of the air must lie on the same wet-bulb temperature line as the state of the inlet air on the psychrometric chart.
- An enthalpy change known as the *heat of mixing* or *heat of solution* is associated with the mixing of certain liquids (like acids and water) and the dissolving of some gases or solids in a liquid solvent at a given temperature and pressure. An *ideal solution* is one for which the heat of mixing or solution is negligible, so that the enthalpy of the solution is the sum of the enthalpies of the pure solution components at the same temperature and pressure. All gas mixtures are ideal, as are mixtures of structurally similar liquid compounds (like benzene, toluene, and xylene). Table B.11 gives heats of mixing at 25°C and 1 atm for aqueous sulfuric acid solutions and heats of solution at the same temperature and pressure for aqueous solutions of HCl(g) (hydrochloric acid) and NaOH(s) (caustic soda).
- To perform energy balance calculations on processes involving nonideal solutions, take the pure components at 25°C as references. To determine the specific enthalpy of a feed or product solution, look it up on an *enthalpy–concentration chart* if one is available (e.g., Figure 8.5-1 for sulfuric acid solutions or Figure 8.5-2 for aqueous ammonia solutions). Otherwise, form the solution at 25°C [$\Delta\hat{H} = \Delta\hat{H}_s(25°C)$] and heat or cool it to its state in the process $\left(\Delta\hat{H} = \int_{25°C}^{T} C_p\, dT\right)$. For the latter step, either find heat capacity data for the solution or (for dilute solutions) assume that the heat capacity is that of the pure solvent.

PROBLEMS

8.1. The specific internal energy of formaldehyde (HCHO) vapor at 1 atm and moderate temperatures is given by the formula

$$\hat{U}(\text{J/mol}) = 25.96T + 0.02134T^2$$

where T is in °C.

(a) Calculate the specific internal energies of formaldehyde vapor at 0°C and 200°C. What reference temperature was used to generate the given expression for $\hat{U}$?

(b) The value of $\hat{U}$ calculated for 200°C is not the true value of the specific internal energy of formaldehyde vapor at this condition. Why not? (*Hint:* Refer back to Section 7.5a.) Briefly state the physical significance of the calculated quantity.

(c) Use the closed system energy balance to calculate the heat (J) required to raise the temperature of 3.0 mol HCHO at constant volume from 0°C to 200°C. List all of your assumptions.

(d) From the definition of heat capacity at constant volume, derive a formula for $C_v(T)$[J/(mol·°C)]. Then use this formula and Equation 8.3-6 to calculate the heat (J) required to raise the temperature of 3.0 mol of HCHO(v) at constant volume from 0°C to 200°C. [You should get the same result you got in Part (c).]

8.2. The heat capacity at constant pressure of hydrogen cyanide is given by the expression

$$C_p[\text{J/(mol}\cdot\text{°C)}] = 35.3 + 0.0291T(\text{°C})$$

(a) Write an expression for the heat capacity at constant volume for HCN, assuming ideal-gas behavior.

(b) Calculate $\Delta\hat{H}$(J/mol) for the constant-pressure process

$$\text{HCN(v, 25°C, 0.80 atm)} \rightarrow \text{HCN(v, 200°C, 0.80 atm)}$$

(c) Calculate $\Delta\hat{U}$(J/mol) for the constant-volume process

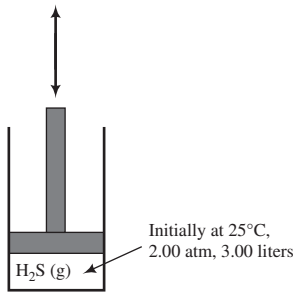
$$\text{HCN(v, 25°C, 50 m}^3\text{/kmol)} \rightarrow \text{HCN(v, 200°C, 50 m}^3\text{/kmol)}$$

(d) If the process of Part (b) were carried out in such a way that the initial and final pressures were each 0.80 atm but the pressure varied during the heating, the value of $\Delta\hat{H}$ would still be what you calculated assuming a constant pressure. Why is this so?

8.3. The heat capacity at constant volume of hydrogen sulfide at low pressures is

$$C_v[\text{kJ/(mol}\cdot\text{°C)}] = 0.0252 + 1.547\times10^{-5}T - 3.012\times10^{-9}T^2$$

where T is in °C. A quantity of H_2S is kept in a piston-fitted cylinder with initial temperature, pressure, and volume equal to 25°C, 2.00 atm, and 3.00 liters, respectively.



(a) Calculate the heat (kJ) required to raise the gas temperature from 25°C to 1000°C if the heating takes place at constant volume (i.e., if the piston does not move), retaining successively one term, two terms, and all three terms of the heat capacity formula. (See Example 8.3-1.) Determine the percentage errors in Q that result from retaining only one and two terms of the heat capacity formula, assuming that the full expression yields the correct result.

(b) For a closed system at constant pressure with negligible kinetic and potential energy changes, the energy balance equation is $Q = \Delta H$. Use Equation 8.3-12 to determine an expression for the heat capacity at constant pressure (C_p) for H_2S, assuming ideal-gas behavior. Then use it to calculate the heat (J) required to raise the gas from 25°C to 1000°C at constant pressure. What would the piston do during this process?

(c) What is the physical significance of the difference between the values of Q calculated in Parts (a) and (b)?

8.4. Use data in Table B.2 to calculate the following:

(a) The heat capacity (C_p) of liquid toluene at 40°C.

(b) The heat capacity at constant pressure of toluene vapor at 40°C.

(c) The heat capacity at constant pressure of solid carbon at 40°C.

(d) $\Delta\hat{H}$(kJ/mol) for toluene vapor going from 40°C to 300°C.

(e) $\Delta\hat{H}$(kJ/mol) for solid calcium carbonate going from 40°C to 300°C.

8.5. Estimate the specific enthalpy of steam (kJ/kg) at 100°C and 1 atm relative to steam at 350°C and 100 bar using:

(a) The steam tables.

(b) Table B.2 or APEx and assuming ideal-gas behavior.

What is the physical significance of the difference between the values of $\hat{H}$ calculated by the two methods?

8.6. Table B.7 of Appendix B gives the following values for steam at 400°C and 150 bar:

$$\hat{H} = 2975\ \text{kJ/kg}, \quad \hat{U} = 2744\ \text{kJ/kg}, \quad \hat{V} = 0.0157\ \text{m}^3\text{/kg}$$

(a) The value 2975 is not the true specific enthalpy of steam at the given condition. Why not? State the process [H_2O(___) → H_2O(___)] for which the specific enthalpy change is 2975 kJ/kg. (Enter the phase, temperature, and pressure of water at the initial and final conditions within the parentheses.)

(b) Estimate the specific enthalpy of steam at 100°C and 1 atm relative to steam at 400°C and 150 bar using the steam tables. Repeat the calculation assuming ideal-gas behavior and Table B.2 or APEx.

(c) What is the physical significance of the difference between the two values calculated in Part (b)?

(d) Given the first and third of the tabulated values at 400°C and 150 bar (i.e., 2975 and 0.0157), calculate the second value. (*Hint:* Begin with the definition of $\hat{H}$.) Don't worry if your calculated value differs slightly from 2744—the difference is just round-off error. If the difference is on the order of 1% or more, however, you've done something wrong.

8.7. Calculate $\Delta\hat{H}$ for each of the following processes. In each case, restate your result as a specific enthalpy relative to a reference state. [The solution—which you should verify—and the restatement for Part (a) are given as an illustration.] Assume that the process pressures are low enough for $\hat{H}$ to be considered independent of pressure, so that the formulas of Table B.2 (which strictly apply at 1 atm) can be used.

(a) CH_3COCH_3(l, 15°C) → CH_3COCH_3(l, 55°C).

Solution: $\boxed{\Delta\hat{H} = 5.180\ \text{kJ/mol}}$

The specific enthalpy of liquid acetone at 55°C relative to liquid acetone at 15°C is 5.180 kJ/mol.

(b) n-C_6H_{14}(l, 25°C) → n-C_6H_{14}(l, 80°C)

(c) n-C_6H_{14}(v, 500°C) → n-C_6H_{14}(v, 0°C). (Make statements about both the specific enthalpy of hexane vapor at 500°C relative to hexane vapor at 0°C and the specific enthalpy of hexane vapor at 0°C relative to hexane vapor at 500°C.)

8.8. Two formulas for the heat capacity of CO are given here:

$$C_p[\text{cal/(mol}\cdot\text{°C)}] = 6.890 + 0.001436T(\text{°C})$$
$$C_p[\text{Btu/(lb-mole}\cdot\text{°F)}] = 6.864 + 0.0007978T(\text{°F})$$

Starting with the second formula, derive the first. (Recall Section 2.5, and remember that the temperature unit in the denominator of C_p refers to a temperature interval.)

8.9. Table B.2 lists values of the heat capacity of liquid ethanol at two temperatures. Use the tabulated values to derive a linear expression for $C_p(T)$; then use the derived expression and data in Table B.1 to calculate the heat transfer rate (kW) required to bring a stream of liquid ethanol flowing at 55.0 L/s from 20°C to the boiling point at 1 atm.

*__8.10.__ The brakes on an automobile act by forcing brake pads, which have a metal support and a lining, to press against a disk (rotor) attached to the wheel. Friction between the pads and the disk causes the car to slow or stop. Each wheel has an iron brake disk with a mass of 15 lb_m and two brake pads, each having a mass of 1 lb_m.

(a) Suppose an automobile is moving at 55 miles per hour when the driver suddenly applies the brakes and brings the car to a rapid halt. Take the heat capacity of the disk and brake pads to be 0.12 Btu/(lb_m·°F) and assume that the car stops so rapidly that heat transfer from the disk and pads has been insignificant. Estimate the final temperature of the disk and pads if the car

* Adapted from a problem developed as part of AIChE's Safety and Chemical Engineering Education (SAChE) program.

MATERIALS

is (i) a Toyota Camry, which has a mass of about 3200 lb_m, or (ii) a Cadillac Escalade, which has a mass of about 5,900 lb_m.

SAFETY

(b) Why are the linings on brake pads no longer made of asbestos? Your answer should provide information on specific issues or concerns caused by the use of asbestos.

8.11. Chlorine gas is to be heated from 120°C and 1 atm to 180°C.

(a) Calculate the heat input (kW) required to heat a stream of the gas flowing at 15.0 kmol/min at constant pressure.

(b) Calculate the heat input (kJ) required to raise the temperature of 15.0 kmol of chlorine in a closed rigid vessel from 120°C and 1 atm to 180°C. (Suggestion: Evaluate $\Delta\hat{U}$ directly from the result of the first calculation, so that you do not have to perform another integration.) What is the physical significance of the numerical difference between the values calculated in Parts (a) and (b)?

(c) To accomplish the heating of Part (b), you would actually have to supply an amount of heat to the vessel greater than the amount calculated. Why?

8.12. The heat required to raise the temperature of m (kg) of a liquid from T_1 to T_2 at constant pressure is

$$Q = \Delta H = m\int_{T_1}^{T_2} C_p(T)\,dT \tag{1}$$

In high school and in first-year college physics courses, the formula is usually given as

$$Q = mC_p\,\Delta T = mC_p(T_2 - T_1) \tag{2}$$

(a) What assumption about C_p is required to go from Equation 1 to Equation 2?

(b) The heat capacity (C_p) of liquid *n*-hexane is measured in a **bomb calorimeter**. A small reaction flask (the bomb) is placed in a well-insulated vessel containing 2.00 L of liquid *n*–C_6H_{14} at $T = 300$ K. A combustion reaction known to release 16.73 kJ of heat takes place in the bomb, and the subsequent temperature rise of the system contents is measured and found to be 3.10 K. In a separate experiment, it is found that 6.14 kJ of heat is required to raise the temperature of everything in the system except the hexane by 3.10 K. Use these data to estimate C_p[kJ/(mol·K)] for liquid *n*-hexane at $T \approx 300$ K, assuming that the condition required for the validity of Equation 2 is satisfied. Compare your result with a tabulated value.

8.13. The heat capacities of a substance have been defined as

$$C_v = \left(\frac{\partial\hat{U}}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial\hat{H}}{\partial T}\right)_P$$

Use the defining relationship between $\hat{H}$ and $\hat{U}$ and the fact that $\hat{H}$ and $\hat{U}$ for ideal gases are functions only of temperature to prove that $C_p = C_v + R$ for an ideal gas (Eq. 8.3-12).

ENVIRONMENTAL

8.14. Your next-door neighbor, Josephine Rackstraw, surprised her husband last January by having a hot tub installed in their back yard while he was away on an ice-fishing trip. It surprised him, all right, but instead of being pleased he was horrified.

"Have you lost your mind, Josephine?" he sputtered. "It will cost a fortune to keep this thing hot, and you know what the President said about conserving energy."

"Don't be silly, Ralph," she replied. "It can't cost more than a few pennies a day, even in the dead of winter."

"No way—just because you have a PhD, you think you're an expert on everything!"

They argued for a while, bringing up several issues that each had been storing for just such an occasion. After calming down and using the tub for a week, they remembered their neighbor (i.e., you) had a chemical engineering education and came to ask if you could settle their argument. You asked a few questions, made several observations, converted everything to metric units, and arrived at the following data, all corresponding to an average outside temperature of 5°C.

- The tub holds 1230 liters of water.
- Ralph normally keeps the tub temperature at 29°C, raises it to 40°C when he plans to use it, keeps it at 40°C for about one hour, and drops it back to 29°C when he is finished.
- During heating, it takes about three hours for the water temperature to rise from 29°C to 40°C. When the heat is shut off, it takes eight hours for the water temperature to drop back to 29°C.
- Electricity costs 10 cents per kilowatt-hour.

Taking the heat capacity of the tub contents to be that of pure liquid water and neglecting evaporation, answer the following questions.

(a) What is the average rate of heat loss (kW) from the tub to the outside air? (*Hint:* Consider the period when the tub temperature is dropping from 40°C to 29°C.)

(b) At what average rate (kW) does the tub heater deliver energy to the water when raising the water temperature? What is the total quantity of electricity (kW·h) that the heater must deliver during this period? [Consider the result of Part (a) when performing the calculation.]

(c) (These answers should settle the argument.) Consider a day in which the tub is used once. Use the results of Parts (a) and (b) to estimate the cost ($) of heating the tub from 29°C to 40°C and the cost ($) of keeping the tub at a constant temperature. (There is no cost for the period in which T is dropping.) What is the total daily cost of running the tub? Assume the rate of heat loss is independent of the tub temperature.

(d) The tub lid, which is an insulator, is removed when the tub is in use. Explain how this fact would probably affect your cost estimates in Part (c).

8.15. Use the *enthalpy* function of APEx to calculate $\Delta\hat{H}$ for each of the processes given below and check your solution to Part (a) by using the heat capacity tabulated in Table B.2. (Include units in your solutions.) Your spreadsheet cell entry for Part (a) should be "=Enthalpy("N2",25,700)".

(a) N_2(g, 25°C) → N_2(g, 700°C)

(b) H_2(g, 800°F) → H_2(g, 77°F)

(c) H_2O(g, 20°C) → H_2O(g, 80°C)

(d) H_2O(l, 20°C) → H_2O(l, 80°C)

(e) Ferric oxide(s, 275K) → Fe_2O_3(s, 438K)

8.16. A stream of carbon monoxide flowing at 300 kg/min is cooled from 450°C to 50°C at a low pressure.

(a) Calculate the required rate of cooling (kW), using the *enthalpy* function of APEx. Check the calculation using the heat capacity formula in Table B.2.

(b) State all the assumptions you made in Part (a). Where in the calculation did you make use of the fact that the cooling was done at a low pressure?

*__8.17.__ Aluminum cans of a liquid baby formula are sterilized with steam in an autoclave before being shipped to wholesale distributors. A batch of the product consists of 500 cans, each of which has a tare (empty) mass of 1.00×10^2 g and contains 0.750 kg of formula. The cans are loaded into the autoclave at 35°C, and saturated steam at 2 bar is used to displace all the air from the autoclave and bring the cans and their contents to the same temperature as the steam. After the autoclave temperature has stabilized, it is held constant for 15 minutes, which is sufficient to achieve the required degree of sterilization. The steam is then vented, the pressure in the autoclave reduced to 1 atm, and the cans of formula are cooled to ambient temperature before being packaged for shipping. The heat capacities of the cans and formula are 0.91 kJ/(kg·°C) and 3.77 kJ/(kg·°C), respectively.

(a) What is the highest temperature (°C) in the autoclave?

(b) Estimate how much steam (kg) condenses as the cans go from their initial temperature to the value in Part (a).

(c) Why is more steam condensate produced in the actual operation than is calculated in Part (c)?

(d) Why is it important that the infant formula be held at the temperature from Part (a) for a period of 15 minutes?

MATERIALS

8.18. Among the best-known building blocks in nanotechnology applications are nanoparticles of noble metals. For example, colloidal suspensions of silver or gold nanoparticles (10–200 nm) exhibit vivid colors because of intense optical absorption in the visible spectrum, making them useful in colorimetric sensors.[16]

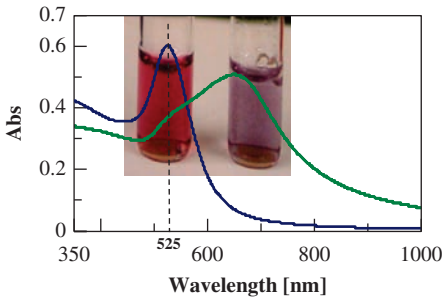
In the illustration shown below, a suspension of gold nanoparticles of a fairly uniform size in water exhibits peak absorption near a wavelength of 525 nm (near the blue region of the visible spectrum of light). When one views the solution in ambient (white) light, the solution appears wine-red because the blue part of the spectrum is largely absorbed. When the nanoparticles aggregate to form large particles, an optical absorption peak near 600–700 nm (near the red region of the visible spectrum) is observed. The breadth of the peak reflects a fairly broad particle size distribution. The solution appears bluish

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater (2010). "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses—Part I," http://pharmahub.org/resources/360.

** Adapted from a problem contributed by Vinay K. Gupta of the University of South Florida.

[16] A. Pyatenko, M. Yamaguchi, and M. Suzuki, *J. Phys. Chem. B*, **109**, 21608(2005).

because the unabsorbed light reaching the eye is dominated by the short (blue-violet) wavelength region of the spectrum.



Since the optical properties of metallic nanoparticles are a strong function of their size, achieving a narrow particle size distribution is an important step in the development of nanoparticle applications. A promising way to do so is *laser photolysis*, in which a suspension of particles of several different sizes is irradiated with a high-intensity laser pulse. By carefully selecting the wavelength and energy of the pulse to match an absorption peak of one of the particle sizes (e.g., irradiating the red solution in the diagram with a 525 nm laser pulse), particles of or near that size can be selectively vaporized.

(a) A spherical silver nanoparticle of diameter D at 25°C is to be heated to its normal boiling point and vaporized with a pulsed laser. Considering the particle a closed system at constant pressure, write the energy balance for this process, look up the physical properties of silver that are required in the energy balance, and perform all the required substitutions and integrations to derive an expression for the energy Q_{abs}(J) that must be absorbed by the particle as a function of D(nm).

(b) The total energy absorbed by a single particle (Q_{abs}) can also be calculated from the following relation:

$$Q_{abs} = FA_p\sigma_{abs}$$

where F(J/m^2) is the energy in a single laser pulse per unit spot area (area of the laser beam) and A_p(m^2) is the total surface area of the nanoparticle. The effectiveness factor, σ_{abs}, accounts for the efficiency of absorption by the nanoparticle at the wavelength of the laser pulse and is dependent on the particle size, shape, and material. For a spherical silver nanoparticle irradiated by a laser pulse with a peak wavelength of 532 nm and spot diameter of 7 mm with D ranging from 40 to 200 nm, the following empirical equation can be used for σ_{abs}.

$$\sigma_{abs} = \frac{1}{4}\left[0.05045 + 2.2876\exp\left(-\left(\frac{D-137.6}{41.675}\right)^2\right)\right]$$

where σ_{abs} and the leading $\frac{1}{4}$ are dimensionless and D has units of nm.

Use the results of Part (a) to determine the minimum values of F required for complete vaporization of single nanoparticles with diameters of 40.0 nm, 80.0 nm, and 120.0 nm. If the pulse frequency of the laser is 10 Hz (i.e., 10 pulses per second), what is the minimum laser power P(W) required for each of those values of D? (*Hint:* Set up a dimensional equation relating P to F.)

(c) Suppose you have a suspension of a mixture of $D = 40$ nm and $D = 120$ nm spherical silver nanoparticles and a 10 Hz/532 nm pulsed laser source with a 7 nm diameter spot and adjustable power. Describe how you would use the laser to produce a suspension of particles of only a single size and state what that size would be.

8.19. A stream of water vapor flowing at a rate of 250 mol/h is brought from 600°C and 10 bar to 100°C and 1 atm.

(a) Estimate the required cooling rate (kW) three ways: (i) from the steam tables, (ii) using heat capacity data in Table B.2, and (iii) using the *Enthalpy* function of APEx.

(b) Which of the answers in Part (a) is most accurate, and why?

(c) What is the physical significance of the difference between the values calculated with methods (i) and (ii)?

8.20. A stream of air at 77°F and 1.2 atm absolute flowing at a rate of 225 ft^3/h is blown through ducts that pass through the interior of a large industrial motor. The air emerges at 500°F. Calculate the rate at

which the air is removing heat generated by the motor. What assumption have you made about the pressure dependence of the specific enthalpy of air?

8.21. Calculate the heat required to raise 50 kg of solid sodium carbonate (Na_2CO_3) from 10°C to 50°C at 1 atm using
(a) the true heat capacity of Na_2CO_3, which is 1.14 kJ/(kg·°C).
(b) a heat capacity estimated by Kopp's rule. Calculate the percentage error in the latter calculation.

8.22. Calculate the heat transfer (kJ) required to cool 55.0 liters of a liquid mixture containing 70.0 wt% acetone and 30.0% 2-methyl-1-pentanol ($C_6H_{14}O$) from 45°C to 20°C. Use Kopp's rule to estimate any heat capacity for which a tabulated value cannot be found. State all assumptions you make.

8.23. Twenty liters of liquid *n*-propyl benzoate ($C_6H_5CO_2C_3H_7$, SG = 1.021) and 15 liters of liquid benzene are mixed and heated from 25°C to 75°C. Calculate the required heat input (kJ), using Kopp's rule when necessary. State all assumptions you make.

8.24. A gas mixture contains one-third methane by volume (recall what that means in terms of mole%) and the balance oxygen at 350°C and 3.0 bar. Calculate the specific enthalpy of this stream in kJ/kg (not per kmol) relative to the pure components at 25°C and 1 atm. *State clearly all assumptions.*

ALTERNATIVE ENERGY
ENVIRONMENTAL

8.25. The radiant energy incident on the earth's surface on a sunny day is roughly 900 W/m^2. Collecting and focusing sunlight and using the focused beam to heat a fluid is an old idea, and as the environmental costs of fossil-fuel combustion mount, solar heating becomes an increasingly attractive alternative.

Suppose a house is to be designed that will have a circulating forced-air central-heating unit, and solar energy is contemplated as a heat source (backed up with a conventional furnace to be used on cloudy days). If air is to be fed at a rate of 1000 m^3/min at 30°C and 1 atm, and the air is to be heated to 55°C before being discharged into the living space, what is the required area of the solar collector plates? Assume 30% of the radiant energy incident on the plates is used to heat the air.

8.26. Propane is to be burned with 25.0% excess air. Before entering the furnace, the air is preheated from 32°F to 575°F.
(a) At what rate (Btu/h) must heat be transferred to the air if the feed rate of propane is 1.35×10^5 SCFH (ft^3/h at STP)?
(b) The stack gas leaves the furnace at 855°F. How is the air likely to be preheated?

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8.27. A fuel gas containing 95 mole% methane and the balance ethane is burned completely with 25% excess air. The stack gas leaves the furnace at 900°C and is cooled to 450°C in a **waste-heat boiler**, a heat exchanger in which heat lost by cooling gases is used to produce steam from liquid water for heating, power generation, or process applications.
(a) Taking as a basis of calculation 100 mol of the fuel gas fed to the furnace, calculate the amount of heat (kJ) that must be transferred from the gas in the waste heat boiler to accomplish the indicated cooling.
(b) How much saturated steam at 50 bar can be produced from boiler feedwater at 40°C for the same basis of calculation? (Assume all the heat transferred from the gas goes into the steam production.)
(c) At what rate (kmol/s) must fuel gas be burned to produce 1280 kg steam per hour (an amount required elsewhere in the plant) in the waste heat boiler? What is the volumetric flow rate (m^3/s) of the gas leaving the boiler?
(d) Briefly explain how the waste-heat boiler contributes to the plant profitability. (Think about what would be required in its absence.)

8.28. Your roommate has learned that burning approximately 3,500 food calories (see Problem 7.3) results in a weight loss of 1 lb_m, and he gets the bright idea of losing weight rapidly by eating ice. His theory is that the energy expended by the body in melting the ice and raising the resulting liquid water to body temperature will do the trick. You burst the poor boy's bubble by telling him the amount of ice he would have to consume. How much ice would be required per pound of weight lost?

ENVIRONMENTAL

*__8.29.__ The flow of groundwater often plagues construction of tunnels and other underground systems. One way of preventing it is with an *ice seal*—freezing the water in the soil so that the ice formed

* Values used in the problem statement are based on the following articles: A. C. Madrigal, *Atlantic Monthly*, August 13, 2013; M. Iwata, *Wall Street Journal*, May 17–18, 2014.

is a barrier to water movement. Such a structure was planned for the Fukushima TEPCO nuclear power plant, which was severely damaged by a 2011 tsunami that created a tremendous environmental challenge. A major concern was potential contamination with radioactive isotopes of groundwater flowing under the plant and into the ocean. A proposal under consideration was to channel the flow around the plant by forming an ice dam with a 1,400-meter perimeter, a depth of 30 m, and a thickness of approximately 2 m. This was to be done by pumping a brine solution at a temperature of −40°C though vertical pipes spaced at 1-m intervals. The brine would exit at a temperature no greater than −25°C. To keep ambient temperature fluctuations from causing occasional melting, the dam was to have a mean temperature of about −20°C.

(a) Estimate the average cooling rate (kW) and associated flow rate of brine (L/min) required to complete formation of the dam within 60 days of starting the refrigeration system. State and give your rationale for each of the assumptions and/or approximations necessary to obtain your result.

(b) From a suitable reference, for which you must provide a citation, find an estimate of the ratio of the heat removed to the work done by a refrigeration system. Use the value to estimate the power usage during the time the dam is being created.

(c) It is expected that substantially less power will be used once the dam has been formed. Explain.

Exploratory Exercises—Research and Discover

(d) Identify the primary radioactive species that were of greatest concern regarding contamination of the groundwater.

(e) Explosions of hydrogen occurred in the power plants after the cooling water system was shut down upon being flooded by the tsunami. What was the source of the hydrogen? Describe the scenario that led to hydrogen formation.

*__8.30.__ Ever wonder why espresso costs much more per cup than regular drip coffee? Part of the reason is the expensive equipment needed to brew a proper espresso. A high-powered burr grinder first shears the coffee beans to a fine powder without producing too much heat. (Heating the coffee in the grinding stage prematurely releases the volatile oils that give espresso its rich flavor and aroma.) The ground coffee is put into a cylindrical container called a *gruppa* and tamped down firmly to provide an even flow of water through it. An electrically heated boiler inside the espresso machine maintains water in a reservoir at 1.4 bar and 109°C. An electric pump takes cold water at 15°C and 1 bar, raises its pressure to slightly above 9 bar, and feeds it into a heating coil that passes through the reservoir. Heat transferred from the reservoir through the coil wall raises the water temperature to 96°C. The heated water flows into the top of the gruppa at 96°C and 9 bar, passes slowly through the tightly packed ground beans, and dissolves the oils and some of the solids in the beans to become espresso, which decompresses to 1 atm as it exits the machine. The water temperature and uniform flow through the bed of packed coffee in the gruppa lead to the more intense flavor of espresso relative to normal drip coffee. Water drawn directly from the reservoir is expanded to atmospheric pressure where it forms steam, which is used to heat and froth milk for lattes and cappuccinos.

(a) Sketch this process, using blocks to represent the pump, reservoir, and gruppa. Label all heat and work flows in the process, including electrical energy.

(b) To make a 14-oz latte, you would steam 12 ounces of cold milk (3°C) until it reaches 71°C and pour it over 2 ounces of espresso. Assume that the steam cools but none of it condenses as it bubbles through the milk. For each latte made, the heating element that maintains the reservoir temperature must supply enough energy to heat the espresso water plus enough to heat the milk, plus additional energy. Assuming

$$(C_p)_{\text{milk}} = 3.93 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}}, \quad \text{SG}_{\text{milk}} = 1.03$$

calculate the quantity of electrical energy that must be provided to the heating element to accomplish those two functions. Why would more energy than what you calculate be required? (There are several reasons.)

* Adapted from a problem contributed by Justin Wood of N.C. State University. The energy balances required to solve the problem are straightforward, but working through the complete problem provides insights into a number of familiar phenomena.

(c) Coffee beans contain a considerable amount of trapped carbon dioxide, not all of which is released when the beans are ground. When the hot pressurized water percolates through the ground beans, some of the carbon dioxide is absorbed in the liquid. When the liquid is then dispensed at atmospheric pressure, fine CO_2 bubbles come out of solution. In addition, one of the chemical compounds formed when the coffee beans are roasted and extracted into the espresso is melanoidin, a *surfactant*. Surfactant molecules are asymmetrical, with one end being *hydrophilic* (drawn to water) and the other end *hydrophobic* (repelled by water). When the bubbles (thin water films containing CO_2) pass through the espresso liquid, the hydrophilic ends of the melanoidin molecules attach to the bubbles and the dissolved bean oils in turn attach to the hydrophobic ends. The result is that the bubbles emerge coated with the oils to form the *crema*, the familiar reddish-brown stable foam at the surface of good espresso. Speculate on why you don't see crema in normal drip coffee. (*Hint:* Henry's law should show up in your explanation.) *Note:* All soaps and shampoos contain at least one surfactant species. (A common one is sodium lauryl sulfate.) Its presence explains why if you have greasy hands, washing with plain water may leave the grease untouched but washing with soap removes the grease.

(d) Explain in your own words (i) how espresso is made, (ii) why espresso has a more intense flavor than regular drip coffee, (iii) what the crema in espresso is, how it forms, and why it doesn't appear in regular drip coffee, and (iv) why washing with plain water does not remove grease but washing with soap does. (*Note:* Many people automatically assume that all chemical engineers are extraordinarily intelligent. If you can explain those four things, you can help perpetuate that belief.)

Equipment Encyclopedia
heat exchanger

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8.31. Propane gas enters a continuous adiabatic heat exchanger[17] at 40°C and 250 kPa and exits at 240°C. Superheated steam at 300°C and 5.0 bar enters the exchanger flowing countercurrently to the propane and exits as a saturated liquid at the same pressure.

(a) Taking as a basis 100 mol of propane fed to the exchanger, draw and label a process flowchart. Include in your labeling the volume of propane fed (m^3), the mass of steam fed (kg), and the volume of steam fed (m^3).

(b) Calculate values of the labeled specific enthalpies in the following inlet–outlet enthalpy table for this process.

References: H_2O(l, 0.01°C), C_3H_8(g, 40°C)

Species	n_{in}	$\hat{H}_{in}$	n_{out}	$\hat{H}_{out}$
C_3H_8	100 mol	$\hat{H}_a$(kJ/mol)	100 mol	$\hat{H}_c$(kJ/mol)
H_2O	m_w(kg)	$\hat{H}_b$(kJ/kg)	m_w(kg)	$\hat{H}_d$(kJ/kg)

(c) Use an energy balance to calculate the required mass feed rate of the steam. Then calculate the volumetric feed ratio of the two streams (m^3 steam fed/m^3 propane fed). Assume ideal-gas behavior for the propane but not the steam and recall that the exchanger is adiabatic.

(d) Calculate the heat transferred from the water to the propane (kJ/m^3 propane fed). (*Hint:* Do an energy balance on either the water or the propane rather than on the entire heat exchanger.)

(e) Over a period of time, scale builds up on the heat-transfer surface, resulting in a lower rate of heat transfer between the propane and the steam. What changes in the outlet streams would you expect to see as a result of the decreased heat transfer?

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8.32. Saturated steam at 300°C is used to heat a countercurrently flowing stream of methanol vapor from 65°C to 260°C in an adiabatic heat exchanger. The flow rate of the methanol is 6500 standard liters per minute, and the steam condenses and leaves the heat exchanger as liquid water at 90°C.

(a) Calculate the required flow rate of the entering steam in m^3/min.

(b) Calculate the rate of heat transfer from the water to the methanol (kW).

(c) Suppose the outlet temperature of the methanol is measured and found to be 240°C instead of the specified value of 260°C. List five possible realistic explanations for the 20°C difference.

[17] An adiabatic heat exchanger is one for which no heat is exchanged with the surroundings. All of the heat lost by the hot stream is transferred to the cold stream.

8.33. Pure ethane is burned completely with preheated 20% excess air. The combustion product gas passes through an insulated heat exchanger (the preheater) in which it transfers heat to the air that will continue on to the furnace. The following data are recorded for the preheater inlet and outlet streams:

	Flow rate in (L/s)	T_{in} (°C)	P_{in} (torr)	Flow rate out (L/s)	T_{out} (°C)	P_{out} (torr)
Product gas	—	945	830	1.98×10^5	850	912
Air	5.53×10^4	30	684	—	—	836

The temperature of the air leaving the preheater is not known because the thermocouple mounted in that pipe has malfunctioned.

(a) Calculate the molar flow rates (mol/s) of the two streams flowing through the preheater and the temperature of the air leaving the preheater.

(b) The preheated air thermocouple is replaced and gives a reading of 161°C. List possible reasons for the discrepancy between what you predicted and what was measured. (Think about all of the assumptions built into your calculations.)

(c) Careful re-measurements are made of the process stream flow rates, temperatures, and pressures, and all of the given values are replicated. What is the most likely reason for the difference between the measured exit air temperature and the temperature predicted in Part (a)? What would you recommend to correct the problem?

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membrane

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8.34. An adiabatic membrane separation unit is used to dry (remove water vapor from) a gas mixture containing 10.0 mole% H_2O(v), 10.0 mole% CO, and the balance CO_2. The gas enters the unit at 30°C and flows past a semipermeable membrane. Water vapor permeates through the membrane into an air stream. The dried gas leaves the separator at 30°C containing 2.0 mole% H_2O(v) and the balance CO and CO_2. Air enters the separator at 50°C with an absolute humidity of 0.002 kg H_2O/kg dry air and leaves at 48°C. Negligible quantities of CO, CO_2, O_2, and N_2 permeate through the membrane. All gas streams are at approximately 1 atm.

(a) Draw and label a flowchart of the process and carry out a degree-of-freedom analysis to verify that you can determine all unknown quantities on the chart.

(b) Calculate (i) the ratio of entering air to entering gas (kg humid air/mol gas) and (ii) the relative humidity of the exiting air.

(c) List several desirable properties of the membrane. (Think about more than just what it allows and does not allow to permeate.)

8.35. A gas containing water vapor has a dry-basis composition of 7.5 mole% CO, 11.5% CO_2, 0.5% O_2, and 80.5% N_2. The gas leaves a catalyst regeneration unit at 620°C and 1 atm with a dew point of 57°C at a flow rate of 28.5 SCMH [m^3(STP)/h]. Valuable solid catalyst particles entrained in the gas are to be recovered in an electrostatic precipitator, but the gas must first be cooled to 425°C to prevent damage to the precipitator electrodes. The cooling is accomplished by spraying water at 20°C into the gas.

(a) Use simultaneous material and energy balances on the spray cooler to calculate the required water feed rate (kg/h). Treat the spray cooler as adiabatic and neglect the heat transferred from the entrained solid particles as they cool.

(b) In terms that a high school senior could understand, explain the operation of the spray cooler in this problem. (What happens when the cold water contacts the hot gas?)

BIOENGINEERING →

8.36. On a cold winter day the temperature is 2°C and the relative humidity is 15%. You inhale air at an average rate of 5500 mL/min and exhale a gas saturated with water at body temperature, roughly 37°C. If the mass flow rates of the inhaled and exhaled air (excluding water) are the same, the heat capacities (C_p) of the water-free gases are each 1.05 J/(g·°C), and water is ingested into the body as a liquid at 22°C, at what rate in J/day do you lose energy by breathing? Treat breathing as a continuous process (inhaled air and liquid water enter, exhaled breath exits) and neglect work done by the lungs.

8.37. Sixty-five liters of liquid ethanol at 70.0°C and 55 L of liquid water at 20.0°C are to be mixed in a well-insulated flask. The energy balance for this constant pressure process is $Q = \Delta H$.

(a) Neglecting evaporation and the heat of mixing, estimate the final mixture temperature. (As part of the calculation, use data in Table B.2 to estimate a linear formula for the heat capacity of liquid ethanol.)

(b) If the experiment were actually performed and the final mixture temperature were measured, it would almost certainly not equal the value estimated in Part (a). List as many reasons as you can to explain the observation. (There are at least seven of them, most involving approximations made in the estimation.)

8.38. A stream of air at 500°C and 835 torr with a dew point of 30°C flowing at a rate of 1515 L/s is to be cooled in a spray cooler. A fine mist of liquid water at 15°C is sprayed into the hot air at a rate of 110.0 g/s and evaporates completely. The cooled air emerges at 1 atm.

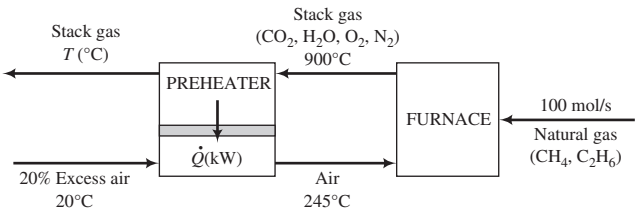
(a) Calculate the final temperature of the emerging air stream, assuming that the process is adiabatic. (*Suggestion:* Derive expressions for the enthalpies of dry air and water at the outlet air temperature, substitute them into the energy balance, and use a spreadsheet to solve the resulting fourth-order polynomial equation.)

(b) At what rate (kW) is heat transferred from the hot air feed stream in the spray cooler? What becomes of this heat?

(c) In a few sentences, explain how this process works in terms that a high school senior could understand. Incorporate the results of Parts (a) and (b) in your explanation.

8.39. In the manufacture of nitric acid, ammonia and preheated air are mixed to form a gas containing 10.0 mole% NH_3 at 600°C. The ammonia is then catalytically oxidized to form NO_2, which is absorbed in water to form HNO_3. If ammonia enters the gas blending unit at 25°C at a rate of 520 kg/h and heat is lost from the mixer to its surroundings at a rate of 7.00 kW, determine the temperature to which the air must be preheated. (See Example 8.3-6.)

8.40. A natural gas containing 95 mole% methane and the balance ethane is burned with 20.0% excess air. The stack gas, which contains no unburned hydrocarbons or carbon monoxide, leaves the furnace at 900°C and 1.2 atm and passes through a heat exchanger. The air on its way to the furnace also passes through the heat exchanger, entering it at 20°C and leaving it at 245°C.



(a) Taking as a basis 100 mol/s of the natural gas fed to the furnace, calculate the required molar flow rate of air, the molar flow rate and composition of the stack gas, the required rate of heat transfer in the preheater, $\dot{Q}$ (write an energy balance on the air), and the temperature at which the stack gas leaves the preheater (write an energy balance on the stack gas). *Note:* The problem statement does not give you the fuel feed temperature. Make a reasonable assumption, and state why your final results should be nearly independent of what you assume.

(b) What would $\dot{Q}$ be if the actual feed rate of the natural gas were 350 SCMH [standard cubic meters per hour, m^3(STP)/h]? Scale up the flowchart of Part (a) rather than repeating the entire calculation.

8.41. The heat capacity at constant pressure of a gas is determined experimentally at several temperatures, with the following results:

T(°C)	0	100	200	300	400	500	600
C_p[J/(mol·°C)]	33.5	35.1	36.7	38.4	40.2	42.0	43.9

(a) Calculate the heat (kW) required to raise 150 mol/s of the gas from 0°C to 600°C, using Simpson's rule (Appendix A.3) to integrate the tabulated heat capacities.

(b) Use the method of least squares (Appendix A.1) to derive a linear expression for $C_p(T)$ in the range 0°C to 600°C, and use this expression to estimate once again the heat (kW) required to raise 150 mol/s of the gas from 0°C to 600°C. If the estimates differ, in which one would you have more confidence, and why?

8.42. As part of a design calculation, you must evaluate an enthalpy change for an obscure organic vapor that is to be cooled from 1800°C to 150°C in a heat exchanger. You search through all the standard references for tabulated enthalpy or heat capacity data for the vapor but have no luck at all, until you finally stumble on an article in the May 1922 *Antarctican Journal of Obscure Organic Vapors* that contains a plot of C_p[cal/(g·°C)] on a logarithmic scale versus $[T(°C)]^{1/2}$ on a linear scale. The plot is a straight line through the points ($C_p = 0.329$, $T^{1/2} = 7.1$) and ($C_p = 0.533$, $T^{1/2} = 17.3$).

(a) Derive an equation for C_p as a function of T.

(b) Suppose the relationship of Part (a) turns out to be

$$C_p = 0.235 \exp[0.0473 T^{1/2}]$$

and that you wish to evaluate

$$\Delta\hat{H}(\text{cal/g}) = \int_{1800°C}^{150°C} C_p \, dT$$

First perform the integration analytically, using a table of integrals if necessary; then write a spreadsheet or computer program to do it using Simpson's rule (Appendix A.3). Have the program evaluate C_p at 11 equally spaced points from 150°C to 1800°C, estimate and print the value of ΔH, and repeat the calculation using 101 points. What can you conclude about the accuracy of the numerical calculation?

8.43. A stream of toluene vapor at its normal boiling point and 1 atm flowing at a rate of 175 kg/min is to be condensed at constant pressure. The product stream from the condenser is liquid toluene at the condensation temperature.

(a) Using data in Table B.1, calculate the rate (kW) at which heat must be transferred from the condenser.

(b) If heat were transferred at a lower rate than that calculated in Part (a), what would the state of the product stream be? (Deduce as much as you can about the phase and the temperature of the stream.)

(c) If heat were transferred at a higher rate than that calculated in Part (a), what could you deduce about the state of the product stream? Sketch a phase diagram (see Figure 6.1-1) and use it to explain your answer.

8.44. **(a)** Determine the specific enthalpy (kJ/mol) of *n*-pentane vapor at 200°C and 2.0 atm relative to *n*-pentane liquid at 20°C and 1.0 atm, assuming ideal-gas behavior for the vapor. Show clearly the process path you construct for this calculation and give the enthalpy changes for each step. State where you used the ideal-gas assumption.

(b) What is the enthalpy of *n*-pentane liquid at 20°C and 1.0 atm relative to *n*-pentane vapor at 200°C and 2.0 atm? (This part should not take much time to complete.)

(c) Beginning with the value of $\hat{H}$ calculated in Part (a) and still assuming ideal-gas behavior, determine the specific internal energy of the vapor at 200°C and 2.0 atm. Once again, state where you used the ideal-gas assumption.

8.45. Calculate the heat of vaporization of water (kJ/mol) at 50°C and low pressures from the tabulated heat of vaporization in Table B.1 and data in Table B.2 and Table B.8. Show clearly the process path you construct for the calculation. Compare your answer with the value of $\Delta\hat{H}_v(50°C)$ given in Table B.5 (convert it to kJ/mol for the comparison). What might account for the difference between the two values?

MATERIALS

Equipment Encyclopedia
nozzle

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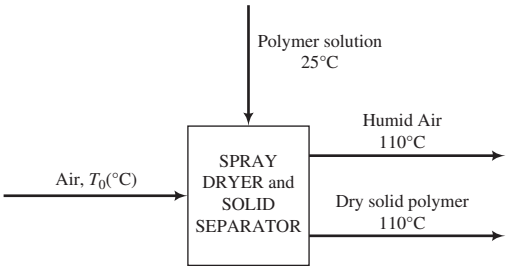
*8.46. Polyvinylpyrrolidone (PVP) is a polymer product used as a binding agent in pharmaceutical applications as well as in personal-care items such as hairspray. In the manufacture of PVP, a spray-drying process is used to collect solid PVP from an aqueous suspension, as shown in the flowchart on the next page. A liquid solution containing 65 wt% PVP and the balance water at 25°C is pumped through an atomizing nozzle at a rate of 1500 kg/h into a stream of preheated air flowing at a rate of 1.57×10^4 SCMH. The water evaporates into the stream of hot air and the solid PVP particles are suspended in the humidified air. Downstream, the particles are separated from the air with a filter and collected. The process is designed so that the exiting solid product and humid air are in thermal

* Adapted from a problem contributed by Jeffrey Seay of the University of Kentucky.

equilibrium with each other at 110°C. For convenience, the spray-drying and solid-separation processes are shown as one unit that may be considered adiabatic.



(a) Draw and completely label the process flow diagram and perform a degree-of-freedom analysis.
(b) Calculate the required temperature of the inlet air, T_0, and the volumetric flow rate (m^3/h) and relative humidity of the exiting air. Assume that the polymer has a heat capacity per unit mass one-third that of liquid water, and only use the first two terms of the polynomial heat-capacity formula for air in Table B.2.
(c) Why do you think the polymer solution is put through an atomizing nozzle, which converts it to a mist of tiny droplets, rather than being sprayed through a much less costly nozzle of the type commonly found in showers?
(d) Due to a design flaw, the polymer solution does not remain in the dryer long enough for all the water to evaporate, so the solid product emerging from the separator is a wet powder. How will this change the values of the outlet temperatures of the emerging gas and powder and the volumetric flow rate and relative humidity of the emerging gas (increase, decrease, can't tell without doing the calculations)? Explain your answers.

Equipment Encyclopedia
condenser

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8.47. Benzene vapor at 480°C is cooled and converted to a liquid at 25°C in a continuous condenser. The condensate is drained into 1.75-m^3 drums, each of which takes 2.0 minutes to fill. Calculate the rate (kW) at which heat is transferred from the benzene in the condenser.

Equipment Encyclopedia
adsorption column

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8.48. In gas adsorption a vapor is transferred from a gas mixture to the surface of a solid. (See Section 6.7.) An approximate but useful way of analyzing adsorption is to treat it simply as condensation of vapor on a solid surface.

Suppose a nitrogen stream at 35°C and 1 atm containing carbon tetrachloride with a 15% relative saturation is fed at a rate of 10.0 mol/min to a 6-kg bed of activated carbon. The temperature and pressure of the gas do not change appreciably from the inlet to the outlet of the bed, and there is no CCl_4 in the gas leaving the adsorber. The carbon can adsorb 40% of its own mass of carbon tetrachloride before becoming saturated, at which point it must be either regenerated (remove the carbon tetrachloride) or replaced with a fresh bed of activated carbon. Neglect the effect of temperature on the heat of vaporization of CCl_4 when solving the following problems:

(a) Estimate the rate (kJ/min) at which heat must be removed from the adsorber to keep the process isothermal, and the time (min) it will take to saturate the bed.
(b) The surface-to-volume ratio of spherical particles is $(3/r)$ (cm^2 outer surface)/(cm^3 volume). First, derive that formula. Second, use it to explain how decreasing the average diameter of the particles in the carbon bed might make the adsorption process more efficient. Third, since most of the area on which adsorption takes place is provided by pores penetrating the particle, explain why the surface-to-volume ratio, as calculated by the above expression, might be relatively unimportant.

8.49. If carbon dioxide is cooled at 1 atm, it condenses directly to a solid (**dry ice**) at −78.4°C. The heat of sublimation at this temperature is $\Delta\hat{H}_{sub}(-78.4°C) = 6030$ cal/mol.

(a) Calculate the heat removal rate (kW) required to produce 300 kg/h of dry ice at 1 atm and −78.4°C if CO_2(v) at 20°C is the feed.
(b) Suppose the process is carried out at 9.9 atm instead of 1 atm with the same initial and final temperatures. Referring to Figure 6.1-1*b*, write an expression for the required heat removal rate in terms of heat capacities and latent heats of CO_2 in different phases.

8.50. Molten sodium chloride is to be used as a constant-temperature bath for a high-temperature chemical reactor. Two hundred kilograms of solid NaCl at 300 K is charged into an insulated vessel, and a 3000 kW electrical heater is turned on, raising the salt to its melting point of 1073 K and melting it at a constant pressure of 1 atm.

(a) The heat capacity (C_p) of solid NaCl is 50.41 J/(mol·K) at $T = 300$ K, and 53.94 J/(mol·K) at $T = 500$ K, and the heat of fusion of NaCl at 1073 K is 30.21 kJ/mol. Use these data to determine a linear expression for $C_p(T)$ and to calculate $\Delta\hat{H}$ (kJ/mol) for the transition of NaCl from a solid at 300 K to a liquid at 1073 K.

(b) Write and solve the energy balance equation for this closed system isobaric process to determine the required heat input in kilojoules.

(c) If 85% of the full power of 3000 kW goes into heating and melting the salt, how long does the process take?

8.51. Estimate the heat of vaporization of diethyl ether at its normal boiling point using Trouton's rule and Chen's rule and compare the results with a tabulated value of this quantity. Calculate the percentage error that results from using each estimation. Then estimate $\Delta\hat{H}_v$ at 100°C using Watson's correlation.

8.52. You are writing energy balances for a compound for which you cannot find heat capacity or latent heat data. All you know about the material are its molecular formula ($C_7H_{12}N$) and that it is a liquid at room temperature and has a normal boiling point of 200°C. Use this information to estimate the enthalpy of the vapor of this substance at 200°C relative to the liquid at 25°C. (Recall Section 8.3c.)

8.53. Estimate the heat of vaporization (kJ/mol) of benzene at 25°C, using each of the following correlations and data:

(a) The heat of vaporization at the normal boiling point and Watson's correlation.

(b) The Clausius–Clapeyron equation and boiling points at 50 mm Hg and 150 mm Hg.

(c) Tables B.1 and B.2.

(d) Find a tabulated value of the heat of vaporization of benzene at 25°C. (*Suggestion:* Do the same thing you do when you want to find almost any item of information.) Then calculate the percentage errors that result from the estimations of Parts (a), (b), and (c).

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8.54. A stream of pure cyclopentane vapor flowing at a rate of 1550 L/s at 150°C and 1 atm enters a cooler in which 65% of the feed is condensed at constant pressure.

(a) What is the temperature at the condenser outlet? Explain how you know (a single sentence should suffice).

(b) Prepare and fill in an inlet–outlet enthalpy table and calculate the required cooling rate in kW.

BIOENGINEERING

*__8.55.__ An adult human being at rest produces roughly 0.40 mJ/h of thermal energy through metabolic activity. Use that fact to solve the following problems.

(a) A college student who weighs 128 pounds put off a major assignment until the day before it was due and worked for eight hours to complete it. If she is modeled as a closed adiabatic system at constant pressure, her heat capacity and molecular weight are approximately the same as that of liquid water, and her temperature was normal when she began to work, what would her temperature have been by the time the assignment was finished?

(b) Now model the student as an open system and assume that evaporation of perspiration (evaporative cooling) is the only mechanism for heat loss. How much weight would she have lost through evaporation if she maintained a constant body temperature?

(c) Are either of the models in Parts (a) and (b) reasonable? Explain. What is the most likely explanation of what happened to the metabolic energy produced in her body?

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8.56. Humid air at 50°C and 1.0 atm with 2°C of superheat is fed to a condenser. Gas and liquid streams leave the condenser in equilibrium at 20°C and 1 atm.

(a) Assume a basis of calculation of 100 mol inlet air, draw and label a flowchart (including Q in the labeling), and carry out a degree-of-freedom analysis to verify that all labeled variables can be determined.

* Adapted from a problem contributed by John Falconer and Garret Nicodemus of the University of Colorado at Boulder.

(b) Write in order the equations you would solve to calculate the mass of water condensed (kg) per cubic meter of air fed to the condenser. Circle the unknown variable for which you would solve each equation. Do not do any of the calculations.

(c) Prepare an inlet–outlet enthalpy table, inserting labels for unknown specific enthalpies ($\hat{H}_1$, $\hat{H}_2$, . . .). Write expressions for the labeled specific enthalpies, substituting values or formulas for heat capacities and latent heats but not calculating the values of the specific enthalpies. Then write an expression for the rate at which heat must be transferred from the unit (kJ per cubic meter of air fed to the condenser).

(d) Solve your equations by hand to calculate kg H_2O condensed/m^3 air fed and kJ transferred/m^3 air fed.

(e) Use APEx to perform the calculations of Part (d).

(f) What cooling rate (kW) would be required to process 250 m^3 air fed/h?

8.57. An air conditioner cools 226 m^3/min of humid air at 36°C and 98% relative humidity to 10°C.

(a) Do a degree-of-freedom analysis to prove that enough information is available to determine the required cooling duty (rate of heat transfer).

(b) Calculate the rate of condensation of water in the unit and the cooling duty in tons (1 ton = 12,000 Btu/h).

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8.58. A gas stream containing *n*-hexane in nitrogen with a relative saturation of 90% is fed to a condenser at 75°C and 3.0 atm absolute. The product gas emerges at 0°C and 3.0 atm at a rate of 746.7 m^3/h.

(a) Calculate the percentage condensation of hexane (moles condensed/mole fed) and the rate (kW) at which heat must be transferred from the condenser.

(b) Suppose the feed stream flow rate and composition and the heat transfer from the condenser are the same as in Part (a), but the condenser and outlet stream pressure is only 2.5 atm instead of 3.0 atm. How would the outlet stream temperatures and flow rates and the percentage condensations of hexane calculated in Parts (a) and (b) change (increase, decrease, no change, no way to tell)? Don't do any calculations, but explain your reasoning.

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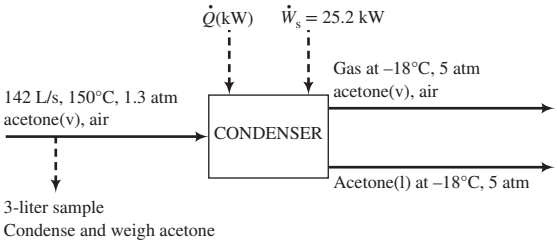
8.59. A gas stream containing acetone in air flows from a solvent recovery unit at a rate of 142 L/s at 150°C and 1.3 atm. The stream flows into a condenser which condenses most of the acetone, and the liquid and gas outlet streams are in equilibrium at −18°C and 5.0 atm. Shaft work is delivered to the system at a rate of 25.2 kW to achieve the compression from 1.3 atm to 5.0 atm. To determine the condenser feed stream composition, a 3.00-liter sample of the gas is taken and cooled to a temperature at which essentially all the acetone in the sample is recovered as a liquid. The liquid is poured into an empty flask with a mass of 4.017 g. The flask containing the liquid acetone is weighed and found to have a mass of 4.973 g.



(a) Carry out a degree-of-freedom analysis to show that enough information is available to determine the compositions of all streams and the required heat transfer rate.

(b) Write out a complete set of equations for the molar flow rates of all streams, the mole fractions of acetone in the feed and product gas streams, and the rate (kW) at which heat must be removed in the condenser. *Do no calculations.*

(c) Solve the equations of Part (b) by hand.

(d) Solve the equations of Part (b) using APEx.

8.60. A mixture of *n*-hexane vapor and air leaves a solvent recovery unit and flows through a 70-cm diameter duct at a velocity of 3.00 m/s. At a sampling point in the duct the temperature is 40°C, the pressure is 850 mm Hg, and the dew point of the sampled gas is 25°C. The gas is fed to a condenser in which it is cooled at constant pressure, condensing 70% of the hexane in the feed.

(a) Perform a degree-of-freedom analysis to show that enough information is available to calculate the required condenser outlet temperature (°C) and cooling rate (kW).
(b) Perform the calculations.
(c) If the feed duct diameter were 35 cm for the same molar flow rate of the feed gas, what would be the average gas velocity (volumetric flow rate divided by cross-sectional area)?
(d) Suppose you wanted to increase the percentage condensation of hexane for the same feed stream. Which three condenser operating variables might you change, and in which direction?

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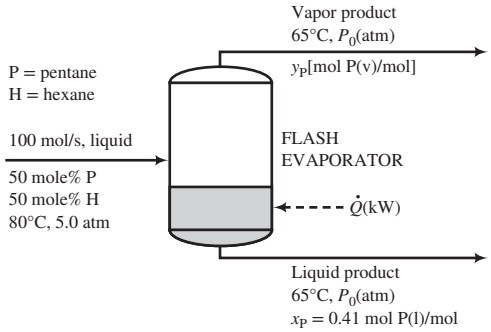
8.61. An equimolar liquid mixture of *n*-pentane and *n*-hexane at 80°C and 5.00 atm is fed into a flash evaporator at a rate of 100.0 mol/s. When the feed is exposed to the reduced pressure in the evaporator, a substantial amount is vaporized. The temperature in the tank is maintained at 65°C by adding heat. The vapor and liquid phases, which are in equilibrium with each other, are separated and discharged as separate streams. The liquid product stream contains 41.0 mole% pentane. A flowchart and an inlet–outlet enthalpy table for the process are given below.



References: P(l, 65°C), H(l, 65°C)

Substance	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
P(l)	$\dot{n}_a$	$\hat{H}_a$	$\dot{n}_c$	$\hat{H}_c$
P(v)	—	—	$\dot{n}_d$	$\hat{H}_d$
H(l)	$\dot{n}_b$	$\hat{H}_b$	$\dot{n}_e$	$\hat{H}_e$
H(v)	—	—	$\dot{n}_f$	$\hat{H}_f$

(a) Using Raoult's law for vapor–liquid equilibrium calculations, calculate (i) the system pressure, P_0(atm), (ii) the mole fraction of pentane in the vapor product, y_P, (iii) the volumetric flow rate of the vapor product, $\dot{V}$(L/s), and (iv) the fractional vaporization of pentane, f(mol vaporized/mol fed).
(b) Determine values for all the $\dot{n}$'s and $\hat{H}$'s in the enthalpy table and calculate the required rate of heat addition to the evaporator, $\dot{Q}$(kW).
(c) How would each of the variables calculated in Parts (a) and (b) change if the evaporator temperature were increased (increase, decrease, no change, cannot tell)? Explain your reasoning.

Equipment Encyclopedia
evaporator

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8.62. A liquid stream containing 50.0 mole% benzene and the balance toluene at 25°C is fed to a continuous single-stage evaporator at a rate of 1320 mol/s. The liquid and vapor streams leaving the evaporator are both at 95.0°C. The liquid contains 42.5 mole% benzene and the vapor contains 73.5 mole% benzene.
(a) Calculate the heating requirement for this process in kW.
(b) Using Raoult's law (Section 6.4b) to describe the equilibrium between the vapor and liquid outlet streams, determine whether or not the given benzene analyses are consistent with each other. If they are, calculate the pressure (torr) at which the evaporator must be operating; if they are not, give several possible explanations for the inconsistency.

8.63. The off-gas from a reactor in a process plant in the heart of Freedonia has been condensing and plugging up the vent line, causing a dangerous pressure buildup in the reactor. Plans have been made to send the gas directly from the reactor into a cooling condenser in which the gas and liquid condensate will be brought to 25°C.
(a) You have been called in as a consultant to aid in the design of this unit. Unfortunately, the chief (and only) plant engineer has disappeared and nobody else in the plant can tell you what the off-gas is (or what anything else is, for that matter). However, a job is a job, and you set out to do what you can. You find an elemental analysis in the engineer's notebook indicating that the gas formula is $C_5H_{12}O$. On another page of the notebook, the off-gas flow rate is given as 235 m^3/h at 116°C and 1 atm. You take a sample of the gas and cool it to 25°C, where it proves to be a solid. You then heat the solidified sample at 1 atm and note that it melts at 52°C and boils at 113°C. Finally, you make several assumptions and estimate the heat removal rate in kW required to bring the off-gas from 116°C to 25°C. What is your result?
(b) If you had the right equipment, what might you have done to get a better estimate of the cooling rate?

Equipment Encyclopedia
dryer

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8.64. A sheet of cellulose acetate film containing 5.00 wt% liquid acetone enters an adiabatic dryer where 90% of the acetone evaporates into a stream of dry air flowing over the film. The film enters the dryer at $T_{f1} = 35°C$ and leaves at T_{f2}(°C). The air enters the dryer at T_{a1}(°C) and 1.01 atm and exits the dryer at $T_{a2} = 49°C$ and 1 atm with a relative saturation of 40%. C_p may be taken to be 1.33 kJ/(kg·°C) for dry film and 0.129 kJ/(mol·°C) for liquid acetone. Make a reasonable assumption regarding the heat capacity of dry air. The heat of vaporization of acetone may be considered independent of temperature. Take a basis of 100 kg film fed to the dryer for the requested calculations.

(a) Estimate the feed ratio [liters dry air (STP)/kg dry film].

(b) Derive an expression for T_{a1} in terms of the film temperature change, $(T_{f2} - 35)$, and use it to answer Parts (c) and (d).

(c) Calculate the film temperature change if the inlet air temperature is 120°C.

(d) Calculate the required value of T_{a1} if the film temperature falls to 34°C, and the value if it rises to 36°C.

(e) If you solved Parts (c) and (d) correctly, you found that even though the air temperature is consistently higher than the film temperature in the dryer, so that heat is always transferred from the air to the film, the film temperature can drop from the inlet to the outlet. How is this possible?

Equipment Encyclopedia
heat exchanger

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8.65. Saturated propane vapor at 2.00×10^2 psia is fed to a well-insulated heat exchanger at a rate of 3.00×10^3 SCFH (standard cubic feet per hour). The propane leaves the exchanger as a saturated liquid (i.e., a liquid at its boiling point) at the same pressure. Cooling water enters the exchanger at 70°F, flowing cocurrently (in the same direction) with the propane. The temperature difference between the outlet streams (liquid propane and water) is 15°F.

(a) What is the outlet temperature of the water stream? (Use the Antoine equation.) Is the outlet water temperature less than or greater than the outlet propane temperature? Briefly explain.

(b) Estimate the rate (Btu/h) at which heat must be transferred from the propane to the water in the heat exchanger and the required flow rate (lb_m/h) of the water. (You will need to write two separate energy balances.) Assume the heat capacity of liquid water is constant at 1.00 Btu/(lb_m·°F) and neglect heat losses to the outside and the effects of pressure on the heat of vaporization of propane.

ENVIRONMENTAL

***8.66.** Fish and wildlife managers have determined that a sudden temperature increase greater than 5°C would be harmful to the marine ecosystem of a river. Warmer waters contain less dissolved oxygen and cause organisms in a river to increase their metabolism; if the temperature increase is sudden, the organisms do not have time to adapt to the new environment and likely will die. (Changes in river temperatures of five degrees and more due to seasonal temperature variations are common, but those temperature changes are gradual.)

A proposed chemical plant plans to use river water for process cooling. The river flows at a rate of 15.0 m^3/s at a temperature of 15°C, and a fraction of it will be diverted to the plant. Preliminary calculations reveal that the cooling water will remove 5.00×10^5 kJ/s of heat from the plant. A portion of the extracted water will evaporate from the plant into the atmosphere, and the remainder will be returned to the river at a temperature of 35°C.

(a) Draw and completely label a flowchart of the process and prove that there is enough information available to calculate all of the unknown stream flow rates on the chart.

(b) Estimate the fraction of the river flow that must be diverted to the plant and the percentage of the cooling water that evaporates. Assume that water has a constant heat capacity of 4.19 kJ/(kg·°C) and a heat of vaporization roughly that of water at the normal boiling point, and also assume that the specific enthalpy of the water vapor relative to liquid water at 15°C equals the heat of vaporization.

(c) Write (but don't evaluate) an expression for the enthalpy change neglected by the assumption about the specific enthalpy of the steam.

Equipment Encyclopedia
evaporator

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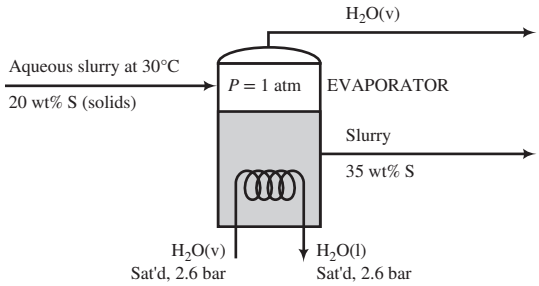
8.67. An aqueous slurry at 30°C containing 20.0 wt% solids is fed to an evaporator in which enough water is vaporized at 1 atm to produce a product slurry containing 35.0 wt% solids. Heat is supplied to the evaporator by feeding saturated steam at 2.6 bar absolute into a coil immersed in the liquid. The steam condenses in the coil, and the slurry boils at the normal boiling point of pure water. The heat capacity of the solids may be taken to be half that of liquid water.

* Adapted from a problem contributed by J. Patrick Abulencia of Manhattan College.



(a) Calculate the required steam feed rate (kg/h) for a slurry feed rate of 1.00×10^3 kg/h.

(b) **Vapor recompression** is often used in the operation of an evaporator. Suppose that the vapor (steam) generated in the evaporator described above is compressed to 2.6 bar and simultaneously heated to the saturation temperature at 2.6 bar, so that no condensation occurs. The compressed steam and additional saturated steam at 2.6 bar are then fed to the evaporator coil, in which isobaric condensation occurs. How much additional steam is required?

(c) What more would you need to know to determine whether or not vapor recompression is economically advantageous in this process?

Equipment Encyclopedia
distillation column
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8.68. A mixture that contains 46 wt% acetone (CH_3COCH_3), 27% acetic acid (CH_3COOH), and 27% acetic anhydride [$(CH_3CO)_2O$] is distilled at $P = 1$ atm. The feed enters the distillation column at $T = 348$ K at a rate of 15,000 kg/h. The distillate (overhead product) is essentially pure acetone, and the bottoms product contains 1% of the acetone in the feed.

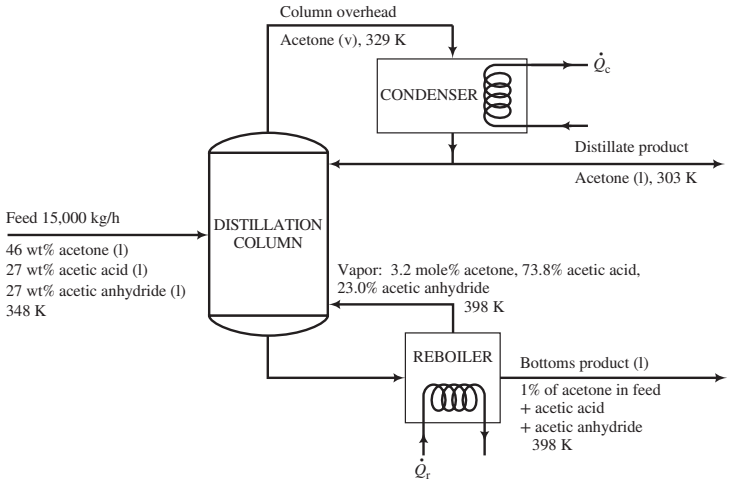
The vapor effluent from the top of the column enters a condenser at 329 K and emerges as a liquid at 303 K. Half of the condensate is withdrawn as the overhead product, and the remainder is refluxed back to the column. The liquid leaving the bottom of the column goes into a steam-heated reboiler, in which it is partially vaporized. The vapor leaving the reboiler is returned to the column at a temperature of 398 K, and the residual liquid, also at 398 K, constitutes the bottoms product. A flowchart of the process and thermodynamic data for the process materials follow.

(a) Calculate the mass flow rates and compositions of the product streams.

(b) Calculate the condenser cooling requirement $\dot{Q}_c$(kJ/h).

(c) Use an overall energy balance to determine the reboiler heating requirement $\dot{Q}_r$(kJ/h).

(d) If the reboiler heat is provided by the condensation of saturated steam at 10 bar gauge, at what rate must steam be fed?



Thermodynamic Data (All temperatures are in kelvins)

Acetone: $C_{pl} = 2.30$ kJ/(kg·K)

$$C_{pv}[\text{kJ/(kg·K)}] = 0.459 + 3.15 \times 10^{-3} T - 0.790 \times 10^{-6} T^2$$

$$\Delta\hat{H}_v(329\text{ K}) = 520.6\text{ kJ/kg}$$

Acetic acid: $C_{pl} = 2.18\ \text{kJ/(kg·K)}$

$C_{pv}[\text{kJ/(kg·K)}] = 0.688 + 1.87 \times 10^{-3}T - 0.411 \times 10^{-6}T^2$

$\Delta\hat{H}_v(391\ \text{K}) = 406.5\ \text{kJ/kg}$

Acetic anhydride: $C_{pl}[\text{kJ/(kg·K)}] = ?$ (Estimate it—see Section 8.3c.)

$C_{pv}[\text{kJ/(kg·K)}] = 0.751 + 1.34 \times 10^{-3}T - 0.046 \times 10^{-6}T^2$

$\Delta\hat{H}_v(413\ \text{K}) = ?$ (Estimate it—see Section 8.4b.)

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evaporator
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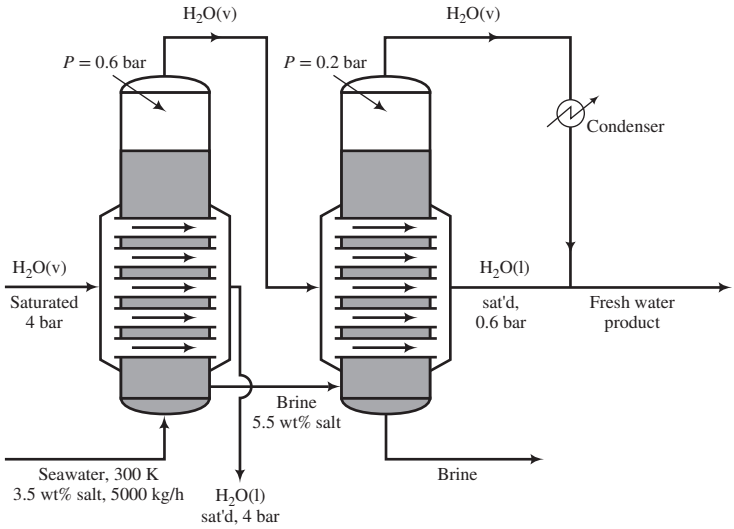
8.69. A **double-effect evaporator** (two evaporators in series) is used to produce fresh water from seawater containing 3.5 wt% dissolved salts. A flowchart for the process is shown here.



Seawater enters the first effect at 300 K at a rate of 5000 kg/h, and saturated steam at 4.00 bar absolute is fed into a tube bundle in the first effect. The steam condenses at 4.00 bar, and the condensate is withdrawn at the saturation temperature corresponding to this pressure.

The heat given up by the steam condensing in the tubes causes water to evaporate from the brine solution at the pressure of 0.60 bar maintained in the effect. The exiting brine contains 5.5 wt% salt. The steam generated in the first effect is fed to a tube bundle in the second effect. The condensate from the bundle and the steam generated in the second effect at a pressure of 0.20 bar constitute the fresh water produced in the process.

In solving the problems to be given, assume that the brine solutions in both effects have the physical properties of pure water and that the effects operate adiabatically.

(a) Draw and label a flowchart of this process, giving the temperature and specific enthalpy of each stream.

(b) At what rate must steam be fed to the first effect?

(c) What is the production rate of fresh water? What is the salt concentration (weight percent) of the final brine solution? Why is it inappropriate to add the condensate from the first effect to the production rate of fresh water?

(d) Why is it necessary that the pressure decrease from one effect to the next?

(e) Suppose a single-effect evaporator were used, operating at $P = 0.20$ bar. Calculate the feed rate of saturated steam at $P = 4.00$ bar that would be required to achieve the same production rate of fresh water. What more would you need to know to determine which process is more economical?

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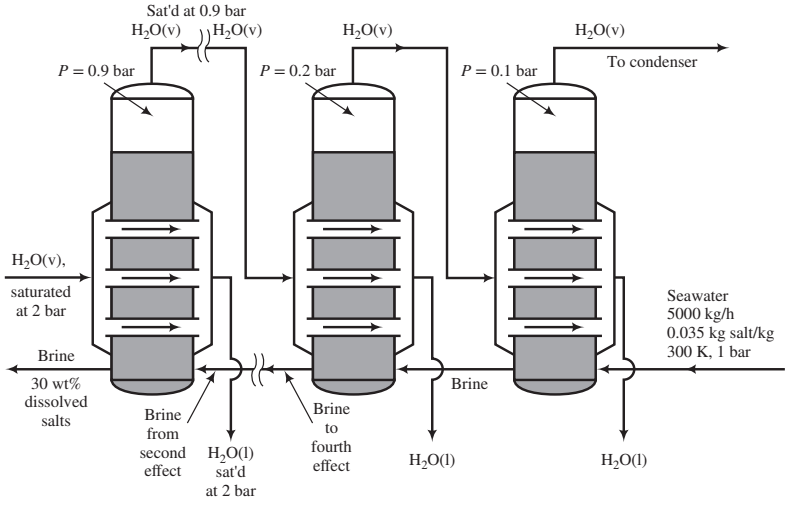
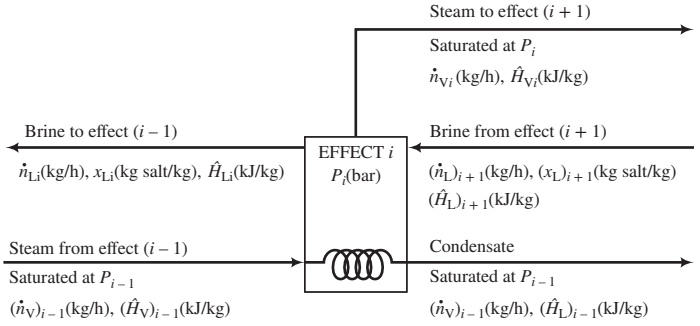
8.70. Seawater containing 3.5 wt% dissolved salts is to be desalinated in an adiabatic six-effect evaporator. (See Problem 8.69.) Backward feed is to be used: the seawater is fed to the last evaporator, and successively concentrated brine solutions flow countercurrent to the direction of flow of steam from one effect to the next. Saturated steam at $P = 2$ bar is fed to the tube bundle in the first effect. The

operating pressures in bars of the six effects are, respectively, 0.9, 0.7, 0.5, 0.3, 0.2, and 0.1. The brine leaving the first effect contains 30 wt% salt. The flowchart shows Effects 1, 5, and 6.



Following is a labeled diagram of the i^{th} effect:



In terms of the variables defined in this diagram,

$$\dot{n}_{L7} = 5000\ \text{kg/h}$$
$$x_{L7} = 0.035\ \text{kg salt/kg}$$
$$x_{L1} = 0.30\ \text{kg salt/kg}$$
$$\dot{n}_{V0} = \text{feed rate of steam to the first effect}$$

(a) Use a salt balance to calculate $\dot{n}_{L1}$. Then use this result to determine how much fresh water is produced in the process.

(b) Prepare a table as follows:

	P (bar)	T (K)	$\dot{n}_L$ (kg/h)	x_L	$\hat{H}_L$ (kJ/kg)	$\dot{n}_V$ (kg/h)	$\hat{H}_V$ (kJ/kg)
Fresh steam	2.0		—	—	—		
Effect 1	0.9			0.30			
2	0.7						
3	0.5						
4	0.3						
5	0.2						
6	0.1						
(7)	1.0	300	5000	0.035		—	—

Fill in all *known* variable values (do not calculate any yet), including values obtained from the steam tables, *assuming that the physical properties of the brine solution are those of pure water.*

(c) Show that the following equations can be derived from balances:

$$x_{Li} = (\dot{n}_L)_{i+1}(x_L)_{i+1}/\dot{n}_{Li} \quad \textbf{(1)}$$

$$(\dot{n}_V)_{i-1} = \frac{\dot{n}_{Vi}\hat{H}_{Vi} + \dot{n}_{Li}\hat{H}_{Li} - (\dot{n}_L)_{i+1}(\hat{H}_L)_{i+1}}{(\hat{H}_V)_{i-1} - (\hat{H}_L)_{i-1}} \quad \textbf{(2)}$$

$$(\dot{n}_L)_{i-1} = \dot{n}_{Li} - (\dot{n}_v)_{i-1} \quad \textbf{(3)}$$

(d) Solve the equations of Part (c) for all six effects using Excel's Solver or another equation-solving program. Fill in the table of Part (b).

8.71. A liquid is placed in a well-insulated container, which is then sealed. Initially, the container and its contents (the liquid and pure nitrogen) are at 93°C and 1 atm; the liquid volume is 70 cm^3, and the gas volume is 3.00 L. The liquid partially evaporates, and the system cools down and eventually comes to thermal equilibrium at 85°C with liquid still present. Physical property data for the liquid and its vapor are:

$$\Delta\hat{U}_v = 20 \text{ kcal/mol at } 90°C$$
$$(C_p)_{liq} = 20 \text{ cal/(mol·°C)}$$
$$(C_p)_{vap} = 10 \text{ cal/(mol·°C)}$$
$$(SG)_{liq} = 0.90$$
$$MW = 42$$

(a) Determine $(C_v)_{liq}$ and $(C_v)_{vap}$. (See Equations 8.3-11 and 8.3-12.)

(b) Draw and label a flowchart for this closed system process, and write and simplify the energy balance equation, assuming adiabatic operation.

(c) Use the energy balance to calculate the mass of liquid that evaporates, taking 4.97 cal/(mol·°C) as the heat capacity of nitrogen.

(d) Calculate the vapor pressure of the liquid at 85°C, assuming that the gas volume remains constant at 3.00 L.

BIOENGINEERING

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8.72. A small pharmaceutical firm plans to manufacture a new drug and has hired you as a consultant to design a condenser to remove the drug from a gas–vapor mixture. The mixture, which contains 20 mole% of the drug and the balance nitrogen, will be fed to the condenser at 510 K and 1 atm at a rate of 3.5 L/s. Of the drug fed to the unit, 90% must be condensed. No physical property data are available for the drug, and part of your job is to acquire the data needed to design the condenser. The company has sent you a large sample of the liquid drug for this purpose.

You acquire an insulated 2.000-liter container with a known heat capacity and a built-in electrical heating coil that can deliver a known heat input to the contents of the container. A calibrated thermocouple is used to measure the temperature in the vessel, and the pressure is measured with a mercury manometer.

You carry out a series of experiments on a day when atmospheric pressure is 763 mm Hg.

Experiment 1. Fill the container with the liquid, then seal and weigh.

$$\text{mass of container + liquid} = 4.4553 \text{ kg}$$
$$\text{mass of evacuated container} = 3.2551 \text{ kg}$$

Next, starting at each of two temperatures (T_0), add a fixed quantity of heat to the liquid, observe the final temperature (T_f), and subtract the heat absorbed by the container from the total heat input to determine the amount of the heat added to the liquid, Q_a.

$$T_0 = 283.0 \text{ K}, Q_a = 800.0 \text{ J} \Longrightarrow T_f = 285.4 \text{ K}$$
$$T_0 = 330.0 \text{ K}, Q_a = 800.0 \text{ J} \Longrightarrow T_f = 332.4 \text{ K}$$

Assume that the liquid heat capacity may be expressed as a linear function of temperature ($C_v = aT + b$) when analyzing these results.

Experiment 2. Pour a small quantity of the drug into the container, place the container in a liquid nitrogen bath to freeze the drug, evacuate all of the air, and seal the container. Weigh the container after it comes back to room temperature.

$$\text{mass of container + drug} = 3.2571\ \text{kg}$$

Next heat the sealed container until all of the liquid evaporates, and repeat Experiment 1.

$$T_0 = 363.0\ \text{K}, h_{\text{manometer}} = -500\ \text{mm}, Q_a = 1.30\ \text{J} \Longrightarrow T_f = 366.9\ \text{K}$$
$$T_0 = 490.0\ \text{K}, h_{\text{manometer}} = -408\ \text{mm}, Q_a = 1.30\ \text{J} \Longrightarrow T_f = 492.7\ \text{K}$$

Assume that the vapor heat capacity may be expressed as a linear function of temperature when analyzing these results.

Experiment 3. Fill approximately half the container with the drug, freeze, evacuate the air, and seal. Measure the pressure at several temperatures, verifying that liquid is present in the container at each temperature.

$$T = 315.0\ \text{K}, h_{\text{manometer}} = -564\ \text{mm}$$
$$T = 334.0\ \text{K}, h_{\text{manometer}} = -362\ \text{mm}$$
$$T = 354.0\ \text{K}, h_{\text{manometer}} = -2\ \text{mm}$$
$$T = 379.0\ \text{K}, h_{\text{manometer}} = +758\ \text{mm}$$

(a) Using the given data, determine the following physical properties of the drug: (i) liquid specific gravity, (ii) molecular weight, (iii) linear expressions for the heat capacities at constant volume [in J/(mol·K)] for both the liquid and vapor [$C_v = a + bT(K)$], (iv) linear expressions for C_p for both liquid and vapor, (v) a Clausius–Clapeyron expression for $p^*(T)$, (vi) the normal boiling point, and (vii) the heat of vaporization (in J/mol) at the normal boiling point.

(b) Calculate the required condenser temperature, assuming operation at 1 atm.

(c) Calculate the rate at which heat must be removed in the condenser, taking the heat capacity of nitrogen to be constant at 29.0 J/(mol·K).

8.73. Freeze drying is a technique for dehydrating substances at low temperatures, thereby avoiding the degradation that may accompany heating. The material to be dried is cooled to a temperature at which all of the water present turns to ice. The frozen substance is then placed in a vacuum chamber and may also be subjected to radiant or microwave heating; the ice in the food sublimes, and the vapor is carried off by the vacuum pump.

Steaks are to be freeze-dried in a heated chamber at 1 torr (1 mm Hg). The steaks, which contain 72% water by mass, enter the chamber at −26°C at a rate of 50 kg/min. Of the water entering with the steaks, 96% leaves as a vapor at 60°C; the remainder leaves as a liquid with the steaks at 50°C.

(a) Use the heat capacity data given below and additional tabulated data for water to calculate the required heat input in kilowatts.

$$(C_p)_{\text{ice}} = 2.17\ \text{J/(g·°C)}$$
$$(C_p)_{\text{dry meat}} = 1.38\ \text{J/(g·°C)}$$

(b) When large temperature changes are not involved in a phase-change operation, a reasonable estimate of the required heat transfer rate may be obtained by neglecting contributions of temperature changes to the overall process enthalpy change (i.e., by taking only phase changes into account). Moreover, it is often reasonable to use any available values of latent heats, neglecting their dependence on temperature and pressure. In the case of the freeze-drying process, the approximation might be to calculate only the heat needed to melt all the water and vaporize 96% of it, using latent heats at the normal melting and boiling points (Table B.1) and neglecting the heat required to raise the temperature of the meat and water. What percentage error in the calculated value of $\dot{Q}$ would result from this approximation? Take the value determined in Part (a) to be exact.

BIOENGINEERING →

(c) Many substances, such as food and drugs, spoil if exposed too long to high temperatures (which accelerate rates of degradation) or to liquid water (which provides an environment for growth of microbial species that cause degradation). Also, rates of evaporation and sublimation increase as

temperature increases and pressure decreases. Use those observations to construct a one-paragraph explanation of how freeze-drying works and the reason for each step of the process. (For example, why is the sublimation done in a vacuum chamber?) Your explanation should be clear to someone with a nontechnical or nonscientific background.

BIOENGINEERING

*8.74. The manufacturers of a new oatmeal product want to determine the least expensive way to safeguard and transport their product. They choose *lyophilization* (freeze drying), which removes most of the water from the product, making it lighter and therefore less costly to transport over long distances, and substantially increases its shelf life. Lyophilization also removes some of the impurities introduced by industrial farming methods.

A solid feed stream containing 70.0 wt% oatmeal, 27% water (ice), and the balance organic impurities enters a heated vacuum chamber at a rate of 1.0×10^3 kg/h at a temperature of −10°C. In the vacuum chamber, 97% of the water and 99% of the organic impurities in the feed sublime (vaporize). The dried product is then packaged and shipped. A vapor stream emerges from the chamber at 15°C. During the process, 7.95×10^5 kJ/h of heat is transferred to the system.

(a) Draw and completely label a flowchart of the process and perform a degree-of-freedom analysis.

(b) Calculate the compositions and flow rates of the product and waste streams.

(c) Find the temperature of the product stream, using the following values for heat capacity and heat of sublimation and neglecting the contribution of the organic impurities to the energy balance.

$$C_p[H_2O(s)] = 2.11 \text{ kJ/(kg·°C)}$$
$$C_p[H_2O(v)] = 1.86 \text{ kJ/(kg·°C)}$$
$$C_p(\text{oatmeal}) = 1.5 \text{ kJ/(kg·°C)}$$
$$(\Delta\hat{H}_{\text{subl}})_{H_2O} = 2845 \text{ kJ/kg}$$

(d) Evaporation is a more conventional way to dry a wet solid—that is, heating the solid at atmospheric pressure to a temperature close to the boiling point of the liquid (in this case, water) and holding it there long enough to drive off essentially all of the liquid. Give at least two reasons why freeze drying is a better alternative for drying the oatmeal.

BIOENGINEERING

8.75. Freeze concentration is used to produce a fruit-juice concentrate. A stream of fresh juice containing 12 wt% soluble solids in water at 20°C is combined with a recycle stream to form a preconcentrate, which is fed to a crystallizer. The mixture is cooled in the crystallizer to −7°C, thereby crystallizing 20,000 kg/h of ice. A slurry leaves the crystallizer containing 10 wt% ice and is fed to a filter. The filtrate, which contains 45 wt% dissolved solids, is removed as the process product. The remaining slurry, which contains all the ice and some concentrate (also containing 45% dissolved solids), is sent to a separator that cleanly removes all of the ice. The residual liquid is the recycle stream that combines with the fresh feed to form the preconcentrate.

(a) Determine the rates (kg/h) at which fresh fruit juice is fed and concentrate is produced, and the mass flow rate (kg/h) and solids concentration of the preconcentrate.

(b) Calculate the cooling requirement (kW) for the freezer, assuming that the temperature of the recycle stream is 0°C and the heat capacity of all solutions is 4.0 kJ/(kg·°C).

(c) An alternative to freeze concentration is to evaporate some of the water from the juice at atmospheric pressure, producing a concentrate with 45% dissolved solids. There are two reasons this process may be less attractive: one is applicable to any solute, and the second applies particularly to a food product. Speculate on what they are.

(d) A second alternative would also involve vaporization, but at low pressure. Why might this alternative be preferable to the one in Part (c), and what would determine whether it would be preferable to freeze concentration?

Equipment Encyclopedia
heat exchanger

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8.76. A mixture containing 35.0 mole% *n*-butane and the balance isobutane at 10°C enters a heat exchanger at a rate of 24.5 kmol/h and a pressure high enough for the mixture to be a liquid. The exchanger has been designed to heat and vaporize the liquid and heat the vapor mixture to 180°C. The heating fluid is a high molecular weight liquid with a constant heat capacity $C_p = 2.62$ kJ/(kg·°C). It enters the exchanger at 215°C and flows countercurrently to the hydrocarbon mixture.

* Adapted from a problem contributed by J. P. Abulencia of Manhattan College.

(a) Estimate the minimum pressure (bar) required for the hydrocarbon feed to be a liquid.

(b) Assuming that the heat capacities and heats of vaporization of *n*-butane and isobutane are independent of pressure (so that the values in Tables B.1 and B.2 may be used), calculate the enthalpy change $\Delta\dot{H}$(kJ/h) undergone by the hydrocarbon mixture in the heat exchanger. Show the process paths you use for *n*-butane and *i*-butane in your calculation. (*Hint:* Since you don't have heat capacities for liquid *n*-butane and *i*-butane in this text, use process paths that don't require them.)

(c) According to the heat exchanger design calculations, the heating fluid exit temperature should be 45°C. Assuming that all the heat lost by the heating fluid is transferred to the hydrocarbon mixture, what is the required mass flow rate of the heating fluid, $\dot{m}_{hf}$(kg/h)?

(d) When the heat exchanger is run with $\dot{m}_{hf}$ equal to the value calculated in Part (b), the exit temperature of the hydrocarbon mixture is measured and found to be only 155°C instead of the design value of 180°C. The process operator observes that the outside of the exchanger is hot to the touch, indicating that some of the heat lost by the heating fluid is escaping into the plant instead of being transferred to the hydrocarbon mixture. After discussing the situation with a production engineer, the operator gradually increases the flow rate of the heating fluid while continuing to monitor the outlet temperature of the hydrocarbon. When the flow rate reaches 2540 kg/h, the outlet fluid temperatures level out at their design values (180°C for the hydrocarbon and 45°C for the heating fluid). At what rate (kJ/h) is heat being transferred from the exchanger to the plant air?

(e) When the heating fluid leaves the exchanger, it passes through a heater, which raises its temperature back to 215°C, and is recycled back to the exchanger. How is the profitability of the process being decreased by the heat loss from the exchanger to the surroundings? (Try to think of two costs that result from the heat loss.)

(f) The engineer proposes adding more insulation to the heat exchanger, which would cut down on the heat loss and reduce the required heating fluid flow rate. What are advantages and disadvantages of the two responses to the heat loss problem (adding insulation versus increasing the heating fluid flow rate)? Which would you guess would be the preferable response in the long run, and why?

BIOENGINEERING →

*__8.77.__ Ketchup contains tomatoes, corn syrup, vinegar, sugar, water, and a variety of seasonings. A recipe for homemade ketchup involves combining the ingredients and pouring them into sterile canning jars, leaving some head space (air) at the top; covering each jar with a metal lid that has a rubber seal on its bottom side; and loosely screwing a metal band onto the threaded top of the jar to keep the lid in place while allowing steam and air to escape. The jars are immersed in boiling water for about 30 minutes and then removed; the bands are tightened to assure a tight seal between the lid and the jar contents; and the jars cool to room temperature. As long as the seal remains tight, a jar can be stored for up to a year.

Suppose the canning jar diameter is 2¼ inches, and a half-inch of headspace is left after the ketchup has been added to the jar. Room temperature is 25°C. In the calculations that follow, assume that water is the only volatile component of ketchup and that the head space volume remains constant at its initial value.

(a) During this process, what is the lowest pressure (atm) in the head space of the jar?

(b) Estimate the molar composition of the gas in the head space when the canning process is complete, stating all assumptions you make.

(c) Calculate the energy (kJ) transferred from the head space during the cooling process. Again, state your assumptions.

(d) Speculate on the likely reason for boiling the ketchup.

(e) When the band is removed from the top of a jar of ketchup, the lid remains firmly attached to the top of the jar and sometimes may need to be pried off. Why?

Exploratory Exercises—Research and Discover

(f) A concern in preparing any item for human consumption is the existence of pathogens, some of which prosper in oxygen-rich environments (aerobic) and some in oxygen-lean environments (anerobic). Among the most deadly bacteria found in improperly canned foods is *clostridium botulinum*.

(i) Identify the conditions under which growth of *clostridium botulinum* is favored.

(ii) Botulinum spores are present on the surfaces of most fresh foods. Why is this relatively harmless?

(iii) Explain why pressure canners may be recommended with some foods and locations.

* Adapted from a problem contributed by Paul Blowers of the University of Arizona.

8.78. A liquid mixture of benzene and toluene containing 50.0 wt% benzene at 100°C and pressure P_0 is fed at a rate of 32.5 m^3/h into a heated *flash tank* maintained at a pressure $P_{tank} \ll P_0$. When the feed is exposed to the reduced pressure in this unit, a portion of it evaporates. The liquid and vapor product streams are in equilibrium at 75°C and P_{tank}. The liquid product contains 43.9 mole% benzene. When carrying out the requested calculations, assume volume additivity of liquid benzene and toluene, use Raoult's law and the Antoine equation where necessary, and neglect the effect of pressure on enthalpy.

(a) Calculate the molar flow rate (mol/s) and molar composition (component mole fractions) of the feed stream. Then calculate the minimum value of P_0(atm) needed to keep the feed stream in the liquid state until it enters the flash tank.

(b) Calculate P_{tank}(atm), the mole fraction of benzene in the vapor, and the molar flow rates of the liquid and vapor products.

(c) Calculate the required heat input rate in kilowatts.

(d) An hour after the system is started up, a chromatographic analysis of the vapor product is run and the benzene mole fraction is found to be 3% higher than the value calculated in Part (b). The system temperature and pressure are rechecked and found to have the correct values. Give several possible explanations of the discrepancy between the calculated and measured values.

(e) Briefly explain why the product temperature is lower than the feed temperature. What would be required to run the unit isothermally?

8.79. A continuous adiabatic flash tank is to be used to separate a liquid mixture of two substances (A and B). The feed enters at temperature T_F and a high pressure and flashes to a low pressure, P, whereupon its temperature drops to T. For an assumed basis of 1 mol/s of feed, let

$$\begin{aligned}
\dot{n}_L, \dot{n}_V &= \text{molar flow rates of liquid product and vapor product} \\
x_F, x, y &= \text{mole fractions of A in the feed, liquid product, and vapor product} \\
p^*_A(T), p^*_B(T) &= \text{vapor pressures of A and B} \\
T_{RA}, T_{RB} &= \text{reference temperatures for enthalpy calculations}
\end{aligned}$$

$$\left.\begin{matrix} \hat{H}_{AF}(T_F), \hat{H}_{AL}(T), \hat{H}_{AV}(T) \\ \hat{H}_{BF}(T_F), \hat{H}_{BL}(T), \hat{H}_{BV}(T) \end{matrix}\right\} \text{ specific enthalpies of A and B in the feed, liquid product, and vapor product, relative to } T_{RA} \text{ and } T_{RB}$$

(a) Derive the following relations from Raoult's law and material and energy balances on the flash tank:

$$x = \frac{P - p^*_B(T)}{p^*_A(T) - p^*_B(T)} \tag{1}$$

$$y = x p^*_A(T)/P \tag{2}$$

$$\dot{n}_L = \frac{y - x_F}{y - x} \tag{3}$$

$$\dot{n}_V = 1 - \dot{n}_L \tag{4}$$

$$\begin{aligned}
\Delta\dot{H} = \dot{n}_L[x\hat{H}_{AL}(T) + (1-x)\hat{H}_{BL}(T)] + \dot{n}_V[y\hat{H}_{AV}(T) + (1-y)\hat{H}_{BV}(T)] \\
- [x_F\hat{H}_{AF}(T_F) + (1-x_F)\hat{H}_{BF}(T_F)] = 0
\end{aligned} \tag{5}$$

(b) Write a spreadsheet program to perform flash calculations for a feed mixture of *n*-pentane and *n*-hexane. When calculating enthalpies of these species, the following heat capacity formulas should be used for liquid and vapor, respectively:

$$\begin{aligned}
C_{pl} &= a_l \\
C_{pv} &= a_v + b_v T(°C)
\end{aligned}$$

The spreadsheet should have the following form. Some values are given, others should be looked up in data tables, and the remainder should be calculated from Equations 1 to 5 and appropriate formulas for specific enthalpies.

Problem 8.79								
Tref = 25 deg. C								
Compound	A	B	C	al	av	bv	Tb	DHv
n-pentane	6.84471	1060.793	231.541	0.195	0.115	3.41E-4	36.07	25.77
n-hexane				0.216	0.137	4.09E-4		
xF	0.5	0.5	0.5	0.5				
Tf(deg.C)	110	110	150					
P(mm Hg)	760	1000	1000					
HAF (kJ/mol)								
HBF (kJ/mol)								
T(deg.C)	80.0							
pA* (mm Hg)								
pB* (mm Hg)								
x								
y								
nL (mol/s)								
nV (mol/s)								
HAL (kJ/mol)								
HBL (kJ/mol)								
HAV (kJ/mol)								
HBV (kJ/mol)								
DH (kJ/s)	−51.333							

In this table, A, B, and C are Antoine equation constants, al, av, and bv are the coefficients of the given heat capacity formulas; Tb(°C) and DHv(kJ/mol) ($\Delta\hat{H}_v$) are the normal boiling point and heat of vaporization, xF(mol pentane/mol) is the mole fraction of pentane in the feed, Tf(°C) is the feed temperature, P(mm Hg) is the system pressure, HAF ($\hat{H}_{AF}$) and HBF ($\hat{H}_{BF}$) are the specific enthalpies of pentane and hexane in the feed stream, pA* is the vapor pressure of *n*-pentane (to be determined using the Antoine equation), x and nL (x and $\dot{n}_L$) are the mole fraction of pentane in the liquid product stream and the molar flow rate of that stream, respectively, y and nV are the corresponding properties of the vapor product stream, HAL is the specific enthalpy of pentane in the liquid product stream, and DH ($\Delta\dot{H}$) is the expression given in Equation 5 for the change in total enthalpy from inlet to outlet.

Enter the appropriate constants and formulas for A, B, C, al, av, bv, Tb, and DHv for *n*-pentane and *n*-hexane, an initial guess for T in Column 2 (= 80.0), and the appropriate formulas for the rest of the variables in Column 2. Then vary the value of T until the value of $\Delta\dot{H}$ is suitably close to zero, using the Goal Seek tool. The value of $\Delta\dot{H}$ (−51.33 kJ/s) corresponding to the initial guess of 80°C is shown in the second column of the table. Your spreadsheet should generate the same value.

After completing the calculations in the second column, copy the formulas into the third and fourth columns and perform the calculations for these two sets of input parameter values. State how increasing the system pressure and feed temperature affect the fraction of the feed vaporized (nV) and the final system temperature (T), and briefly explain why your results make sense.

Equipment Encyclopedia
distillation column

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8.80. A saturated vapor stream containing 10.9 mole% propane, 75.2% isobutane, and 13.9% *n*-butane passes from the top of a distillation column to a total condenser. Seventy-five percent of the condensate is returned to the column as reflux, and the remainder is removed as the overhead column product at a rate of 2500 kmol/h.

A decision must be made on whether to use a refrigerant or cooling water in the condenser. If the refrigerant is used, it will be fed to the condenser as a liquid and vaporized by the heat released by the condensing column vapor. The refrigerant pressure will be such that the vaporization takes place at −6°C, at which temperature $\Delta\hat{H}_v = 151$ kJ/kg. The other option calls for cooling water to be taken from a nearby river at its average summer temperature of 25°C. To avoid environmental problems, the temperature of the water returned to the river can be no greater than 34°C. With either system, the temperature of the condensate should be 6°C greater than the outlet temperature of the coolant, so that if the refrigerant is used the saturated condensate should have a temperature of 0°C, and if cooling water is used the saturated condensate should be at 40°C. The condenser pressure will be set to the minimum value needed to condense all of the vapor, which is to say the condensate will be at its bubble-point temperature at the condenser pressure. Raoult's law may be used for all bubble-point and dew-point calculations (see Section 6.4c).

(a) Suppose the refrigerant is used for cooling. Estimate the condenser pressure P(mm Hg); the temperature T_f(°C) of the vapor fed to the condenser, assuming that the vapor is at its dew point at pressure P; and the required coolant flow rate (kg/h).

(b) Repeat Part (a) assuming that cooling water is fed to the condenser.

(c) What more would you need to know to be able to choose between the two options?

Equipment Encyclopedia
reactor, boiler, heat exchanger, absorption column

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8.81. Formaldehyde is produced from methanol in a catalytic oxidation reactor. The following reactions take place:

$$CH_3OH \rightarrow HCHO + H_2$$
$$2H_2 + O_2 \rightarrow 2H_2O$$

A stream of methanol is joined by a recycle stream, also methanol, and the combined stream is fed to the conversion reactor. Also entering the reactor are air (to oxidize some of the hydrogen produced in the methanol conversion reaction) and steam (to control the reactor temperature). The product gas from the reactor contains 19.9 mole% formaldehyde, 8.34% methanol, 30.3% nitrogen, 0.830% oxygen, 5.0% hydrogen, and 35.6% water vapor and is at 600°C and 1 atm.

The following process is used to separate the formaldehyde from the unreacted methanol and noncondensable gases. The gases leaving the reactor are fed to a waste-heat boiler, in which they are cooled to 145°C, in the process generating steam at 3.1 bar from saturated liquid water (i.e., liquid water at its boiling point) at the same pressure. The gases are cooled further to 100°C in a heat exchanger, where they come into thermal contact with cooling water fed at 30°C. To reduce scaling on the heat exchanger tubes, the temperature increase of the cooling water is limited to 15°C. The cooled gases are fed to an absorption column, where methanol and formaldehyde are absorbed in water. Pure water at 20°C is fed to the top of the column. The gas leaving the absorber is saturated with water vapor at 27°C and 1 atm and contains 200 parts of formaldehyde per million parts (by volume) of total gas. The aqueous solution leaving the bottom of the absorber at 88°C is fed to a distillation column that operates at 1 atm. The final product solution, which contains 37 wt% formaldehyde, 1% methanol, and the balance water, is removed from the reboiler at the bottom of the column, while pure methanol vapor emerges as the overhead product and is condensed at 1 atm. A portion of the condensate is refluxed to the top of the column, and the rest is recycled to the methanol conversion reactor. The reflux ratio, or ratio of methanol refluxed to methanol recycled to the reactor, is 2.5:1.

(a) Taking as a basis of calculation 100 mol of gas leaving the conversion reactor, draw and completely label a flowchart of this process. Then calculate the moles of fresh methanol feed, formaldehyde product solution, recycled methanol, and absorber off-gas, the kg of steam generated in the waste-heat boiler, and the kg of cooling water fed to the heat exchanger between the waste-heat boiler and the absorber. Finally, calculate the heat (kJ) that must be removed in the distillation column overhead condenser, assuming that methanol enters as a saturated vapor at 1 atm and leaves as a saturated liquid at the same pressure.

(b) By what factor must all of the calculated quantities be multiplied to scale the flowchart to a production rate of 3.6×10^4 metric tons per year of formaldehyde solution, assuming that the process is on-stream 350 days per calendar year?

Equipment Encyclopedia
thermometer

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8.82. An outside-air sample is taken on a day when the temperature is 78°F and the relative humidity is 40%.
(a) Use the psychrometric chart to state as many physical properties of the air as you can without doing any calculations. For each one, provide a brief description of the property in your own words.
(b) A thermometer is mounted on the back porch of your house. What temperature would it read?
(c) A sample of outside air is cooled at constant pressure. At what temperature would condensation begin?
(d) You step out of your neighborhood pool and feel quite cold until you dry off. Explain why. Estimate your skin temperature while you were still wet. Explain your answer. What would be different if the relative humidity were 98%?

8.83. An open vessel containing 0.205 lb_m of liquid water is placed in an empty room 5 ft wide, 4 ft deep, and 7 ft high, which initially contains dry air at 90°F. All the water evaporates without changing the room temperature.
(a) Use the psychrometric chart to estimate the final relative humidity, wet-bulb temperature, humid volume, dew-point temperature, and specific enthalpy of the room air. Take the molecular weight of dry air to be 29.0, and for simplicity, assume the mass of dry air in the room stays constant at its initial value.
(b) To answer Part (a), you had to make a significant assumption besides the one given in the problem statement. What was it? (*Hint:* You could test it by measuring the calculated quantities in different parts of the room.)

Equipment Encyclopedia
psychrometer

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8.84. A **sling psychrometer** is a device to measure the humidity of air. A porous cloth (the **wick**) is wrapped around the bulb of a mercury thermometer, which is then whirled around in the air. As the water in the wick evaporates, the temperature of the thermometer bulb drops, and finally stabilizes at the wet-bulb temperature of the air. The dry-bulb temperature is read from a second thermometer mounted on the sling.

One summer day, the weather bureau reports a temperature of 33°C and a relative humidity of 40%. You wipe the sweat from your forehead and remark to a friend that you'd bet $5 that the report is wrong, and the relative humidity is higher than 80%. He immediately puts a $5 bill on the table, accepting your challenge. You bring out your sling psychrometer, whirl it around, and read a dry-bulb temperature of 35°C and a wet-bulb temperature of 29°C. Who wins the bet?

8.85. Humid air is enclosed in a 2.00-liter flask at 40°C. The flask is slowly cooled. When the temperature reaches 20°C, drops of moisture become visible on the flask wall. Although the pressure in the flask changes when the temperature drops, it remains close enough to 1 atm for the psychrometric chart to provide a close representation of the behavior of the system throughout the process. Use the chart to solve the following problems.
(a) What were the relative humidity, absolute humidity, and wet-bulb temperature of the air at 40°C?
(b) Calculate the mass of the water in the flask. (See Example 8.4-5.)
(c) Calculate the enthalpy change in joules undergone by the air in going from 40°C to 20°C.
(d) Write an energy balance for this closed-system process, taking the wet air in the flask as the system, and use it to calculate the heat in joules that must be transferred from the air to accomplish the cooling. (Assume ideal-gas behavior, so that $\hat{H} = \hat{U} + RT$.)
(e) You assumed that the pressure in the flask remained constant at 1 atm throughout the cooling process so you could use the psychrometric chart. What would the pressure in the flask actually have done, and why? How would your answers to Part (a) change if you took the pressure change into account (increase, decrease, no change, can't tell without more information)? Explain your answers.

Equipment Encyclopedia
dryer

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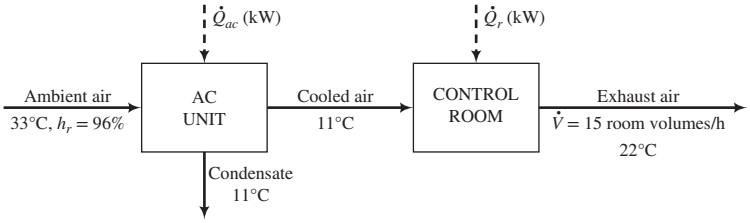
8.86. Wet solids pass through a continuous dryer. Hot dry air enters the dryer at a rate of 400 kg/min and mixes with the water that evaporates from the solids. Humid air leaves the dryer at 50°C containing 2.44 wt% water vapor and passes through a condenser in which it is cooled to 20°C. The pressure is constant at 1 atm throughout the system.
(a) At what rate (kg/min) is water evaporating in the dryer?
(b) Use the psychrometric chart to estimate the wet-bulb temperature, relative humidity, dew point, and specific enthalpy of the air leaving the dryer.
(c) Use the psychrometric chart to estimate the absolute humidity and specific enthalpy of the air leaving the condenser.
(d) Use the results of Parts (b) and (c) to calculate the rate of condensation of water (kg/min) and the rate at which heat must be transferred from the condenser (kW).
(e) If the dryer operates adiabatically, what can you conclude about the temperature of the entering air? Briefly explain your reasoning. What additional information would you need to calculate this temperature?

SAFETY

Equipment Encyclopedia
humidity measurement
www.wiley.com/college/felder

*8.87. Workers in the petrochemical industry often wear flame-retardant jumpsuits. Unfortunately, the material from which they are made hinders evaporation of perspiration, and consequently heat stress can be a hazard in plants where it is hot and humid.

A control room in a petrochemical facility with dimensions 20 ft × 40 ft × 10 ft is used by workers to relax periodically in a cool environment. One summer day, the ambient air temperature is 33°C and the relative humidity is 96%. The air conditioning (AC) unit in the control room takes in ambient air and cools it to 11°C, which causes condensation of water that is discharged to a drain, and delivers the cooled air to the control room. The room air is maintained at 22°C, and there are 15 changes of room air per hour. The process may be shown schematically as follows.



(a) Use the psychrometric chart to estimate the following properties of the ambient air, cooled air, and exhaust air: moisture content, dew point, humid volume, and enthalpy at the process condition. Also estimate the volumetric flow rate (m^3/h) and relative humidity of the exhaust air. (*Hint:* What can you say about the moisture content of the cooled air and the exhaust air?) How could you know simply by inspection of the ambient air properties that some of the water entering the air conditioner would be condensed?

(b) Draw and fully label a flowchart of the process. (*Suggestion:* Label the molar flow rates of each stream component.) Then calculate the rate of condensation of water (kg/h).

(c) Prepare an inlet–outlet enthalpy table for an energy balance on the air conditioner, taking the same reference conditions used to prepare Figure 8.4-1 (given in the figure caption). Calculate the cooling load on the air conditioner [$-\dot{Q}_{ac}$(kW)].

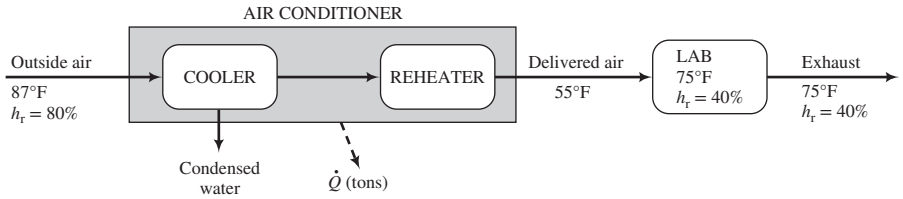
(d) Calculate the net rate of heat transfer to the air in the room, $\dot{Q}_r$(kW). List probable sources of this heat.

(e) In practice, about 80% of the exhaust air would be recycled to the air conditioner inlet. State at least two benefits of doing so.

Equipment Encyclopedia
condenser, heat exchanger
www.wiley.com/college/felder

8.88. On an uncomfortable summer day, the air is at 87°F and 80% relative humidity. A laboratory air conditioner is to deliver 1.00×10^3 ft^3/min of air at 55°F in order to maintain the interior air at an average temperature of 75°F and a relative humidity of 40%.

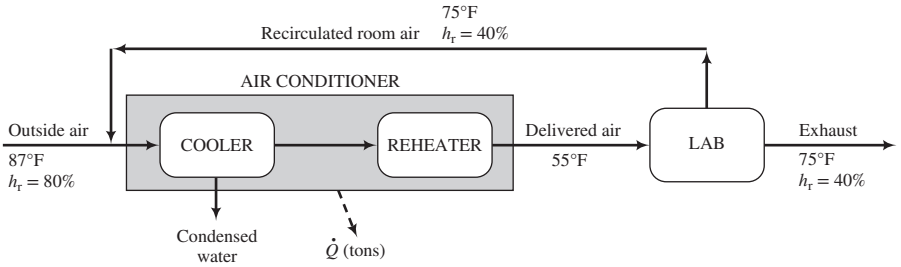
(a) If the vent switch on the air conditioner is turned to the "open" position, outside air enters the unit as shown below.



In the air conditioner, the air is cooled to a temperature low enough to condense the necessary amount of water and reheated to 55°F, at which point it has the same absolute humidity as the room air. Use the psychrometric chart to estimate the rate (lb_m/min) at which water is condensed, the temperature to which the air must be cooled to condense water at this rate, and the net tons of cooling required ($\dot{Q}$), where 1 ton of cooling = −12,000 Btu/h. [*Note:* The humid volume of the delivered air (at 55°F), which is difficult to read from the psychrometric chart, is 13.07 ft^3/lb_m dry air, and the heat capacity of liquid water is 1.0 Btu/(lb_m·°F).]

* Adapted from a problem contributed by Carol Clinton of the National Institute for Occupational Safety and Health (NIOSH).

(b) If the vent switch is set to the "closed" position (as it normally would be), inside air would be recirculated through the air conditioner as shown in the following diagram.



The recycle ratio (ft^3 recirculated/ft^3 exhausted) is 6:1. Calculate the condensation rate and the overall cooling requirement in tons if conditioned air is delivered at the same rate, temperature, and relative humidity as in Part (a). What percentage of the cooling load on the air conditioner is saved by recirculating the air? Explain in your own words why the cooling rate is lower when room air is recirculated instead of bringing all the air in from the outside.

(c) An even lower cooling load would be required if *all* of the air passing through the conditioner were recirculated rather than just 6/7 of it, thereby eliminating the need for outside air and exhaust. Why would this be a bad idea? (*Hint:* Think about the people working in the laboratory.)

Equipment Encyclopedia
dryer

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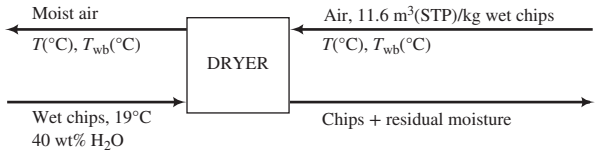
8.89. Wet wood chips are dried in a continous rotary dryer that operates at atmospheric pressure. The chips enter at 19°C with a water content of 40 wt% and must leave with a moisture content of less than 15%. Hot air is fed to the dryer at a rate of 11.6 m^3(STP)/kg wet chips.

To monitor the performance of the dryer by sampling the exiting chips and determining their moisture content directly would be a cumbersome procedure and almost impossible to automate. Instead, wet- and dry-bulb thermometers are mounted in both the inlet and outlet air lines, and the moisture content of the exiting chips is determined by a material balance.



After the unit goes on-stream, the inlet dry-bulb temperature is found to be 100°C, and the wet-bulb temperature is low enough so that the moisture content of the air may be neglected. The dry-bulb temperature of the exiting air is found to be 38°C, and the wet-bulb temperature is 29°C.

(a) Use the psychrometric chart to calculate the absolute humidity (kg H_2O/kg dry air) and specific enthalpy (kJ/kg dry air) of the outlet air stream. Then calculate the mass of water in the exiting air per kilogram of wet chips fed, assuming dry air has a molecular weight of 29.0.

(b) Calculate the moisture content of the emerging chips and determine whether the design specification of less than 15% H_2O has been achieved.

(c) Suppose a sample of the moist chips leaving the dryer is taken, the moisture content is measured, and the result is significantly different from the value calculated in Part (b). First briefly state how the moisture content was probably measured (keep it simple); then list possible reasons for the difference between the two values; and finally state in which value you would have more confidence and explain why.

(d) If the unit is operating adiabatically and the heat capacity of the dry chips is 1.70 kJ/(kg·°C), what is the exit temperature of the chips? (In estimating the specific enthalpy of the entering air, recall that the reference temperature for dry air used in constructing the psychrometric chart of Figure 8.4-1 is 0°C.)

Equipment Encyclopedia
humidifier

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8.90. Air at 45°C (dry bulb) and 10% relative humidity is to be humidified adiabatically to 70% relative humidity.

(a) Use the psychrometric chart to estimate the adiabatic saturation temperature of the air.

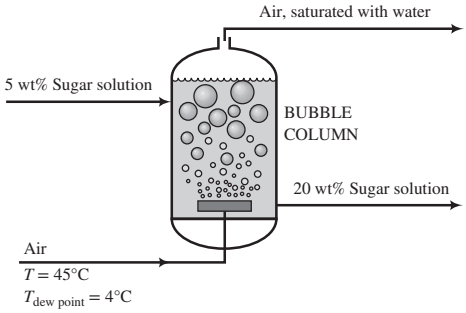
(b) Estimate the final temperature of the air and the rate at which water must be added to humidify 15 kg/min of the entering air. (See Example 8.4-7.)

(c) What have you assumed in carrying out this calculation?

Equipment Encyclopedia
dryer
www.wiley.com/college/felder

8.91. Air at 50°C with a dew point of 4°C enters a textile dryer at a rate of 11.3 m^3/min and leaves saturated. The dryer operates adiabatically. Use the psychrometric chart to determine the absolute humidity and humid volume of the entering air, and then use the results to determine the flow rate of *dry* air (kg/min) through the dryer, the final temperature of the air, and the rate (kg/min) at which water is evaporated in the dryer. (*Hint:* Refer to Section 8.4e.) What have you assumed in carrying out this calculation?

8.92. A solution of sugar in water is to be concentrated from 5 wt% sugar to 20% sugar. The solution is at about 45°C when it is fed continuously to a bubble column. Air at 45°C with a dew point of 4°C is bubbled through the column and emerges saturated. The humidification of the air may be considered adiabatic.



Use the psychrometric chart to solve the following problems:

(a) What are the absolute humidities of the entering and exiting air?

(b) How many kilograms of dry air must be fed per kilogram of the entering sugar solution? What is the corresponding volume of the entering wet air? (Use the chart for the latter problem as well.)

(c) Suppose that instead of feeding the air through a sparger (a device that resembles a showerhead and releases the gas into the liquid as tiny bubbles), the air enters the column through a simple pipe. Speculate on the probable changes that would occur in the two outlet streams and briefly explain your reasoning.

8.93. Cold air at 20°F, 760 mm Hg pressure, and 70% relative humidity is conditioned by being passed through a bank of heating coils, then through a water spray, and finally through a second set of heating coils. In passing through the first coil bank, the air is heated to 75°F. The temperature of the water supplied to the spray chamber is adjusted to the wet-bulb temperature of the air admitted to the chamber, so that the humidifying unit may be assumed to operate adiabatically. It is required that the air emerging from the conditioning unit be at 70°F and 35% relative humidity. Use Figure 8.4-2 to solve the following problems.

(a) Calculate the temperature of the water supplied to the spray chamber and the relative humidity and dry-bulb temperature of the air leaving the spray chamber.

(b) Calculate the mass of water evaporated (lb_m) per cubic foot of air fed to the conditioning unit.

(c) Calculate the required heat transfer rates (Btu/ft^3 entering air) in each of the heating coil banks.

(d) Sketch a psychrometric chart and show the path followed by the air in each of the three steps of this process.

Equipment Encyclopedia
cooling tower
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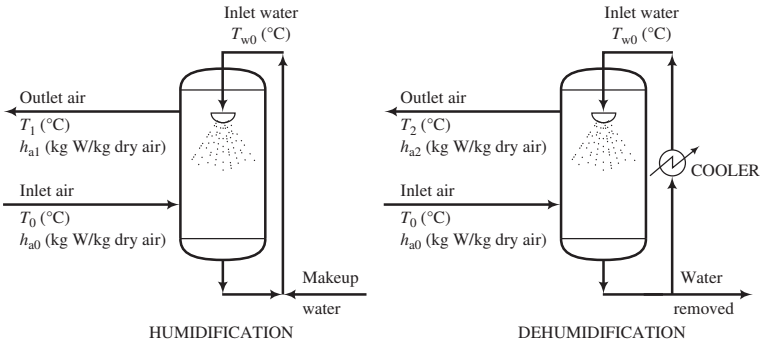
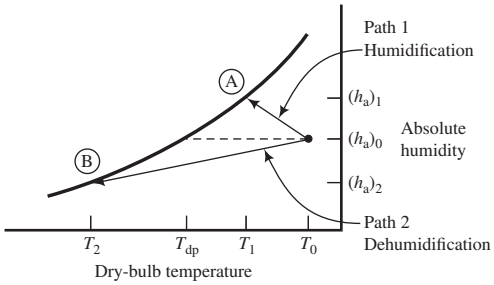
8.94. **Spray cooling** is a technique for cooling and either humidifying or dehumidifying air by contacting it with a spray of liquid water.



The liquid water leaving the tower is recirculated and, in the case of dehumidification, cooled before reentering the tower.

Two possible paths on the psychrometric chart corresponding to two different entering liquid temperatures are shown below. On the chart, T_0 and T_{dp} are the dry-bulb temperature and dew point, respectively, of the entering air.



Path Ⓐ**:** The entering liquid temperature (T_{w0}) is above the dew point of the entering air. Liquid water evaporates into the superheated air, causing the absolute humidity of the air to increase (the path rises) and both the evaporation and the contact with the cold liquid cause the air temperature to decrease (the path moves to the left).

Path Ⓑ**:** The entering liquid temperature is below the dew point of the entering air. The temperature of the air contacted by the cold spray drops below the dew point (the path again moves to the left), and water vapor condenses out of the air (the path moves down).

We thus arrive at the interesting conclusion that *you can remove water from air by spraying water into the air*, provided that the entering liquid temperature is below the dew point of the entering air.

Use the psychrometric chart to solve the following spray-cooling problems.

(a) A spray tower is used to cool and humidify air with dry-bulb and wet-bulb temperatures of 40°C and 18°C, respectively. The air emerges from the tower at 20°C. The tower operation is such that the air follows an adiabatic humidification curve (a constant wet-bulb temperature line on the psychrometric chart). How much water must be added as makeup per kg of dry air treated?

(b) A stream of air at 37°C and 50% relative humidity flowing at a rate of 1250 kg/h is to be cooled to 15°C and dehumidified in a spray tower. The air is saturated as it emerges from the tower. Liquid water leaves the tower at 12°C; some is withdrawn, and the rest is cooled and recirculated. No heat is transferred between the tower and its surroundings. Calculate the rate (kg/h) at which water must be withdrawn from the recirculation loop and the heat duty on the cooler (kW). (*Suggestion:* Use an overall energy balance for the latter calculation.)

(c) A non-engineering friend of yours heard someone say that you can remove water from air by spraying water into it. He thought that sounded strange and came to you to you for clarification. He first asks "Is that possible?" and then adds, "If it is, how does it work?" In a short paragraph, state what you would tell him.

8.95. The heat of solution of ammonia in water at 1 atm is

$$\Delta\hat{H}_s(25°C, r = 2 \text{ mol } H_2O/\text{mol } NH_3) = -78.2 \text{ kJ/mol}$$

(a) Calculate the enthalpy change that accompanies the dissolution of 200 mol of NH_3 in 400 mol of water at 25°C and 1 atm.

(b) If you actually bubbled 200 mol of ammonia at 25°C through 400 mol of water initially at 25°C and calculated the heat released in the process as $Q = \Delta H$, why would Q not equal the value you calculated in Part (a)? (Give two reasons.)

8.96. Use Table B.11 to determine the specific enthalpy (kJ/mol HCl) of hydrochloric acid containing 1 mol HCl/5 mol H_2O at 25°C relative to:

(a) HCl(g) and H_2O(l) at 25°C

(b) H_2O (l) and an infinitely dilute HCl solution at 25°C. (Note Equation 8.5-2.)

8.97. Sodium hydroxide is dissolved in enough water to make up a 20.0 mole% solution.

(a) If the NaOH and water are initially at 77°F (25°C), how much heat (Btu/lb product solution) must be removed for the solution also to be at 77°F. Assume the process is carried out at constant pressure, so that $Q = \Delta H$, and use Table B.11 to evaluate $\Delta \hat{H}_s$.

(b) If the dissolution is done adiabatically, estimate the final temperature of the solution. Assume that the heat capacity of the solution is approximately that of pure liquid water.

(c) If the process of Part (b) were actually carried out, the final temperature would be less than the value calculated. Why? (Neglect errors caused by the assumptions of adiabatic dissolution and a solution heat capacity equal to that of pure water.)

8.98. A sulfuric acid solution is labeled 8 N (where 1 N = 1 g-equivalent/L, and 1 mol of H_2SO_4 contains two g-equivalents). The specific gravity of the solution is 1.230, and its heat capacity is 3.00 J/(g·°C). Calculate the specific enthalpy of this solution (kJ/mol H_2SO_4) at 60°C relative to pure H_2O and an infinitely dilute solution at 25°C.

8.99. You are about to dilute 2.00 mol of 100% sulfuric acid with enough water to produce a 30 mole% aqueous solution. The acid and water are initially at 25°C.

(a) How much heat would have to be removed to keep the final solution at 25°C?

(b) Suppose the flask has a mass of 150 g, and that the heat capacity of the flask and its contents is 3.30 J/(g·°C). If the flask is sufficiently insulated to be considered adiabatic, what will be the final solution temperature?

Equipment Encyclopedia
absorption column

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8.100. An 8-molar hydrochloric acid solution [SG = 1.12, C_p = 2.76 J/(g·°C)] is produced by absorbing hydrogen chloride [HCl(g)] in water. Liquid water enters the absorber at 25°C and gaseous HCl is fed at 20°C and 790 torr absolute. Essentially all of the HCl fed to the column is absorbed. Take one liter of product solution as a basis of calculation.

(a) Estimate the volume (liters) of HCl that must be fed to the absorber.

(b) Estimate the heat (kJ) that must be transferred from the absorber if the product solution is to emerge at 40°C.

(c) Estimate the final solution temperature if the absorber operates adiabatically.

(d) Briefly describe how you might have used this experimental system with the absorption column heavily insulated to estimate

$$(\Delta \hat{H}_s)_{HCl(g)}(25°C, r = 5.75 \text{ mol } H_2O/\text{mol HCl})$$

Equipment Encyclopedia
evaporator

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8.101. A 0.1 mole% caustic soda (NaOH) solution is to be concentrated in a continuous evaporator. The solution enters the unit at 25°C at a rate of 150 mol/min and is concentrated to 5 mole% at 60°C. Hot dry air at 200°C and 1.1 bar absolute is bubbled through the evaporator and leaves saturated with water at 60°C and 1 atm. Calculate the required volumetric flow rate of the entering air and the rate at which heat must be transferred to or from the unit. Assume that the heat capacity per unit mass of all liquid solutions is that of pure water.

8.102. Water is added to pure sulfuric acid in a well-insulated flask initially at 25°C and 1 atm to produce a 4.00-molar sulfuric acid solution (SG = 1.231). The final temperature of the product solution is to be 25°C, so that the water added must be chilled liquid ($T < 25$°C), or a mixture of liquid water and ice. Take as a basis of calculation one liter of the product solution and assume $Q = \Delta H$ for the process. If you need to know the heat capacity of ice, take it to be half that of liquid water.

(a) If only liquid water is added, what masses (g) of H_2SO_4 and H_2O should be mixed and what should be the initial temperature of the water?

(b) If a mixture of liquid water and ice is added, how many grams of each should be fed?

Equipment Encyclopedia
evaporator

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8.103. Ortho-phosphoric acid (H_3PO_4) is produced as a dilute aqueous solution that must be concentrated before further use. In one facility, 100 tons/day of a 28 wt% P_2O_5 solution [see Part (a) of this problem] at 125°F is to be concentrated in a single evaporator to 42 wt% P_2O_5. Heat is supplied to the evaporator by condensing saturated steam at 27.5 psia. The evaporator is to operate at 3.7 psia, and there is a boiling point elevation of 37°F for the 42 wt% P_2O_5 solution in the evaporator (see Section 6.5c). The heat of solution of H_3PO_4 at 77°F may be taken to be −5040 Btu/lb-mole H_3PO_4 relative to H_3PO_4 (l) and H_2O(l). The heat capacity of the 28% solution is 0.705 Btu/(lb_m·°F) and that of the 42% solution is 0.583 Btu/(lb_m·°F).

(a) It is conventional for the compositions of phosphoric acid solutions to be expressed in terms of wt% P_2O_5. Write the stoichiometric equation for the formation of ortho-phosphoric acid

(MW = 98.00) from phosphorus pentoxide (MW = 141.96), and use it to derive the expression

$$\text{wt\% } H_3PO_4 = 1.381(\text{wt\% } P_2O_5)$$

(b) Calculate the ratio (lb_m water evaporated/lb_m feed solution).

(c) Suppose the water evaporated is subsequently condensed at a constant pressure of 3.7 psia. Determine the condensate flow rate in gal/min. How much heat (Btu/min) can be recovered through condensation of this water? At what temperature is this heat available? (To put it another way, if this heat were to be transferred to another stream, what is an upper bound on the temperature of that stream?)

(d) How much steam (lb_m/h) must be supplied to the system to evaporate the required amount of water? Recast your answer in terms of lb_m steam per lb_m water evaporated.

Equipment Encyclopedia
crystallizer
@
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8.104. Two hundred kilograms per hour of an aqueous solution containing 20.0 mole% sodium acetate ($NaC_2H_3O_2$) enters an evaporative crystallizer at 60°C. When the solution is exposed to the low pressure in the evaporator, 16.9% of the water evaporates, concentrating the remaining solution and causing crystals of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) to form. The product is an equilibrium mixture of crystals and a saturated aqueous solution containing 15.4 mole% $NaC_2H_3O_2$. The effluents (crystals, solution, and water vapor) are all at 50°C.

(a) Calculate the feed rate to the crystallizer in kmol/h.

(b) Calculate the production rate (kg/h) of trihydrate crystals and the mass flow rate (kg/h) of the liquid solution in which the crystals are suspended.

(c) Estimate the rate (kJ/h) at which heat must be transferred to or from the crystallizer (state which), using the following physical property data:

$$(C_p)_{\text{all solutions}} = 3.5 \text{ kJ/(kg·°C)}$$
$$(C_p)_{\text{crystals}} = 1.2 \text{ kJ/(kg·°C)}$$
$$(C_p)_{H_2O(v)} = 32.4 \text{ kJ/(kmol·°C)}$$
$$(\Delta\hat{H}_v)_{H_2O} = 4.39 \times 10^4 \text{ kJ/kmol}$$

Heat of solution of anhydrous sodium acetate:

$$\Delta\hat{H}_s(25°C) = -1.71 \times 10^4 \text{ kJ/kmol } NaC_2H_3O_2$$

Heat of hydration: $NaC_2H_3O_2(s) + 3H_2O(l) \rightarrow NaC_2H_3O_2 \cdot 3H_2O(s)$

$$\Delta\hat{H}(25°C) = -3.66 \times 10^4 \text{ kJ/kmol } NaC_2H_3O_2$$

(d) In a commercial process to produce crystalline sodium acetate trihydrate, what are several processing steps the slurry leaving the crystallizer might undergo?

8.105. Fifty milliliters of 100% H_2SO_4 at 25°C and 84.2 mL of liquid water at 15°C are mixed. The heat capacity of the product solution is 2.43 J/(g·°C).

(a) Estimate the maximum temperature attainable by the product solution and state the conditions under which this temperature would be attained, using heat of mixing data from Table B.11.

(b) Give several reasons why the temperature calculated in Part (a) could not be attained in practice.

(c) Estimate how much heat would have to be transferred from the mixing vessel to keep the temperature of the product solution at 25°C. (You should be able to solve this problem quickly by looking back at the enthalpy table of Part (a).)

8.106. Suppose $m_A(g)$ of species A {molecular weight M_A, heat capacity C_{pA}[J/(g·°C)]} at temperature T_{A0}(°C) and m_B(g) of species B (M_B, C_{pB}) at temperature T_{B0} are mixed adiabatically. The heat of mixing of A and B at 25°C is $\Delta\hat{H}_m$(r) (J/mol A in solution), where $r = (m_B/M_B)/(m_A/M_A)$. The heat capacity of the product solution is C_{ps}[J/(g·°C)]. All heat capacities may be considered independent of temperature.

(a) Derive an expression for T_{max}, the highest temperature attainable by the product solution, in terms of the other quantities defined. State the conditions that would have to be met for this temperature to be approached.

(b) Use your expression to estimate T_{max} for a process in which 100.0 g of sodium hydroxide at 25°C and 225.0 g of water at 40°C are combined to form a product solution with a heat capacity of 3.85 J/(g·°C).

8.107. One g-mole of pure liquid sulfuric acid at temperature T_0(°C) is mixed with r g-moles of liquid water, also at temperature T_0(°C), in an adiabatic container. The final solution temperature is T_s(°C). The heat capacities of the pure acid, pure water, and the product solution [J/(g·°C)] are C_{pa}, C_{pw}, and C_{ps}, respectively, all of which may be taken to be independent of temperature.

(a) Without doing any calculations, sketch the plot of T_s versus r you would expect to obtain for r varying between 0 and ∞. (*Hint:* Think first about what you would expect T_s to be at the extreme values of r.)

(b) Use an energy balance to derive an expression for T_s in terms of the initial acid and water temperatures, the heat capacities, the water/acid mole ratio (r), and the heat of mixing, $\Delta\hat{H}_m(r, 25°C)$ (kJ/mol H_2SO_4).

(c) A series of 1.00 mol samples of pure liquid sulfuric acid are added to 11 insulated flasks containing varying amounts of water. The quantities of water in the flasks and the mass heat capacities of the product solutions are tabulated below:

r (mol H_2O)	0.5	1.0	1.5	2.0	3.0	4.0	5.0	10.0	25.0	50.0	100.0
C_p [J/(g·°C)]	1.58	1.85	1.89	1.94	2.10	2.27	2.43	3.03	3.56	3.84	4.00

The heat capacities of pure sulfuric acid and pure water may be determined from the molar heat capacities in Table B.2 evaluated at 25°C. All heat capacities should be taken to be independent of temperature.

Unfortunately, the laboratory air conditioner has been out of order for three weeks (Physical Plant promises they will get to it any day now) and the temperature on the July afternoon of the experiment (which also equals the initial acid and water temperatures) is an uncomfortable 40°C. Prepare a spreadsheet to generate a table and then a plot of T_s, the final temperature in each flask, versus r, the water/acid mole ratio of the solution in the flask. (*Suggestion:* Make the r axis logarithmic.) Assume that mixing is adiabatic.

(d) The actual experimental plot of T_s versus r would lie below the one determined in Part (c). Why?

*__8.108.__ Instant cold packs are used for first aid when ice is not available. In one such device, a small pouch containing 2.00×10^2 grams of ammonium nitrate (NH_4NO_3) is placed in a bag containing 2.00×10^2 milliliters of water initially at 25°C. When the pouch is broken, the ammonium nitrate dissolves in the water and the cold pack reaches a final temperature of −2°C.

(a) Calculate $\Delta\hat{H}_s$ for the solution in the cold pack, assuming that the pack loses a negligible amount of heat to the surroundings during the dissolution process and that the heat capacity of the solution is that of pure water.

(b) What would be the final temperature of a pack containing 300 grams of ammonium nitrate and 300 mL of water?

8.109. A stirred tank with volume V_t(L) is charged with V_l(L) of a liquid, B. The space above the liquid (volume $V_g = V_t - V_l$) is filled with a pure gas, A, at an initial pressure P_0(atm). The initial system temperature is T_0(K). The stirrer in the tank is turned on, and A begins to dissolve in B. The dissolution continues until the liquid is saturated with A at the final system temperature (T) and pressure (P).

The equilibrium solubility of A in B is governed by the following expression, which relates the molar A/B ratio in the liquid to the partial pressure of A in the gas phase (which in turn equals the pressure in the tank, since the gas is pure A):

$$r(\text{mol A/mol B}) = k_s p_A(\text{atm})$$

where

$$k_s[\text{mol A/(mol B·atm)}] = c_0 + c_1 T(\text{K})$$

When performing the requested calculations, use the following variable definitions:

- M_A, M_B = molecular weights of A and B
- C_{vA}, C_{vB}, C_{vS}[J/(g·K)] = constant-volume heat capacities of A(g), B(l), and solutions of A in B, respectively

* Adapted from Stephanie Farrell, Mariano J. Savelski, and C. Stewart Slater (2010). "Integrating Pharmaceutical Concepts into Introductory Chemical Engineering Courses—Part I," http://pharmahub.org/resources/360.

- SG_B = specific gravity of B(l)
- $\Delta\hat{U}_s$ (J/mol A dissolved) = internal energy of solution at 298 K (independent of composition over the range of concentrations to be considered)
- n_{A0}, n_{B0} = g-moles of A(g) and B(l) initially charged into the tank
- $n_{A(l)}, n_{A(v)}$ = g-moles of A dissolved and remaining in the gas phase at equilibrium, respectively

Make the following assumptions:

- A negligible amount of B evaporates.
- The tank is adiabatic and the work input to the tank from the stirrer is negligible.
- The gas phase behaves ideally.
- The volumes of the liquid and gas phases may be considered constant.
- The heat capacities C_{vA}, C_{vB}, and C_{vs} are constant, independent of temperature and (in the case of C_{vs}) solution composition.

(a) Use material balances, the given equilibrium solubility relation, and the ideal-gas equation of state to derive expressions for n_{A0}, n_{B0}, $n_{A(v)}$, $n_{A(l)}$, and P in terms of the final temperature, T(K), and variables $M_A, M_B, SG_B, V_t, V_l, T_0, P_0, c_0$, and c_1. Then use an energy balance to derive the following equation:

$$T = 298 + \frac{n_{A(l)}(-\Delta\hat{U}_s) + (n_{A0}M_A C_{vA} + n_{B0}M_B C_{vB})(T_0 - 298)}{n_{A(v)}M_A C_{vA} + (n_{A(l)}M_A + n_B M_B)C_{vs}}$$

(b) Prepare a spreadsheet to calculate T from specified values of $M_A(= 47)$, $M_B(= 26)$, $SG_B(= 1.76)$, $V_t(= 20.0)$, $V_l(= 3.0)$, $c_0(= 1.54 \times 10^{-3})$, $c_1(= -1.60 \times 10^{-6})$, $C_{vA}(= 0.831)$, $C_{vB}(= 3.85)$, $C_{vs}(= 3.80)$, and $\Delta\hat{U}_s(= -1.74 \times 10^5)$, and a number of different values of T_0 and P_0. The spreadsheet should have the structure given below. (Calculated values are shown for one initial temperature and pressure.)

Problem 8.109										
Vt	MA	CvA	MB	CvB	SGB	c0	c1	DUs	Cvs	
20.0	47.0	0.831	26.0	3.85	1.76	0.00154	-1.60E-06	-174000	3.80	
Vl	T0	P0	Vg	nB0	nA0	T	nA(v)	nA(l)	P	Tcalc
3.0	300	1.0								
3.0	300	5.0								
3.0	300	10.0	17.0	203.1	6.906	320.0	5.222	1.684	8.1	314.2
3.0	300	20.0								
3.0	330	1.0								
3.0	330	5.0								
3.0	330	10.0								
3.0	330	20.0								

The values of V_g, n_{B0}, and n_{A0} should first be calculated from the given values of the other variables. Next, a value of T should be guessed (in the example in the table, the guessed value is 320 K), the values of $n_{A(v)}$, $n_{A(l)}$, and P should be calculated from the equations derived in Part (a), and the temperature should be recalculated from the energy balance in the column labeled T_{calc} (it equals 314.2 in the example). The value of T should then be varied until it equals the recalculated value of T_{calc}. (*Suggestion:* Create a new cell as $T - T_{calc}$ and use Goal Seek to find the value of T that drives $T - T_{calc}$ to zero.)

Enter the formulas in the cells for $V_1 = 3.0$ L, $T_0 = 300$ K, and $P_0 = 10.0$ atm, and verify that your cell values match those shown above. Then find the correct value of T using the procedure just described, copy the formulas into the other rows of the table, and determine T for each set of initial conditions. Summarize the effects of the initial temperature and pressure on the adiabatic temperature rise and briefly explain why your results make sense.

8.110. An aqueous solution containing 85.0 wt% H_2SO_4 at 60°F (specific gravity = 1.78) is diluted with pure liquid water at the same temperature. The feed solution volume is 350 mL. The mixing may be considered adiabatic, and the pressure is constant at 1 atm.

(a) The product solution is to contain 30.0 wt% H_2SO_4. Calculate the volume (mL) of water needed for the dilution, ideally using a single-dimensional equation.

(b) Use the enthalpy–concentration chart of Figure 8.5-1 to estimate the specific enthalpies (Btu/lb_m) of the feed solution and the water. Then write an energy balance on this closed system constant-pressure process and solve it for the specific enthalpy of the product solution. Finally, use Figure 8.5-1 to verify your calculated value of $\hat{H}_{\text{product}}$ and to estimate the product solution temperature. (See Example 8.5-3.)

(c) Use Figure 8.5-1 to estimate the maximum temperature that could be attained by mixing the feed solution with pure water and the concentration (wt% H_2SO_4) of the product solution.

(d) Good laboratory practice calls for adding acid to water when carrying out dilutions rather than vice versa. Use Figure 8.5-1 to justify this rule for the dilution of the feed solution in this problem.

8.111. Aqueous sulfuric acid solutions containing 15.0 wt% H_2SO_4 and 80.0 wt% H_2SO_4 are mixed to form a 30.0 wt% product solution. The 15% solution was in a laboratory in which the temperature was 77°F. The 80% solution had just been taken from a storage cabinet in an air-conditioned stockroom and was at a temperature of 60°F when the mixing occurred.

(a) The mass of the 15% solution is 2.30 lb_m. What mass of 80% solution should be weighed out?

(b) Use Figure 8.5-1 to estimate the product solution temperature if the mixing is adiabatic. (See Example 8.5-3.)

(c) The product solution temperature eventually drops to (77°F). How much heat (Btu) is transferred from the solution to the laboratory air in this constant-pressure cooling process?

(d) The dilution can be carried out either by slowly adding the 15% solution to the 80% solution or vice versa. Use Figure 8.5-1 to determine the maximum temperature that would be attained using each procedure. Which procedure would be safer?

8.112. Taking as references pure liquid sulfuric acid at 77°F and pure liquid water at 32°F and without using Figure 8.5-1, calculate $\hat{H}$(Btu/lb_m) for each of the following substances. For each substance, also report the value you would read from Figure 8.5-1.

(a) H_2O (l, 120°F)

(b) H_2SO_4 (l, 200°F)

(c) 60 wt% H_2SO_4 (aq, 200°F)

8.113. You have analyzed an aqueous ammonia solution and find that it contains 30 wt% NH_3.

(a) Use Figure 8.5-2 to determine the mass fraction of NH_3 in the vapor that would be in equilibrium with this solution in a closed flask at 1 atm and the corresponding system temperature.

(b) If the liquid phase in Part (a) accounts for 90% of the total system mass, calculate the overall system composition and specific enthalpy using balances. (See Example 8.5-3.)

8.114. An NH_3–H_2O mixture containing 60 wt% NH_3 is brought to equilibrium in a closed container at 140°F. The total mass of the mixture is 250 g. Use Figure 8.5-2 to determine the masses of ammonia and of water in each phase of the system.

8.115. An ammonia solution at a high pressure is flash-vaporized at a rate of 200 lb_m/h. The solution contains 0.70 lb_m NH_3/lb_m, and its enthalpy relative to H_2O(l, 32°F) and NH_3(l, −40°F) is −50 Btu/lb_m. Liquid and gas streams emerge from the unit at 1 atm and 80°F. Use Figure 8.5-2 to determine the mass flow rates and ammonia mass fractions of the vapor and the liquid product streams and the rate (Btu/h) at which heat must be transferred to the vaporizer. (See Example 8.5-4.)

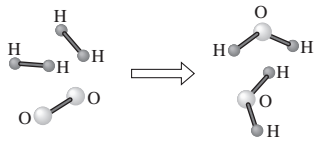
CHAPTER 9

Balances on Reactive Processes

Consider the familiar reaction in which water is formed from hydrogen and oxygen:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(v)$$

On the molecular level, the reaction might be depicted as follows:



Each time this reaction takes place, three chemical bonds are broken (two between hydrogen atoms and one between oxygen atoms) and four bonds are formed among the atoms of the two water molecules. As it happens, more energy is released when the water molecule bonds form than it takes to break the hydrogen and oxygen molecule bonds. For the reactor temperature to remain constant, the net energy released (about 250 kJ per mol of water formed) must be transferred from the system; otherwise, the release of energy can raise the temperature substantially.

In *any* reaction between stable molecules, energy is required to break the reactant chemical bonds, and energy is released when the product bonds form. If the first process absorbs less energy than the second process releases (as in the water formation reaction), the reaction is **exothermic**: the product molecules at a given temperature and pressure have lower internal energies (and hence lower enthalpies) than the reactant molecules at the same temperature and pressure. The net energy released—the **heat of reaction**—must be transferred from the reactor as heat or work, or else the system temperature increases. On the other hand, if less energy is released when the product bonds form than it took to break the reactant bonds, the reaction is **endothermic**: energy must be added to the reactor as heat or work to keep the temperature from decreasing.

The large internal energy and enthalpy changes commonly associated with chemical reactions can play major roles in the design and operation of chemical processes. If a reaction is endothermic, the energy needed to keep the reactor temperature (and hence the reaction rate) from dropping too much may cost enough to turn a profitable process into an unprofitable one. On the other hand, if the reaction is exothermic, heat usually must be transferred from the reactor to keep the temperature below a value that leads to safety or product quality problems. The heat transferred may be an asset, as when the reactor is a combustion furnace and the heat is used to generate steam in a boiler. It may also be a liability: for example, a momentary failure of a reactor temperature-control system can lead to rapid overheating and possibly an explosion.

An energy balance on a reactor tells the process engineer how much heating or cooling the reactor requires in order to operate at the desired conditions. In this chapter we show how enthalpy changes that accompany chemical reactions are determined from tabulated physical properties of the reactants and products and how calculated enthalpies of reaction are incorporated in energy balances on reactive processes.

Test Yourself

(Answers, p. 659)

1. Explain in your own words the concepts of exothermic and endothermic reactions. The terms "chemical bonds" and "heat of reaction" should appear in your explanation.

2. The following two sentences seem to contain a self-contradiction.

> *In an exothermic reaction, the products are at a lower energy level than the reactants. However, if the reactor is not cooled, the products are hotter than the reactants, which means they must be at a higher energy level than the reactants.*

Identify the logical error in this paragraph.

CREATIVITY EXERCISE

Suppose an exothermic reaction takes place in a continuous reactor. Think of several ways the heat of reaction might be removed, illustrating your suggestions with sketches. (For example, pass a cold fluid through a hollow metal tube immersed in the reactor, so that heat is transferred from the hot reacting fluid to the coolant.)

9.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- Explain in your own words the concepts of heat of reaction; exothermic and endothermic reactions; heat of formation; combustion; heat of combustion; standard heats of formation, combustion, and reaction; heating value of a fuel; adiabatic flame temperature; ignition temperature; ignition lag; lower and upper flammability limits and flash point of a fuel; a flame; blue and yellow flames; flashback; and detonation.
- Given (a) the amount of any reactant consumed or any product generated in a reaction at a given temperature and pressure and (b) the heat of the reaction at that temperature and pressure, calculate the total enthalpy change.
- Determine a heat of reaction from heats of other reactions using Hess's law. Determine standard enthalpies and internal energies of reaction from known standard heats of formation and heats of combustion.
- Write and solve an energy balance on a chemical reactor using either the heat of reaction method (taking reactant and product species as references for enthalpy calculations) or the heat of formation method (taking elemental species as references), and specify which method is preferable for a given process. Write the process path implicitly adopted when each method is used.
- Solve reactive-system energy-balance problems for (a) the heat transfer required for specified inlet and outlet conditions, (b) the outlet temperature corresponding to a specified heat input (e.g., for an adiabatic reactor), and (c) the product composition corresponding to a specified heat input and a specified outlet temperature.
- Solve energy-balance problems for processes involving solutions for which heats of solution are significant.
- Convert a higher heating value of a fuel to a lower heating value and vice versa.

9.1 HEATS OF REACTION

When a chemical reaction occurs, energy is consumed as chemical bonds between atoms in reactant molecules are broken, and energy is released as the atoms form new bonds in product molecules. The result is a change in the internal energy—and therefore the enthalpy—of the

system. The **heat of reaction**, $\Delta H_r(T, P)$, is the enthalpy difference when stoichiometric quantities of reactants at a specified temperature and pressure react completely and the products are at the same temperature and pressure.

For example, consider the reaction between solid calcium carbide and liquid water to form solid calcium hydroxide and gaseous acetylene:

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g) \quad \textbf{(9.1-1)}$$

$$\Delta H_r(25°C,\ 1\ atm) = -125.4\ kJ^{[1]} \quad \textbf{(9.1-2)}$$

In this text, when a heat of reaction is given in kJ, the stoichiometric quantities referred to are in gram-moles (mol). (See Footnote 1.) Equation 9.1-2 indicates that when 1 mol of solid calcium carbonate and 2 mol of liquid water react completely to form 1 mol of solid calcium hydroxide and 1 mol of gaseous acetylene, and the reactants and products are all at 25°C and 1 atm, the enthalpy change is −125.4 kJ. We may write this result in any of the following ways:

$$\frac{-125.4\ kJ}{1\ mol\ CaC_2\ consumed}, \frac{-125.4\ kJ}{2\ mol\ H_2O\ consumed}, \frac{-125.4\ kJ}{1\ mol\ Ca(OH)_2\ generated}, \frac{-125.4\ kJ}{1\ mol\ C_2H_2\ generated}$$

If you know the amount or rate of consumption or generation of any reactive species at the specified conditions, you can calculate the associated enthalpy change from the heat of reaction. For example:

$$100\ mol\ Ca(OH)_2\ generated \Longrightarrow \Delta H = \frac{100\ mol\ Ca(OH)_2\ gen}{} \left| \frac{-125.4\ kJ}{mol\ Ca(OH)_2\ gen} \right. = -1.254 \times 10^4\ kJ$$

$$100\ \frac{mol\ H_2O\ consumed}{s} \Longrightarrow \Delta \dot{H} = \frac{100\ mol\ H_2O\ cons}{s} \left| \frac{-125.4\ kJ}{2\ mol\ H_2O\ cons} \right. = -0.627 \times 10^4\ \frac{kJ}{s}$$

We may generalize the preceding result to any reaction for which the heat of reaction, $\Delta H_r(T_0, P_0)$, is known at a reference temperature and pressure T_0 and P_0. If $(n_i - n_{i0})$ is the amount of Species i that reacts (it would be positive if i is a product and negative if it is a reactant), and the reactants and products are all at temperature T_0 and pressure P_0, then the enthalpy change for the reaction is

$$\Delta H(kJ) = \frac{\Delta H_r(T_0, P_0)(kJ)}{\nu_i(mol\ i)}(n_i - n_{i0})(mol\ i) = \frac{\Delta H_r(T_0, P_0)}{|\nu_i|} n_{ir}$$

where n_{ir} is the amount of Species i that has been either consumed or produced by the reaction and ν_i(mol i) is the stoichiometric coefficient of Species i (positive for products, negative for reactants). For a continuous system,

$$\Delta \dot{H}(kJ/s) = \frac{\Delta H_r(T_0, P_0)(kJ)}{\nu_i(mol\ i)}(\dot{n}_i - \dot{n}_{i0})(mol\ i/s) = \frac{\Delta H_r(T_0, P_0)}{|\nu_i|} \dot{n}_{ir}$$

[1] *Note:* In many textbooks you will see heats of reaction given with the dimension energy/mole (most commonly, kJ/mol). The value of ΔH_r with such units has exactly the same meaning as in the definition we have given—the enthalpy change when stoichiometric amounts of reactants react completely. The mol in the denominator simply indicates the molar unit to be used (mol, kmol, lb-mole, etc.) when specifying those stoichiometric amounts, as opposed to meaning per mol of a particular species. In this text, whenever heats of reaction are given in kJ, the molar unit will always be mol, and if they are in Btu, the unit will be lb-mole.

In Chapter 4, we defined the extent of reaction, ξ, as a measure of how far a reaction has proceeded. From Equation 4.6-3, this quantity is

$$\xi = \begin{cases} \textit{Batch:} \quad \dfrac{(n_{i,\text{out}} - n_{i,\text{in}})(\text{mol } i)}{\nu_i(\text{mol } i)} = \dfrac{n_{ir}}{|\nu_i|} \\ \textit{Continuous:} \quad \dfrac{(\dot{n}_{i,\text{out}} - \dot{n}_{i,\text{in}})(\text{mol } i/\text{time})}{\dot{\nu}_i(\text{mol } i/\text{time})} = \dfrac{\dot{n}_{ir}}{|\dot{\nu}_i|} \end{cases} \tag{9.1-3}$$

From the preceding equations, it follows that if a reaction occurs with a heat of reaction $\Delta H_r(T_0, P_0)(\text{kJ})$, all the reactants and products are at temperature T_0 and pressure P_0, and the extent of reaction is ξ, then the enthalpy change is

$$\boxed{\Delta H(\text{kJ}) = \xi \Delta H_r(T_0, P_0)} \tag{9.1-4a}$$

A similar expression applies to a continuous reactor at steady state, but the algebra needed to get there is a bit more complex. Now the rate of enthalpy change for the reaction is

$$\Delta \dot{H}(\text{kJ/time}) = \frac{\Delta H_r(T_0, P_0)(\text{kJ})}{\nu_i(\text{mol } i)} (\dot{n}_i - \dot{n}_{i0})(\text{mol } i/\text{time})$$

(An example of this equation was given above when the rate of enthalpy change was calculated to be 2500 kJ/s.) As given in Equation 9.1-3, the extent of reaction for a continuous reactor is

$$\xi = \frac{(\dot{n}_i - \dot{n}_{i0})(\text{mol } i/\text{time})}{\dot{\nu}_i(\text{mol } i/\text{time})} \Longrightarrow (\dot{n}_i - \dot{n}_{i0}) = \xi \dot{\nu}_i$$

Combining the two previous equations leads to the result

$$\Delta \dot{H}(\text{kJ/time}) = \xi \Delta H_r(T_0, P_0)(\text{kJ}) \left[\frac{\dot{\nu}_i \left(\dfrac{\text{mol}}{\text{time}} \right)}{\nu_i(\text{mol})} \right]$$

The factor in brackets has a numerical value of 1 and a dimension of time^{-1}. If $\Delta H_r = 148$ kJ, then $\Delta \dot{H}_r = 148$ kJ/time, where the time unit would be the same one used to express stream flow rates ($\dot{n}$) and stoichiometric coefficients ($\dot{\nu}$) in the process. The last two equations yield the result:

$$\boxed{\Delta \dot{H}(\text{kJ/time}) = \xi \Delta \dot{H}_r(T_0, P_0)} \tag{9.1-4b}$$

If you are confused by this derivation, no one could blame you, but the calculations you will need to do are straightforward. If you are analyzing a process with species amounts expressed in moles, use Eq. (9.1-4a), and if the amounts are expressed as molar flow rates, use Eq. (9.1-4b).

Following are several important terms and observations related to heats of reaction.

1. If $\Delta H_r(T, P)$ is negative the reaction is **exothermic** at temperature T and pressure P, and if $\Delta H_r(T, P)$ is positive the reaction is **endothermic** at T and P. These definitions of exothermic and endothermic are equivalent to the ones given earlier in terms of chemical bond strengths. (Convince yourself.)

2. *At low and moderate pressures, $\Delta H_r(T, P)$ is nearly independent of pressure*. We will presume this independence in the balance of this chapter and write the heat of reaction as $\Delta H_r(T)$.

3. *The value of the heat of a reaction depends on how the stoichiometric equation is written*. For example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l): \quad \Delta H_{r1}(25°C) = -890.3\ kJ$$
$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l): \quad \Delta H_{r2}(25°C) = -1780.6\ kJ$$

This result should seem reasonable to you if you look back at the definition of ΔH_r. The first line states that the combined enthalpy of 1 gram-mole of CO_2 plus 2 gram-moles of liquid water is 890.3 kJ lower than the combined enthalpy of 1 gram-mole of methane plus 2 gram-moles of oxygen at 25°C. Doubling the quantity of reactants at a given condition doubles the total enthalpy of the reactants at that condition, and similarly for the products. The difference between the product and reactant enthalpies in the second reaction (by definition, ΔH_{r2}) must therefore be double the enthalpy difference in the first reaction (ΔH_{r1}).

4. *The value of a heat of reaction depends on the phases (gas, liquid, or solid) of the reactants and products*. For example,

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l): \quad \Delta H_r(25°C) = -890.3\ kJ$$
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g): \quad \Delta H_r(25°C) = -802.3\ kJ$$

The only difference between the reactions is that the water formed is a liquid in the first one and a vapor in the second. Since enthalpy is a state function, the difference between the two heats of reaction must be the enthalpy change associated with the vaporization of 2 mol of water at 25°C—that is, $2\Delta\hat{H}_v(25°C)$.

5. The **standard heat of reaction**, ΔH_r°, is the heat of reaction when both the reactants and products are at a specified reference temperature and pressure, usually (and always in this text) 25°C and 1 atm.

Example 9.1-1 Calculation of Heats of Reaction

1. The standard heat of the combustion of *n*-butane vapor is

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l): \quad \Delta H_r^\circ = -2878\ kJ$$

Calculate the rate of enthalpy change, $\Delta\dot{H}$(kJ/s), if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

2. Calculate the standard heat of the reaction

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$$

Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in *this* reaction and the reactants and products are all at 25°C.

3. The heats of vaporization of *n*-butane and water at 25°C are 19.2 kJ/mol and 44.0 kJ/mol, respectively. Calculate the standard heat of the reaction

$$C_4H_{10}(l) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(v)$$

Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

Solution

1. From Equation 9.1-3,

$$\xi = \frac{\dot{n}_{CO_2,r}}{|\dot{\nu}_{CO_2}|} = \frac{2400\ mol/s}{4\ mol/s} = 600$$

$$\Downarrow \text{Equation 9.1-4b}$$

$$\Delta\dot{H} = \xi\left(\frac{\dot{\nu}}{\nu}\right)\Delta H_r^\circ = (600)\left(\frac{4\ mol/s}{4\ mol}\right)(-2878\ kJ) = -1.73 \times 10^6\ kJ/s$$

2. Since doubling the stoichiometric coefficients of a reaction must double the heat of reaction,

$$\Delta\dot{H}^\circ_{r2} = 2\Delta\dot{H}^\circ_{r1} = 2(-2878\ \text{kJ/s}) = -5756\ \text{kJ/s}$$

The enthalpy change associated with the production of 2400 mol/s of CO_2 at 25°C cannot depend on how the stoichiometric equation is written (the same quantities of reactants and products at the same temperatures must have the same enthalpies), and so $\Delta\dot{H}$ must be the value calculated in Part (a). Let us do the calculation and prove it, however. From Equation 9.1-3,

$$\xi = \frac{(\dot{n}_{CO_2})_{out}}{|\dot{\nu}_{CO_2}|} = \frac{2400\ \text{mol/s}}{8\ \text{mol/s}} = 300$$

$$\Downarrow \text{Equation 9.1-4b}$$

$$\Delta\dot{H} = \xi\Delta\dot{H}^\circ_r = (300)(-5756\ \text{kJ/s}) = -1.73 \times 10^6\ \text{kJ/s}$$

3. Compare the two reactions:

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l): \quad (\Delta H^\circ_{r1}) = -2878\ \text{kJ}$$

$$C_4H_{10}(l) + \tfrac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(v): \quad (\Delta H^\circ_{r2}) = ?$$

The total enthalpy of the products in the second reaction [4 mol CO_2(g) + 5 mol H_2O(v) at 25°C] is greater than that of the products in the first reaction [4 mol CO_2(g) + 5 mol H_2O(l) at 25°C] by five times the heat of vaporization of water. Similarly, the total enthalpy of the reactants in the second reaction is lower than that of the reactants in the first reaction by the heat of vaporization of butane. (Why?) Since $\Delta H_r = H_{products} - H_{reactants}$, it follows that

$$(\Delta H^\circ_{r2}) = (\Delta H^\circ_{r1}) + 5\ \text{mol}\ H_2O(\Delta\hat{H}_v)_{H_2O} + 1\ \text{mol}\ C_4H_{10}(\Delta\hat{H}_v)_{C_4H_{10}}$$

$$= [-2878 + 5(44.0) + 19.2]\ \text{kJ} = \boxed{-2639\ \text{kJ}}$$

$$\Delta\dot{H} = \xi\Delta\dot{H}^\circ_{r2} = (600)(-2639\ \text{kJ/s}) = \boxed{-1.58 \times 10^6\ \text{kJ/s}}$$

If a reaction takes place in a closed reactor at constant volume, the heat released or absorbed is determined by the change in internal energy between reactants and products. The **internal energy of reaction**, $\Delta U_r(T)$, is the difference $U_{products} - U_{reactants}$ if stoichiometric quantities of reactants react completely at temperature T.

Suppose a reaction occurs, and ν_i (mol Species i) is the stoichiometric coefficient of the ith gaseous reactant or product. If ideal-gas behavior can be assumed and specific volumes of liquid and solid reactants and products are negligible compared with those of the gases, the internal energy of reaction is related to the heat of reaction by

$$\Delta U_r(T) = \Delta H_r(T) - RT\left(\sum_{\substack{\text{gaseous}\\\text{products}}} |\nu_i| - \sum_{\substack{\text{gaseous}\\\text{reactants}}} |\nu_i|\right) \qquad \textbf{(9.1-5)}$$

For example, for the reaction

$$C_6H_{14}(l) + \tfrac{19}{2}O_2(g) \rightarrow 6CO(g) + 7H_2O(v)$$

the internal energy of reaction is

$$\Delta U_r(T) = \Delta H_r(T) - RT(6 + 7 - \tfrac{19}{2})\ \text{mol}$$

$$= \Delta H_r(T) - RT(\tfrac{7}{2}\ \text{mol})$$

If there are no gaseous reactants or products, then to a good approximation $\Delta U_r = \Delta H_r$.

Example 9.1-2 Evaluation of ΔU_r

The standard heat of the reaction

$$C_2H_4(g) + 2Cl_2(g) \rightarrow C_2HCl_3(l) + H_2(g) + HCl(g)$$

is $\Delta H_r^\circ = -420.8$ kJ/mol. Calculate ΔU_r° for this reaction.

Solution From the stoichiometric equation

$$\sum |\nu_i| \text{ (product gases)} = (1 + 1) \text{ mol} = 2 \text{ mol}$$
$$\sum |\nu_i| \text{ (reactant gases)} = (1 + 2) \text{ mol} = 3 \text{ mol}$$

From Equation 9.1-5

$$\Delta U_r = \Delta H_r - RT(2 - 3) \text{ mol}$$
$$= -420.8 \text{ kJ} - \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \left| \begin{array}{c|c|c} 298 \text{ K} & -1 \text{ mol} & \dfrac{1 \text{ kJ}}{10^3 \text{ J}} \end{array} \right.$$
$$= \boxed{-418.3 \text{ kJ}}$$

Test Yourself

(Answers, p. 659)

1. What is a heat of reaction? A standard heat of reaction?
2. Suppose ΔH_r° is -40 kJ for the reaction $2A \rightarrow B$.
   - **(a)** What is the value of the ratio (kJ/mol A reacted)?
   - **(b)** Is the reaction exothermic or endothermic at 25°C and 1 atm?
   - **(c)** If the reactants and products are at the same temperature, must heat be added to or withdrawn from the reactor? (Assume that the energy balance reduces to $Q = \Delta H$.)
   - **(d)** If the reactor is adiabatic ($Q = 0$), would the products leave at a higher or a lower temperature than that of the entering reactants?
3. $C_6H_{14}(l) + \frac{19}{2}O_2 \rightarrow 6CO_2 + 7H_2O(l)$: $\Delta H_r^\circ = -4163$ kJ
   $C_6H_{14}(g) + \frac{19}{2}O_2 \rightarrow 6CO_2 + 7H_2O(l)$: $\Delta H_r^\circ = -4195$ kJ
   The standard state for the heats of reaction is 25° and 1 atm. What is the physical significance of the difference between the two given values of ΔH_r°?
4. Write the formula for $\Delta U_r(T)$ in terms of $\Delta H_r(T)$ for the reaction $A(g) + 2B(g) + C(l) \rightarrow D(g) + 2E(s)$.
5. Derive Equation 9.1-5 from the definition of $\hat{H}$ as $\hat{U} + P\hat{V}$.

9.2 MEASUREMENT AND CALCULATION OF HEATS OF REACTION: HESS'S LAW

A heat of reaction may be measured in a **calorimeter**—a closed reactor immersed in a fluid contained in a well-insulated vessel. The rise or fall of the fluid temperature can be measured and used to determine the energy released or absorbed by the reaction, and the value of ΔH_r° may then be calculated from that energy and known reactant and product heat capacities.

There are serious limitations to this technique, however. Suppose, for example, you wish to determine ΔH_r° for the reaction

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

You could put 1 mole of carbon and 0.5 mole of oxygen together in a reactor, but you would never get 1 mole of carbon monoxide as the final product. If the reactants are at or near 25°C or lower,

nothing apparent would occur since the rate at which carbon and oxygen react at this temperature is immeasurably low. If, on the other hand, the mixture were heated to a temperature at which C and O_2 react at a measurable rate, the product would be either pure CO_2 or at best a mixture of CO and CO_2, making it impossible to determine the heat of the CO formation reaction alone.

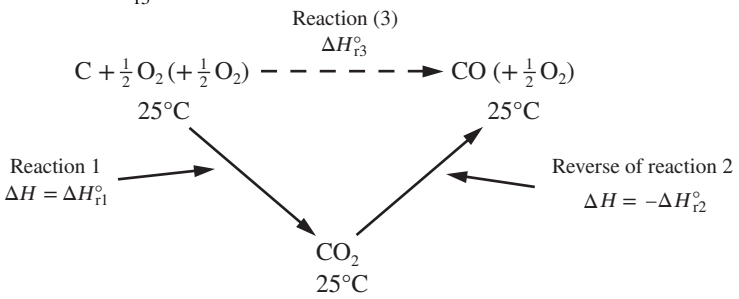
However, you *can* carry out the reactions

1. $C + O_2 \rightarrow CO_2$: $\quad \Delta H^\circ_{r1} = -393.51\ \text{kJ}$

2. $CO + \frac{1}{2}O_2 \rightarrow CO_2$: $\quad \Delta H^\circ_{r2} = -282.99\ \text{kJ}$

and determine their heats of reaction experimentally. You may then construct a process path for the reaction

3. $C + \frac{1}{2}O_2 \rightarrow CO$: $\quad \Delta H^\circ_{r3} = ?$



Since H is a state function,

$$\Delta H^\circ_{r3} = \Delta H^\circ_{r1} + (-\Delta H^\circ_{r2}) = (-393.51 + 282.99)\ \text{kJ} = -110.52\ \text{kJ}$$

You have thus calculated the desired heat of reaction, which could not be measured directly, from two measurable heats of reaction.

This result could have been obtained more concisely by treating the stoichiometric equations for reactions 1 and 2 as algebraic equations. If the equation for reaction 2 is subtracted from that for reaction 1, the result is

$$C + O_2 - CO - \tfrac{1}{2}O_2 \rightarrow CO_2 - CO_2$$

$$\Downarrow$$

$$C + \tfrac{1}{2}O_2 \rightarrow CO \text{ (reaction 3)}$$

The standard heat of reaction 3 may be calculated by applying the same operation to the heats of reactions 1 and 2—that is, $\Delta H^\circ_{r3} = \Delta H^\circ_{r1} - \Delta H^\circ_{r2}$—confirming the result previously obtained.

The general statement of the validity of this procedure is called **Hess's law**: *If the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3, . . . , then the heat of reaction* ΔH°_{r1} *can be obtained by performing the same operations on the heats of reactions* $\Delta H^\circ_{r2}, \Delta H^\circ_{r3}, \ldots$.

Example 9.2-1 Hess's Law

The standard heats of the following combustion reactions have been determined experimentally:

1. $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$: $\quad \Delta H^\circ_{r1} = -1559.8\ \text{kJ}$

2. $C + O_2 \rightarrow CO_2$: $\quad \Delta H^\circ_{r2} = -393.5\ \text{kJ}$

3. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$: $\quad \Delta H^\circ_{r3} = -285.8\ \text{kJ}$

Use Hess's law and the given heats of reaction to determine the standard heat of the reaction

4. $2C + 3H_2 \rightarrow C_2H_6$: $\quad \Delta H^\circ_{r4} = ?$

Solution The stoichiometric equation of the fourth reaction can be obtained as the following linear combination of the first three reactions:

$$(4) = 2 \times (2) + 3 \times (3) - (1) \quad (\textit{verify})$$

From Hess's law

$$\Delta H^\circ_{r4} = 2\Delta H^\circ_{r2} + 3\Delta H^\circ_{r3} - \Delta H^\circ_{r1} = -84.6\ \text{kJ}$$

This heat of reaction could not have been measured directly, since you cannot react carbon and hydrogen in such a way that ethane is the only reaction product.

Test Yourself

(Answers, p. 659)

1. What is Hess's law?
2. Suppose heats of reaction at 25°C are measured experimentally for the following set of reactions:

$$2A + B \rightarrow 2C: \quad \Delta H^\circ_{r1} = -1000\ \text{kJ}$$
$$A + D \rightarrow C + 3E: \quad \Delta H^\circ_{r2} = -2000\ \text{kJ}$$

Use Hess's law to show that for

$$B + 6E \rightarrow 2D: \quad \Delta H^\circ_{r} = +3000\ \text{kJ}$$

9.3 FORMATION REACTIONS AND HEATS OF FORMATION

A **formation reaction** of a compound is the reaction in which the compound is formed from its elemental constituents as they normally occur in nature (e.g., O_2 rather than O). The enthalpy change associated with the formation of 1 mole of the compound at a reference temperature and pressure (usually 25°C and 1 atm) is the **standard heat of formation** of the compound, $\Delta\hat{H}^\circ_f$.

Standard heats of formation for many compounds are listed in Table B.1 of this text and on pp. 2-185 through 200 of *Perry's Chemical Engineers' Handbook*.[2] The values in Table B.1 can also be retrieved using the APEx functions DeltaHfg("compound"), DeltaHfl("compound"), and DeltaHfc("compound") for the specified compound in gaseous, liquid, and solid (crystalline) forms, respectively. For example, $\Delta\hat{H}^\circ_f$ for crystalline ammonium nitrate is given in Table B.1 as −365.15 kJ/mol, where the mol is understood to be of NH_4NO_3. This means the change in enthalpy associated with forming one gram-mole of crystalline ammonium nitrate from its elements is −365.15 kJ. We could also write this in terms of a heat of reaction:

$$N_2(g) + 2H_2(g) + \tfrac{3}{2}O_2 \rightarrow NH_4NO_3(c); \quad \Delta H^\circ_r = -365.14\ \text{kJ}$$

Similarly, for liquid benzene $\Delta\hat{H}^\circ_f = -48.66$ kJ/mol C_6H_6, or

$$6C(s) + 3H_2(g) \rightarrow C_6H_6(l); \quad \Delta H^\circ_r = 48.66\ \text{kJ}$$

These heat of formation values could be determined using APEx by inserting the formulas =DeltaHfc("NH4NO3") and =DeltaHfl("benzene") into cells of an Excel spreadsheet. *Note:* The standard heat of formation of an elemental species (e.g., O_2) is zero. (Why?)

It may be shown using Hess's law that if ν_i(mol Species i) *is the stoichiometric coefficient of the* i^{th} *species participating in a reaction (+ for products, – for reactants) and* $\Delta\hat{H}^\circ_{fi}$ *is the standard*

[2] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York, 2008.

heat of formation of this species, then the standard heat of the reaction is

$$\Delta H_r^\circ = \sum_i \nu_i \Delta \hat{H}_{fi}^\circ = \sum_{\text{products}} |\nu_i| \Delta \hat{H}_{fi}^\circ - \sum_{\text{reactants}} |\nu_i| \Delta \hat{H}_{fi}^\circ \qquad \textbf{(9.3-1)}$$

The standard heats of formation of all elemental species should be set equal to zero in this formula. The validity of Equation 9.3-1 is illustrated in the next example.

Example 9.3-1 Determination of a Heat of Reaction from Heats of Formation

Determine the standard heat of reaction for the combustion of liquid *n*-pentane, assuming $H_2O(l)$ is a combustion product.

$$C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$$

Solution From Equation 9.3-1

$$\Delta H_r^\circ = 5 \text{ mol } CO_2(\Delta \hat{H}_f^\circ)_{CO_2(g)} + 6 \text{ mol } H_2O(\Delta \hat{H}_f^\circ)_{H_2O(l)} - 1 \text{ mol } C_5H_{12}(\Delta \hat{H}_f^\circ)_{C_5H_{12}(l)}$$

$\Downarrow$ Heats of formation from Table B.1 or APEx

$$\Delta H_r^\circ = [5(-393.5) + 6(-285.84) - (-173.0)] \text{ kJ}$$

$$= \boxed{-3509 \text{ kJ}}$$

To verify the formula for ΔH_r°, we may write the stoichiometric equations for the formation reactions of the reactants and products:

1. $5C(s) + 6H_2(g) \rightarrow C_5H_{12}(l)$: $\quad \Delta H_{r1}^\circ = 1 \text{ mol } C_5H_{12}(\Delta \hat{H}_f^\circ)_{C_5H_{12}(l)}$
2. $C(s) + O_2(g) \rightarrow CO_2(g)$: $\quad \Delta H_{r2}^\circ = 1 \text{ mol } CO_2(\Delta \hat{H}_f^\circ)_{CO_2(g)}$
3. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$: $\quad \Delta H_{r3}^\circ = 1 \text{ mol } H_2O(\Delta \hat{H}_f^\circ)_{H_2O(l)}$

The desired reaction,

4. $C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$: $\quad \Delta H_r^\circ = ?$

may be obtained as $5 \times (2) + 6 \times (3) - (1)$ (*verify*), and the given formula for ΔH_r° then follows from Hess's law.

Techniques for estimating heats of formation of compounds with known molecular structures are given by Poling, Prausnitz, and O'Connell.[3]

Test Yourself

(Answers, p. 659)

1. The standard heat of the reaction

$$2CO \rightarrow 2C + O_2$$

is $\Delta H_r^\circ = +221.0$ kJ. Use this result to calculate the standard heat of formation of CO and check your result with a tabulated value.

2. $\Delta \hat{H}_f^\circ$ is −28.64 kcal/mol for $C_3H_8(l)$ and −24.82 kcal/mol for $C_3H_8(g)$. What is the physical significance of the difference between these values?

3. Consider the reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(v)$$

Write the formula for ΔH_r° in terms of the standard heats of formation of the reactants and products.

[3] B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th Edition, McGraw-Hill, New York, 2001.

9.4 HEATS OF COMBUSTION

The **standard heat of combustion** of a substance, $\Delta\hat{H}_c^\circ$, is the heat of the combustion of that substance with oxygen to yield specified products [e.g., $CO_2(g)$ and $H_2O(l)$], with both reactants and products at 25°C and 1 atm (the arbitrary but conventional reference state).

Table B.1 lists standard heats of combustion for a number of substances. The given values are based on the following assumptions: (a) all carbon in the fuel forms $CO_2(g)$, (b) all hydrogen forms $H_2O(l)$, (c) all sulfur forms $SO_2(g)$, and (d) all nitrogen forms $N_2(g)$. The standard heat of combustion of liquid ethanol, for example, is given in Table B.1 as $\Delta\hat{H}_c^\circ = -1366.9$ kJ/mol, where the mol is understood to be of ethanol. This means the change in enthalpy associated with complete combustion of one gram-mole of liquid ethanol with the stoichiometric amount of oxygen is −1366.9 kJ. We could also write this in terms of a heat of reaction:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l); \quad \Delta H_r^\circ = -1366.9\ \text{kJ}$$

The heats of combustion in Table B.1 can also be retrieved using the APEx functions DeltaHcg("compound"), DeltaHcl("compound"), and DeltaHcc("compound") for the specified compound in gaseous, liquid, and solid (crystalline) forms, respectively. Additional heats of combustion are given on pp. 2-195 through 2-200 of *Perry's Chemical Engineers' Handbook* (see Footnote 2).

Standard heats of reactions that involve only combustible substances and combustion products can be calculated from tabulated standard heats of combustion, in another application of Hess's law. A hypothetical reaction path may be constructed in which (a) all combustible reactants are burned with O_2 at 25°C and (b) CO_2 and H_2O combine to form the reaction products plus O_2. Step (b) involves the reverse of the combustion reactions of the reaction products. Since both steps involve only combustion reactions, the total enthalpy change—which equals the desired heat of reaction—can be determined entirely from heats of combustion as

$$\Delta H_r^\circ = -\sum_i \nu_i (\Delta\hat{H}_c^\circ)_i = \sum_{\text{reactants}} |\nu_i| (\Delta\hat{H}_c^\circ)_i - \sum_{\text{products}} |\nu_i| (\Delta\hat{H}_c^\circ)_i \qquad \textbf{(9.4-1)}$$

If any of the reactants or products are themselves combustion products [CO_2, $H_2O(l)$, SO_2, . . .], their $\Delta\hat{H}_c^\circ$ terms in Equation 9.4-1 should be set equal to 0.

Note that this formula is similar to that used to determine ΔH_r° from heats of formation, except that in this case the negative of the sum is taken. The validity of this formula is illustrated in the next example.

Example 9.4-1 Calculation of a Heat of Reaction from Heats of Combustion

Calculate the standard heat of reaction for the dehydrogenation of ethane:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Solution From Table B.1 or using APEx function DeltaHcg,

$$(\Delta\hat{H}_c^\circ)_{C_2H_6} = -1559.9\ \text{kJ/mol}$$
$$(\Delta\hat{H}_c^\circ)_{C_2H_4} = -1411.0\ \text{kJ/mol}$$
$$(\Delta\hat{H}_c^\circ)_{H_2} = -285.84\ \text{kJ/mol}$$

From Equation 9.4-1, therefore,

$$\Delta H_r^\circ = 1\ \text{mol}\ C_2H_6(\Delta\hat{H}_c^\circ)_{C_2H_6} - 1\ \text{mol}\ C_2H_4(\Delta\hat{H}_c^\circ)_{C_2H_4} - 1\ \text{mol}\ H_2(\Delta\hat{H}_c^\circ)_{H_2} = \boxed{136.9\ \text{kJ}}$$

As an illustration, let us demonstrate the validity of this formula using Hess's law. The combustion reactions are

1. $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$

2. $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

3. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

It is easy to show that

4. $C_2H_6 \rightarrow C_2H_4 + H_2$

is obtained as (1) **–** (2) – (3). (Show it.) The desired result follows from Hess's law.

One of the principal applications of Equation 9.4-1 is to determine heats of formation for combustible substances whose formation reactions do not occur naturally. For example, the formation reaction of pentane

$$5C(s) + 6H_2(g) \rightarrow C_5H_{12}(l): \quad \Delta\hat{H}_f^\circ = ?$$

cannot be carried out in a laboratory, but carbon, hydrogen, and pentane can all be burned and their standard heats of combustion determined experimentally. The heat of formation of pentane may then be calculated from Equation 9.4-1 as

$$(\Delta\hat{H}_f^\circ)_{C_5H_{12}(l)} = 5(\Delta\hat{H}_c^\circ)_{C(s)} + 6(\Delta\hat{H}_c^\circ)_{H_2(g)} - (\Delta\hat{H}_c^\circ)_{C_5H_{12}(l)}$$

where it is understood that the coefficients of the first two terms in the equation have units of mol C/mol C_5H_{12} and mol H/mol C_5H_{12}, respectively.

CREATIVITY EXERCISE

When an exothermic reaction takes place, the energy released raises the temperature of the reactor contents unless the reactor is cooled. Suppose such a reaction occurs in a batch reactor.

1. Think of as many reasons as you can why you might not want the reactor temperature to increase. (*Example:* The product might degrade or decompose at higher temperatures.)

2. Think of as many ways as you can to keep the reactor temperature from increasing as the reaction proceeds. (*Example:* Throw in some ice.)

9.5 ENERGY BALANCES ON REACTIVE PROCESSES

9.5a General Procedures

To perform energy balance calculations on a reactive system, proceed much as you did for nonreactive systems: (a) draw and label a flowchart; (b) use material balances and phase equilibrium relationships such as Raoult's law to determine as many stream component amounts or flow rates as possible; (c) choose reference states for specific enthalpy (or internal energy) calculations and prepare and fill in an inlet–outlet enthalpy (or internal energy) table; and (d) calculate $\Delta\dot{H}$ (or ΔU or ΔH), substitute the calculated value in the appropriate form of the energy balance, and complete the required calculation.

Two methods are commonly used to choose reference states for enthalpy calculations and to calculate specific enthalpies and $\Delta\dot{H}$.[4] We outline the two approaches below, using a propane combustion process to illustrate them. For simplicity, the material balance calculations for the illustrative process have been performed and the results incorporated into the flowchart.

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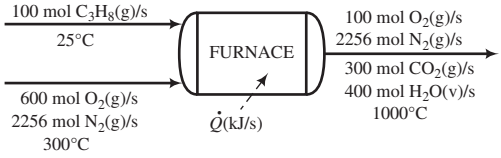
[4] In what follows, we presume that the value of $\Delta\dot{H}$ is needed for the energy balance. If ΔU or ΔH is required, replace each $\dot{H}$ that appears with U or H.



$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l): \quad \Delta H_r^\circ = -2220\ \text{kJ}$$

Heat of Reaction Method. This method is generally preferable when there is a single reaction for which ΔH_r° is known.

1. *Complete the material balance calculations on the reactor to the greatest extent possible.*

2. *Choose reference states for specific enthalpy calculations*. The best choices are generally reactant and product species at 25°C and 1 atm in the states for which the heat of reaction is known [C_3H_8(g), O_2(g), CO_2(g), and H_2O(l) in the example process], and nonreacting species at any convenient temperature, such as the reactor inlet or outlet temperature or the reference condition used for the species in an available enthalpy table [N_2(g) at 25°C and 1 atm, the reference state for Table B.8].

3. *For a single reaction in a continuous process, calculate the extent of reaction, ξ, from Equation 9.1-3*.[5] When writing the equation, choose as species A any reactant or product for which the feed and product flow rates are known. In the example, we may choose any reactant or product since we know all inlet and outlet species flow rates and calculate the rate of consumption or generation of A ($\dot{n}_{A,r}$ in Equation 9.1-3) as $|(\dot{n}_A)_{out} - (\dot{n}_A)_{in}|$. If A is propane,

$$\xi = \frac{|(\dot{n}_{C_3H_8})_{out} - (\dot{n}_{C_3H_8})_{in}|}{|\dot{\nu}_{C_3H_8}|} = \frac{|0 - 100|\text{mol/s}}{1\ \text{mol/s}} = 100$$

As an exercise, let A be O_2, CO_2, or H_2O and verify that the value of ξ is independent of the species chosen.

4. *Prepare the inlet–outlet enthalpy table, inserting known molar amounts (n_i) or flow rates ($\dot{n}_i$) for all inlet and outlet stream components*. If any of the components is at its reference state, insert 0 for the corresponding $\hat{H}_i$. For the example process, the table would appear as follows:

References: C_3H_8(g), O_2(g), N_2(g), CO_2(g), H_2O(l) at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_3H_8	100	0	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

5. *Calculate each unknown stream component enthalpy, $\hat{H}_i$, as $\Delta\hat{H}$ for the species going from its reference state to the process state, and insert the enthalpies in the table*. In the example,

$$\hat{H}_2 = \Delta\hat{H} \text{ for } O_2(25°C) \rightarrow O_2(300°C)$$
$$= 8.47\ \text{kJ/mol (from Table B.8 or the Enthalpy function of APEx)}$$

[5] If multiple reactions occur you would calculate the extents of each independent reaction, $\xi_1, \xi_2, \ldots$ (Equation 4.6-7), but for such processes you are generally better off using the heat of formation method to be described.

We proceed in the same manner to calculate $\hat{H}_3 = 8.12$ kJ/mol, $\hat{H}_4 = 32.47$ kJ/mol, $\hat{H}_5 = 30.56$ kJ/mol, $\hat{H}_6 = 48.60$ kJ/mol, and $\hat{H}_7 = 81.71$ kJ/mol.

Consider the last result. By definition

$$\hat{H}_7 = \Delta\hat{H} \text{ for } H_2O(l, 25°C) \rightarrow H_2O(g, 1000°C)$$

We could either use steam tables to determine $\Delta\hat{H}$ in one step or heat the liquid water from 25°C to 100°C, vaporize it, heat the vapor from 100°C to 1000°C, and calculate

$$\hat{H}_7 = \int_{25°C}^{100°C} C_{pl}\, dT + \Delta\hat{H}_v(100°C) + \int_{100°C}^{1000°C} C_{pv}\, dT$$

The last calculation could be done easily using APEx by entering the following formula into a cell in a spreadsheet:

=Enthalpy("water",25,100,,"l") + Hv("water") + Enthalpy("water",100,1000,,"g")

6. *Calculate $\Delta\dot{H}$ for the reactor*. Use one of the following formulas:

$$\Delta\dot{H} = \xi\Delta\dot{H}_r^\circ + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} \quad \text{(single reaction)} \qquad \textbf{(9.5-1a)}$$

$$\Delta\dot{H} = \sum_{\text{reactions}} \xi_j\Delta\dot{H}_{rj}^\circ + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} \quad \text{(multiple reactions)} \qquad \textbf{(9.5-1b)}$$

A derivation of these equations is outlined following the presentation of the heat of formation method. Substitution of the previously calculated values into Equation 9.5-1a yields $\Delta\dot{H} = -1.26 \times 10^5$ kJ/s.

7. Substitute the calculated value of $\Delta\dot{H}$ in the energy balance ($\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$ for an open system) and complete the required calculations.

Heat of Formation Method: This method is generally preferable for multiple reactions and single reactions for which ΔH_r is not readily available.

1. *Complete the material balance calculations on the reactor to the greatest extent possible.*

2. *Choose reference states for enthalpy calculations*. (This is the step that distinguishes the preceding method from this one.) The choices should be the elemental species that constitute the reactants and products in the states in which the elements are found at 25°C and 1 atm [C(s), H_2(g), etc.] and nonreacting species at any convenient temperature. In the example, the reference states would be C(s), H_2(g), and O_2(g) at 25°C (the elemental species constituting the reactants and products), and N_2 at 25°C (the reference temperature of Table B.8).

3. *Prepare the inlet–outlet enthalpy table, inserting known molar amounts (n_i) or flow rates ($\dot{n}_i$) for all inlet and outlet stream components.* For the example process, the table would appear as follows:

References: C(s), H_2(g), O_2(g), N_2(g) at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_3H_8	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

4. *Calculate each unknown specific enthalpy*. For a reactant or product, start with the elemental species at 25°C and 1 atm (the references) and form 1 mol of the process species at 25°C and 1 atm ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$ from Table B.1). Then bring the species from 25°C and 1 atm to its process state, calculating $\Delta\hat{H}$ using the appropriate heat capacities from Table B.2 or the APEx function Enthalpy, specific enthalpies from Table B.8 or B.9, and latent heats from Table B.1 or the APEx functions Hm (heat of melting) and/or Hv (heat of vaporization). The specific enthalpy that goes in the inlet–outlet table is the sum of the enthalpy changes for each step in the process path.

In the example, we would first calculate the specific enthalpy of the entering propane ($\hat{H}_1$) as follows:

$$3C(s)(25°C, 1\text{ atm}) + 4H_2(g)(25°C, 1\text{ atm}) \rightarrow C_3H_8(g)(25°C, 1\text{ atm})$$

$$\Downarrow$$

$$\hat{H}_1 = (\Delta\hat{H}_f^\circ)_{C_3H_8(g)} = -103.8\text{ kJ/mol (from Table B.1)}$$

This is the enthalpy of propane at 25°C (the process state) relative to C(s) and H_2(g) at 25°C (the reference states). If the propane had entered at a temperature T_0 other than 25°C, a term of the form $\int_{25°C}^{T_0} C_p\,dT$ would be added to the heat of formation of propane.

Next, we calculate the specific enthalpy of O_2 at 300°C (the process state) relative to O_2 at 25°C (the reference state) as $\hat{H}_2 = 8.47$ kJ/mol (from Table B.8 or APEx). There is no heat of formation term, since O_2 is an elemental species. We proceed in the same manner to calculate $\hat{H}_3 = 8.12$ kJ/mol, $\hat{H}_4 = 32.47$ kJ/mol, $\hat{H}_5 = 30.56$ kJ/mol, $\hat{H}_6 = -344.9$ kJ/mol, and $\hat{H}_7 = -204.1$ kJ/mol. To calculate $\hat{H}_6$ and $\hat{H}_7$, we form the corresponding species [CO_2(g) and H_2O(v)] at 25°C from their elements ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$), then heat them from 25°C to 1000°C ($\Delta\hat{H} = \hat{H}_{1000°C}$ from Table B.8 or APEx), and add the formation and heating terms.

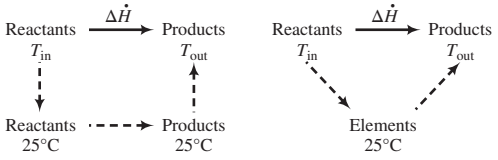
5. *Calculate $\Delta\dot{H}$ for the reactor*. For both single and multiple reactions, the formula is

$$\Delta\dot{H} = \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} \qquad \textbf{(9.5-2)}$$

Note that heat of reaction terms are not required if the elements are chosen as references. The heats of reaction are implicitly included when the heats of formation of the reactants (included in the $\hat{H}_{in}$ terms) are subtracted from those of the products (in the $\hat{H}_{out}$ terms) in the expression for $\Delta\dot{H}$. Substituting the calculated $\dot{n}$ and $\hat{H}$ values into Equation 9.5-2 yields $\Delta\dot{H} = -1.26 \times 10^5$ kJ/s.

6. *Substitute the calculated value of $\Delta\dot{H}$ in the energy balance equation and complete the required calculations*.

The process paths that correspond to the heat of reaction and heat of formation methods are shown below.



(*a*) Process path for heat of reaction method

(*b*) Process path for heat of formation method

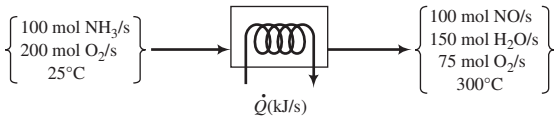
The heat of reaction method amounts to bringing the reactants from their inlet conditions to their reference states at 25°C ($\Delta\dot{H} = -\sum \dot{n}_{in}\hat{H}_{in}$), carrying out the reaction at 25°C (from Equation 9.1-4b, $\Delta\dot{H} = \xi\Delta\dot{H}_r^\circ$ or the summation of such terms for multiple reactions), bringing the products from their reference states at 25°C to their outlet states ($\Delta\dot{H} = \sum \dot{n}_{out}\hat{H}_{out}$), and summing the enthalpy changes for these three steps to calculate $\Delta\dot{H}$ for the overall process. The heat of formation method amounts to bringing the reactants from their inlet conditions to their constituent elements at 25°C $\left(\Delta\dot{H} = -\sum \dot{n}_{in}\hat{H}_{in}\right)$, taking the elements to the products at their outlet states $\left(\Delta\dot{H} = \sum \dot{n}_{out}\hat{H}_{out}\right)$, and summing the enthalpy changes for these two steps to calculate $\Delta\dot{H}$ for the overall process.

Example 9.5-1 Energy Balance About an Ammonia Oxidizer

One hundred mol NH_3/s and 200 mol O_2/s at 25°C are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300°C. Calculate the rate at which heat must be transferred to or from the reactor, assuming operation at approximately 1 atm. The standard heat of reaction for the oxidation of ammonia is given below:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(v): \quad \Delta H_r^\circ = -904.7\ \text{kJ}\left(\Delta \dot{H}_r^\circ = -904.7\ \frac{\text{kJ}}{\text{s}}\right)$$

Solution Basis: Given Feed Rates



(Verify the product flow rates.) Since only one reaction takes place and ΔH_r° is known, we will use the heat of reaction method for the energy balance, choosing as references the reactant and product species in the states for which the heat of reaction is given. The enthalpy table appears as follows:

References: $NH_3(g)$, $O_2(g)$, NO(g), $H_2O(v)$ at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
NH_3	100	0	—	—
O_2	200	0	75	$\hat{H}_1$
NO	—	—	100	$\hat{H}_2$
H_2O	—	—	150	$\hat{H}_3$

Calculate Unknown Enthalpies

$O_2(g, 300°C)$: From Table B.8, $\hat{H}_1 = 8.470$ kJ/mol (Insert value in enthalpy table)

NO(g, 300°C): $\hat{H}_2 = \int_{25°C}^{300°C} (C_p)_{NO}\, dT \xrightarrow{\text{Table B.2}} \hat{H}_2 = 8.453$ kJ/mol (Insert in table)

$H_2O(v, 300°C)$: From Table B.8, $\hat{H}_3 = 9.570$ kJ/mol (Insert in table)

Calculate ξ and $\Delta\dot{H}$

Since 100 mol NH_3/s is consumed in the process (A = NH_3, $\dot{n}_{A,r} = 100$ mol NH_3/s), Equation 9.1-3 becomes

$$\xi = \frac{\dot{n}_{NH_3,r}}{|\dot{\nu}_{NH_3}|} = \frac{100\ \text{mol/s}}{4\ \text{mol/s}} = 25$$

$$\Downarrow \text{Equation 9.5-1a}$$

$$\Delta\dot{H} = \xi\Delta\dot{H}_r^\circ + \underbrace{\sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in}}_{\text{from table}}$$

$$= (25)(-904.7\ \text{kJ/s}) + [(75)(8.470) + (100)(8.453) + (150)(9.570) - (100)(0) - (200)(0)]\ \text{kJ/s} = -19{,}700\ \text{kJ/s}$$

Energy Balance

For this open system,

$$\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$$\Downarrow \quad \dot{W}_s = 0 \quad \text{(no moving parts)}$$

$$\Downarrow \quad \Delta\dot{E}_p = 0 \quad \text{(horizontal unit)}$$

$$\Downarrow \quad \Delta\dot{E}_k \approx 0 \quad \text{(neglect kinetic energy changes)}$$

$$\dot{Q} \approx \Delta\dot{H} = -19{,}700 \text{ kJ/s} = \boxed{-19{,}700 \text{ kW}}$$

Thus, 19,700 kW of heat must be transferred from the reactor to maintain the product temperature at 300°C. If less heat were transferred, more of the heat of reaction would go into the reaction mixture and the outlet temperature would increase.

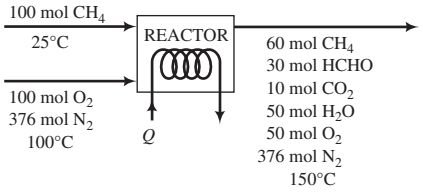
The heat of formation method, which involves taking elemental constituents of the reactants and products in their naturally occurring states as references for enthalpy calculations, is usually convenient for processes that involve several simultaneous reactions. The next example illustrates this approach.

Example 9.5-2 Energy Balance on a Methane Oxidation Reactor

Methane is oxidized with air to produce formaldehyde in a continuous reactor. A competing reaction is the combustion of methane to form CO_2.

1. $CH_4(g) + O_2 \rightarrow HCHO(g) + H_2O(v)$
2. $CH_4(g) + 2O_2 \rightarrow CO_2 + 2H_2O(v)$

A flowchart of the process for an assumed basis of 100 mol of methane fed to the reactor is shown here. All species are gases.



Solution Basis: 100 mol CH_4 Fed

Since the component amounts of all streams are known, we may proceed directly to the energy balance. We choose as references the elemental species that form the reactants and products at 25°C and 1 atm (the state for which heats of formation are known) and the nonreactive species—$N_2(g)$—also at 25°C and 1 atm (the reference state for Table B.8). The inlet–outlet enthalpy table is shown below.

References: C(s), $O_2(g)$, $H_2(g)$, $N_2(g)$ at 25°C and 1 atm

Substance	n_{in} (mol)	$\hat{H}_{in}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{out}$ (kJ/mol)
CH_4	100	$\hat{H}_1$	60	$\hat{H}_4$
O_2	100	$\hat{H}_2$	50	$\hat{H}_5$
N_2	376	$\hat{H}_3$	376	$\hat{H}_6$
HCHO	—	—	30	$\hat{H}_7$
CO_2	—	—	10	$\hat{H}_8$
H_2O	—	—	50	$\hat{H}_9$

Calculate Unknown Enthalpies

All of the quantities shown can be retrieved easily using the appropriate functions in APEx. In the following calculations, values of $\Delta\hat{H}_f^\circ$ come from Table B.1, formulas for $C_p(T)$ come from Table B.2, and values of $\hat{H}(T)$ for O_2 and N_2 are specific enthalpies relative to the gaseous species at 25°C taken from Table B.8. Effects of any pressure changes on enthalpies are neglected.

$$\begin{aligned}
\text{CH}_4(25°\text{C}): \quad \hat{H}_1 &= (\Delta\hat{H}_f^\circ)_{\text{CH}_4} = -74.85\ \text{kJ/mol} \\
\text{O}_2(100°\text{C}): \quad \hat{H}_2 &= \hat{H}_{\text{O}_2}(100°\text{C}) = 2.235\ \text{kJ/mol} \\
\text{N}_2(100°\text{C}): \quad \hat{H}_3 &= \hat{H}_{\text{N}_2}(100°\text{C}) = 2.187\ \text{kJ/mol} \\
\text{CH}_4(150°\text{C}): \quad \hat{H}_4 &= (\Delta\hat{H}_f^\circ)_{\text{CH}_4} + \int_{25°\text{C}}^{150°\text{C}} (C_p)_{\text{CH}_4}\, dT \\
&= (-74.85 + 4.90)\ \text{kJ/mol} = -69.95\ \text{kJ/mol} \\
\text{O}_2(150°\text{C}): \quad \hat{H}_5 &= \hat{H}_{\text{O}_2}(150°\text{C}) = 3.758\ \text{kJ/mol} \\
\text{N}_2(150°\text{C}): \quad \hat{H}_6 &= \hat{H}_{\text{N}_2}(150°\text{C}) = 3.655\ \text{kJ/mol} \\
\text{HCHO}(150°\text{C}): \quad \hat{H}_7 &= (\Delta\hat{H}_f^\circ)_{\text{HCHO}} + \int_{25°\text{C}}^{150°\text{C}} (C_p)_{\text{HCHO}}\, dT \\
&= (-115.90 + 4.75)\ \text{kJ/mol} = -111.15\ \text{kJ/mol} \\
\text{CO}_2(150°\text{C}): \quad \hat{H}_8 &= (\Delta\hat{H}_f^\circ)_{\text{CO}_2} + \hat{H}_{\text{CO}_2}(150°\text{C}) \\
&= (-393.5 + 4.75)\ \text{kJ/mol} = -388.6\ \text{kJ/mol} \\
\text{H}_2\text{O(v, 150°C)}: \quad \hat{H}_9 &= (\Delta\hat{H}_f^\circ)_{\text{H}_2\text{O(v)}} + \hat{H}_{\text{H}_2\text{O(v)}}(150°\text{C}) \\
&= (-241.83 + 4.27)\ \text{kJ/mol} = -237.56\ \text{kJ/mol}
\end{aligned}$$

As each of these values is calculated, it should be substituted in the inlet–outlet enthalpy table. The table finally appears as follows:

References: C(s), O_2(g), H_2(g), N_2(g) at 25°C and 1 atm

Substance	n_{in} (mol)	$\hat{H}_{in}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{out}$ (kJ/mol)
CH_4	100	−74.85	60	−69.95
O_2	100	2.235	50	3.758
N_2	376	2.187	376	3.655
HCHO	—	—	30	−111.15
CO_2	—	—	10	−388.6
H_2O	—	—	50	−237.56

Evaluate ΔH

From Equation 9.5-2,

$$\Delta H = \sum n_{out}\hat{H}_{out} - \sum n_{in}\hat{H}_{in} = -15{,}300\ \text{kJ}$$

If molecular species had been chosen as references for enthalpy calculations, the extents of each reaction (ξ_1 and ξ_2) would have had to be calculated and Equation 9.5-1b used to determine ΔH. When more than one reaction occurs in a process, you are advised to choose elemental species as references and avoid these complications.

Energy Balance

Remember that we are dealing with a continuous process and hence an open system. [The reason we use n(mol) and not $\dot{n}$(mol/s) is that we took 100 mol CH_4 as a basis of calculation.] With ΔE_k, ΔE_p, and W_s neglected, the open system energy balance yields

$$\boxed{Q = \Delta H = -15{,}300\ \text{kJ}}$$

9.5b Processes with Known Heat Inputs: Adiabatic Reactors

In the reactive systems we have looked at so far, the inlet and outlet conditions were specified and the required heat input could be determined from an energy balance.

In another important class of problems, the input conditions, heat input, and product composition are specified, and the outlet temperature is to be calculated. To solve such problems, you must evaluate the enthalpies of the products relative to the chosen reference states in terms of the unknown final temperature, and then substitute the resulting expressions into the energy balance ($\dot{Q} = \Delta\dot{H}$, or $\Delta\dot{H} = 0$ for a continuous adiabatic reactor) to calculate T_{out}. Excel with the APEx add-in makes trial-and-error calculations of this sort particularly easy. The next example illustrates both a manual calculation and the use of APEx.

Example 9.5-3 Energy Balance on an Adiabatic Reactor

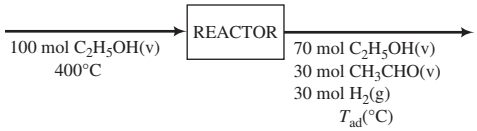
The dehydrogenation of ethanol to form acetaldehyde

$$C_2H_5OH(v) \rightarrow CH_3CHO(v) + H_2(g)$$

is carried out in a continuous adiabatic reactor. Ethanol vapor is fed to the reactor at 400°C, and a conversion of 30% is obtained. Calculate the product temperature (a) using heat capacity formulas from Table B.2, and (b) using APEx.

Solution **Basis: 100 mol Feed**

Material balances lead to the flowchart shown here.



Since only one reaction occurs, we could equally well choose the reactants and products [$C_2H_5OH(v)$, $CH_3CHO(v)$, $H_2(g)$] or their elemental constituents [C(s), $H_2(g)$, $O_2(g)$] as references for enthalpy calculations. Let us choose the molecular species.

References: $C_2H_5OH(v)$, $CH_3CHO(v)$, $H_2(g)$ at 25°C and 1 atm

Substance	n_{in} (mol)	$\hat{H}_{in}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{out}$ (kJ/mol)
C_2H_5OH	100.0	$\hat{H}_1$	70.0	$\hat{H}_2$
CH_3CHO	—	—	30.0	$\hat{H}_3$
H_2	—	—	30.0	$\hat{H}_4$

The open system energy balance neglecting kinetic and potential energy changes and shaft work and setting $Q = 0$ for this adiabatic reactor is

$$\Delta H = \xi \Delta H_r^\circ + \sum n_{out}\hat{H}_{out} - \sum n_{in}\hat{H}_{in} = 0$$

The expression for ΔH is that of Equation 9.5-1a, with the dots above H and n omitted since a molar amount and not a flow rate was chosen as a basis of calculation.

(a) ***Manual Calculation***

Extent of Reaction:

We could use any reactant or product as a basis for calculating ξ. Let us use acetaldehyde. From Equation 9.1-3,

$$\xi = \frac{|(n_{CH_3CHO})_{out} - (n_{CH_3CHO})_{in}|}{|\nu_{CH_3CHO}|} = \frac{|30.0 \text{ mol} - 0 \text{ mol}|}{1 \text{ mol}} = 30.0$$

Standard Heat of Reaction:

From Equation 9.3-1 and Table B.1 (heats of formation),

$$\begin{aligned}\Delta H_r^\circ &= \sum \nu_i \Delta \hat{H}_f^\circ = (-1\text{ mol } C_2H_5OH)(\Delta \hat{H}_f^\circ)_{C_2H_5OH(v)} + (1\text{ mol } CH_3CHO)(\Delta \hat{H}_f^\circ)_{CH_3CHO(v)} \\ &\quad + (1\text{ mol } H_2)(\Delta \hat{H}_f^\circ)_{H_2(g)} \\ &= [(-1)(-235.31) + (1)(-166.2) + (1)(0)]\text{ kJ} = 69.11\text{ kJ}\end{aligned}$$

Inlet Enthalpy:

$$\hat{H}_1 = \int_{25°C}^{400°C} (C_p)_{C_2H_5OH} \xrightarrow{C_p \text{ from Table B.2}} \hat{H}_1 = 33.79\text{ kJ/mol}$$

Outlet Enthalpies:

The heat capacities of ethanol vapor and hydrogen are given in Table B.2. For acetaldehyde vapor, the heat capacity is given by Poling, Prausnitz, and O'Connell[6]:

$$(C_p)_{CH_3CHO}\left(\frac{\text{kJ}}{\text{mol}\cdot°\text{C}}\right) = 0.05048 + 1.326\times10^{-4}T - 8.050\times10^{-8}T^2 + 2.380\times10^{-11}T^3$$

where T is in °C. For the three species in the product stream,

$$\hat{H}_i = \int_{25°C}^{T_{ad}} C_{pi}(T)\,dT, \quad i = 1, 2, 3$$

If the heat capacity formulas for the three species are substituted in this expression and the integrals are evaluated, the results are three fourth-order polynomial expressions for $\hat{H}_2(T_{ad})$, $\hat{H}_3(T_{ad})$, and $\hat{H}_4(T_{ad})$:

$$\begin{aligned}\textbf{\textit{C}}_2\textbf{\textit{H}}_5\textbf{\textit{OH:}} \qquad \hat{H}_2(\text{kJ/mol}) &= 4.958\times10^{-12}T_{ad}^4 - 2.916\times10^{-8}T_{ad}^3 \\ &\quad + 7.860\times10^{-5}T_{ad}^2 + 0.06134T_{ad} - 1.582 \\ \textbf{\textit{CH}}_3\textbf{\textit{CHO:}} \qquad \hat{H}_3(\text{kJ/mol}) &= 5.950\times10^{-12}T_{ad}^4 - 2.683\times10^{-8}T_{ad}^3 \\ &\quad + 6.630\times10^{-5}T_{ad}^2 + 0.05048T_{ad} - 1.303 \\ \textbf{\textit{H}}_2\textbf{\textit{:}} \qquad \hat{H}_4(\text{kJ/mol}) &= -0.2175\times10^{-12}T_{ad}^4 + 0.1096\times10^{-8}T_{ad}^3 \\ &\quad + 0.003825\times10^{-5}T_{ad}^2 + 0.02884T_{ad} - 0.7210\end{aligned}$$

Solve the Energy Balance for T_{ad}

$$\Delta H = \xi \Delta H_r^\circ + (70.0\text{ mol})\hat{H}_2 + (30.0\text{ mol})\hat{H}_3 + (30.0\text{ mol})\hat{H}_4 - (100.0\text{ mol})\hat{H}_1 = 0$$

$$\Downarrow \text{ Substitute for } \xi(=30.0),\ \Delta H_r^\circ(=69.11\text{ kJ}),\ \hat{H}_1(=33.79\text{ kJ/mol}),\text{ and } \hat{H}_2 \text{ through } \hat{H}_4$$

$$\Delta H = 5.190\times10^{-10}T_{ad}^4 + 2.813\times10^{-6}T_{ad}^3 + 7.492\times10^{-3}T_{ad}^2 + 6.673T_{ad} - 1477 = 0$$

This equation can be solved using an equation-solving program or a spreadsheet.[7] The solution is

$$\boxed{T_{ad} = 185°\text{C}}$$

[6] B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th Edition, McGraw-Hill, New York, 2001. The formula given has been derived from the one shown in this reference, which is for the heat capacity in J/(mol·K) with the temperature expressed in kelvin.

[7] To obtain the solution using a spreadsheet, put a guessed value of T_{ad} in one cell and the expression for ΔH in an adjacent cell, and use the Goal Seek tool to determine the value of T_{ad} for which the expression for ΔH equals zero. A first guess might be the value of T_{ad} obtained by dropping all higher-order terms in the expression, leaving $6.673T_{ad} - 1134 = 0 \Longrightarrow T_{ad} \approx 170°\text{C}$.

(b) ***Spreadsheet Calculation.*** Replicate the following solution for yourself in Excel with APEx to make sure you understand it. Each step matches a calculation in Part (a). The numbers and formulas entered in Column B—including an initially guessed temperature of 100°C—are shown below the spreadsheet.

	A	B
1	Example 9.5-3	
2		
3	Xi	30
4	DHr	69.11
5	H1	33.79029
6	T	100
7	H2(T)	5.309161
8	H3(T)	4.381741
9	H4(T)	2.164416
10	DH	−737.703

[B3] 30

[B4] =DeltaHfg("acetaldehyde") – DeltaHfg("ethanol")

[B5] =Enthalpy("ethanol",25,400,,"g")

[B6] 100

[B7] =Enthalpy("ethanol",25,B$6,,"g")

[B8] =0.05048*(B$6−25) + 1.326e−4*(B$6^2−25^2)/2
−8.05e−8*(B$6^3−25^3)/3 + 2.38e−11*(B$6^4−25^4)/4

[B9] =Enthalpy("hydrogen",25,B$6)

[B10] =B3*B4 + 70*B7 + 30*B8 + 30*B9 − 100*B5

Once the cell entries have been made, use Excel's Solver or Goal Seek to set the value in Cell B10 (which equals ΔH) equal to 0 by varying the value in Cell B6 (the temperature). When you click "Solve" or "OK," the value in Cell B6 changes to 185, so that the solution is $\boxed{185°C}$ and the value in Cell B10 changes to -2.4×10^{-7}, more than close enough to zero for our purposes.

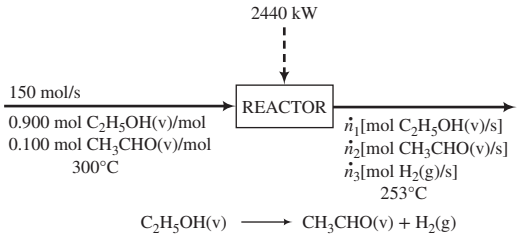
Contrast the ease of this calculation with the cumbersome set of calculations in Part (a). This example would be even easier if the heat capacity formula for acetaldehyde were listed in Table B.2 so that the Enthalpy function of APEx could be used to determine $\hat{H}_3$. Since it isn't, the formula for the integral of the given formula must be entered manually in [B8].

Another class of problems involves processes for which the heat input and outlet temperature are specified but the extent of reaction and product composition are not. Solving such problems requires the simultaneous solution of material and energy balance equations, as the next example illustrates.

Example 9.5-4 Simultaneous Material and Energy Balances

The ethanol dehydrogenation reaction of Example 9.5-3 is carried out with the feed entering at 300°C. The feed contains 90.0 mole% ethanol and the balance acetaldehyde and enters the reactor at a rate of 150 mol/s. To keep the temperature from dropping too much and thereby decreasing the reaction rate to an unacceptably low level, heat is transferred to the reactor. When the heat addition rate is 2440 kW, the outlet temperature is 253°C. Calculate the fractional conversion of ethanol achieved in the reactor.

Solution



A degree-of-freedom analysis based on atomic species balances (see Section 4.7) is as follows:

$$\begin{aligned} &3 \text{ unknown labeled variables } (\dot{n}_1, \dot{n}_2, \dot{n}_3) \\ &-2 \text{ independent atomic species balances (C and H)} \\ &-1 \text{ energy balance} \\ &= 0 \text{ degrees of freedom} \end{aligned}$$

(Convince yourself that there are only two independent atomic balances by writing the C and O balances and observing that they yield the same equation.)

Balance on C

$$\frac{150 \text{ mol}}{\text{s}} \left| \frac{0.900 \text{ mol } C_2H_5OH}{\text{mol}} \right| \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_5OH} + \frac{150 \text{ mol}}{\text{s}} \left| \frac{0.100 \text{ mol } CH_3CHO}{\text{mol}} \right| \frac{2 \text{ mol C}}{1 \text{ mol } CH_3CHO}$$

$$= \frac{\dot{n}_1(\text{mol } C_2H_5OH)}{\text{s}} \left| \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_5OH} \right. + \frac{\dot{n}_2(\text{mol } CH_3CHO)}{\text{s}} \left| \frac{2 \text{ mol C}}{1 \text{ mol } CH_3CHO} \right.$$

$$\Downarrow$$

$$\dot{n}_1 + \dot{n}_2 = 150 \text{ mol/s} \qquad \textbf{(1)}$$

Balance on H

$$[(150)(0.900)(6) + (150)(0.100)(4)] \text{ mol H/s} = 6\dot{n}_1 + 4\dot{n}_2 + 2\dot{n}_3 \quad \text{(Convince yourself)}$$

$$\Downarrow$$

$$3\dot{n}_1 + 2\dot{n}_2 + \dot{n}_3 = 435 \text{ mol H/s} \qquad \textbf{(2)}$$

Energy Balance

In the last example we used molecular species as references for specific enthalpy calculations. This time we will use elemental species [C(s), H_2(g), O_2(g)] at 25°C and 1 atm. (For a single reaction both choices require about the same computational effort.) The energy balance neglecting shaft work and kinetic and potential energy changes becomes

$$\dot{Q} = \Delta\dot{H} = \sum \dot{n}_{\text{out}} \hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}} \hat{H}_{\text{in}}$$

The value of $\dot{Q}$ is 2440 kJ/s and the expression for$\Delta\dot{H}$ is that of Equation 9.5-2. The specific enthalpies of the species at the inlet and outlet of the process relative to their elemental constituents are calculated as

$$\hat{H}_i = \Delta\hat{H}^\circ_{fi} + \int_{25°C}^{T} C_{pi}(T)\, dT$$

where T is 300°C at the inlet and 253°C at the outlet. Taking standard heats of formation from Table B.1 (or APEx function DeltaHfg), formulas for C_p of ethanol vapor and hydrogen from Table B.2 (or APEx function Enthalpy for the integrals of those formulas), and the formula for C_p of acetaldehyde vapor from Example 9.5-3, we calculate the values of $\hat{H}_i$ shown in the inlet–outlet enthalpy table.

References: C(s), H_2(g), O_2(g) at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_2H_5OH	135	−212.19	$\dot{n}_1$	−216.81
CH_3CHO	15	−147.07	$\dot{n}_2$	−150.90
H_2	—	—	$\dot{n}_3$	6.595

The energy balance $\left(\dot{Q} = \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in}\right)$ becomes

$$2440\ \text{kJ/s} = [-216.81\dot{n}_1 - 150.90\dot{n}_2 + 6.595\dot{n}_3 - (135)(-212.19) - (15)(-147.07)]\ \text{kJ/s}$$

$$\Downarrow$$

$$216.81\dot{n}_1 + 150.90\dot{n}_2 - 6.595\dot{n}_3 = 28{,}412\ \text{kJ/s} \qquad \textbf{(3)}$$

Solving Equations 1 through 3 simultaneously (e.g., with Excel's Solver) yields

$$\dot{n}_1 = 92.0\ \text{mol}\ C_2H_5OH/\text{s}$$
$$\dot{n}_2 = 58.0\ \text{mol}\ CH_3CHO/\text{s}$$
$$\dot{n}_3 = 43.0\ \text{mol}\ H_2/\text{s}$$

The fractional conversion of ethanol is

$$x = \frac{(\dot{n}_{C_2H_5OH})_{in} - (\dot{n}_{C_2H_5OH})_{out}}{(\dot{n}_{C_2H_5OH})_{in}} = \frac{(135 - 92.0)\ \text{mol/s}}{135\ \text{mol/s}} = \boxed{0.319}$$

9.5c Thermochemistry of Solutions[8]

The enthalpy change associated with the formation of a solution from the solute elements and the solvent at 25°C is called the **standard heat of formation of the solution**. If a solution contains n moles of solvent per mole of solute, then

$$\boxed{(\Delta\hat{H}_f^\circ)_{solution} = (\Delta\hat{H}_f^\circ)_{solute} + \Delta\hat{H}_s^\circ(n)} \qquad \textbf{(9.5-3)}$$

where $\Delta\hat{H}_s^\circ$ is the heat of solution at 25°C (Section 8.5). From the definitions of $\Delta\hat{H}_f^\circ$ and $\Delta\hat{H}_s^\circ$, the dimensions of the heat of formation of the solution are (energy)/(mole of solute).

The standard heat of a reaction involving solutions may be calculated from heats of formation of the solutions. For example, for the reaction

$$2HNO_3(\text{aq},\ r = 25) + Ca(OH)_2(\text{aq},\ r = \infty) \rightarrow Ca(NO_3)_2(\text{aq},\ r = \infty) + 2H_2O(\text{l})$$

the standard heat of reaction is

$$\begin{aligned}\Delta H_r^\circ &= 1\ \text{mol}\ Ca(NO_3)_2(\Delta\hat{H}_f^\circ)_{Ca(NO_3)_2(\text{aq})} + 2\ \text{mol}\ H_2O(\Delta\hat{H}_f^\circ)_{H_2O(\text{l})} \\ &\quad - 2\ \text{mol}\ HNO_3(\Delta\hat{H}_f^\circ)_{HNO_3(\text{aq},\ r=25)} - 1\ \text{mol}\ Ca(OH)_2(\Delta\hat{H}_f^\circ)_{Ca(OH)_2(\text{aq},\ r=\infty)} \\ &= -114.2\ \text{kJ}\end{aligned}$$

The last equation signifies that if a solution containing 2 mol of HNO_3 in 50 mol of H_2O($r = 25$) is neutralized at 25°C with 1 mol of $Ca(OH)_2$ dissolved in enough water so that the addition of more water would not cause a measurable enthalpy change ($r \rightarrow \infty$), the enthalpy change is −114.2 kJ.

[8] Reviewing Sections 8.5a and 8.5b before reading this section might prove helpful.

If a standard heat of formation is tabulated for a solution involved in a reaction, the tabulated value may be substituted directly into the expression for ΔH_r; otherwise, $(\Delta \hat{H}_f^\circ)_{soln}$ must first be calculated by adding the standard heat of formation of the pure solute to the standard heat of solution.

Example 9.5-5 Standard Heat of a Neutralization Reaction

1. Calculate ΔH_r° for the reaction

$$H_3PO_4(aq,\ r = \infty) + 3NaOH(aq,\ r = 50) \rightarrow Na_3PO_4(aq,\ r = \infty) + 3H_2O(l)$$

2. If 5.00 mol of NaOH dissolved in 250 mol of water is neutralized completely at 25°C with dilute phosphoric acid, what is the attendant enthalpy change?

Solution **1.** $H_3PO_4(aq)$: $\Delta \hat{H}_f^\circ = -309.3$ kcal/mol $= -1294$ kJ/mol [from p. 2-188 of *Perry's Chemical Engineers' Handbook* (see Footnote 2)].

$$\text{NaOH(aq, } r = 50\text{):} \quad (\Delta \hat{H}_f^\circ)_{NaOH(aq)} = (\Delta \hat{H}_f^\circ)_{NaOH(s)} + \Delta \hat{H}_s^\circ(r = 50)$$

$$\Big\Vert \text{ Table B.1 } (\Delta \hat{H}_f^\circ)$$

$$\Big\Downarrow \text{ Table B.11 } (\Delta \hat{H}_s^\circ)$$

$$= (-426.6 - 42.51)\ \text{kJ/mol} = -469.1\ \text{kJ/mol}$$

$Na_3PO_4(aq)$: $\Delta \hat{H}_f^\circ = -471.9$ kcal/mol $= -1974$ kJ/mol (from p. 2-192 of *Perry's Chemical Engineers' Handbook*).

$H_2O(l)$: $\Delta \hat{H}_f^\circ = -285.8$ kJ/mol (from Table B.1)

$$\Delta H_r^\circ = 1\ \text{mol}\ Na_3PO_4(\Delta \hat{H}_f^\circ)_{Na_3PO_4(aq)} + 3\ \text{mol}\ H_2O(\Delta \hat{H}_f^\circ)_{H_2O(l)} - 1\ \text{mol}\ H_3PO_4(\Delta \hat{H}_f^\circ)_{H_3PO_4(aq)}$$
$$- 3\ \text{mol NaOH}(\Delta \hat{H}_f^\circ)_{NaOH(aq,\ r=50)}$$
$$= \boxed{-130.1\ \text{kJ}}$$

2. If 5 mol of dissolved NaOH is neutralized, then

$$\Delta H(25°C) = \frac{-130.1\ \text{kJ}}{3.00\ \text{mol NaOH}} \left| \frac{5.00\ \text{mol NaOH}}{} \right. = \boxed{-217\ \text{kJ}}$$

When you calculate ΔH for a reactive process as

$$\sum_{\text{products}} n_i \hat{H}_i - \sum_{\text{reactants}} n_i \hat{H}_i$$

and one of the reactant or product species is a solution, its specific enthalpy usually has the dimensions (energy)/(mole of solute), so that the corresponding value of n_i must be moles or molar flow rate of the *solute*, and not of the total solution. A complicating factor may be that while the heat of formation of a solution is always obtained in the desired units, solution heat capacities are normally based on a unit mass of the total solution rather than of the solute. To calculate the specific enthalpy of a solution at a temperature T in (energy)/(mole of solute), you must first calculate m, the mass of solution corresponding to 1 mole of dissolved solute, and then add

$$m \int_{25°C}^{T} (C_p)_{solution}\, dT$$

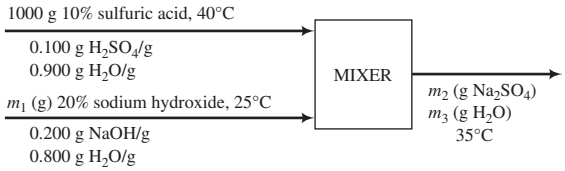
to the standard heat of formation of the solution. The next example illustrates this calculation.

Example 9.5-6 Energy Balance on a Neutralization Process

A 10.0 wt% aqueous solution of H_2SO_4 at 40°C is to be neutralized with a 20.0 wt% aqueous solution of NaOH at 25°C in a continuous reactor. At what rate in kJ/kg H_2SO_4 solution must heat be removed from the reactor if the product solution emerges at 35°C?

Solution Basis: 1 kg H_2SO_4 Solution

$$H_2SO_4(aq,\ 10\%) + 2NaOH(aq,\ 20\%) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$



This is a straightforward problem, but the number of intermediate calculations required to solve it might make it appear more difficult than it is. Let us summarize what must be done:

1. Solve for m_1, m_2, and m_3 by material balances.
2. Calculate the solvent-to-solute mole ratios of all solutions. (The quantities are needed to determine the solution enthalpies from tabulated heats of solution.)
3. Calculate the enthalpies of the solutions. (This will require additional composition calculations to allow the use of tabulated solution heat capacities.)
4. Write the energy balance equation and solve it for the heat removal rate.

Observe that nothing here is really new, and, as we work our way through to the final result, recognize that most of the calculations are simply conversions of solution compositions from mass fractions to mole ratios back to mass ratios—conversions required by the nature of the available data for properties of solutions.

1. ***Solve for m_1, m_2, and m_3 by material balances, and calculate the amount of water formed.***

$$\textit{S balance:}\quad \frac{100\text{ g } H_2SO_4}{98.1\text{ g } H_2SO_4}\left|\frac{32.0\text{ g S}}{}\right. = \frac{m_2\text{(g } Na_2SO_4)}{142\text{ g } Na_2SO_4}\left|\frac{32.0\text{ g S}}{}\right.$$

$$\Downarrow$$

$$m_2 = 145\text{ g } Na_2SO_4$$

$$\textit{Na balance:}\quad \frac{0.200\,m_1\text{(g NaOH)}}{40.0\text{ g NaOH}}\left|\frac{23.0\text{ g Na}}{}\right. = \frac{145\text{ g } Na_2SO_4}{142\text{ g } Na_2SO_4}\left|\frac{46.0\text{ g Na}}{}\right.$$

$$\Downarrow$$

$$m_1 = 408\text{ g NaOH(aq)}$$

$$\textit{Total mass balance:}\quad 1000\text{ g} + 408\text{ g} = 145\text{ g} + m_3 \Longrightarrow m_3 = 1263\text{ g } H_2O(l)$$

$$\textit{Mass of product solution:}\quad m = m_2 + m_3 = 1408\text{ g}$$

$$\text{Water formed by reaction} = \frac{145\text{ g } Na_2SO_4\text{ formed}}{142\text{ g}}\left|\frac{1\text{ mol}}{1\text{ mol } Na_2SO_4}\right.\left|\frac{2\text{ mol } H_2O}{}\right.$$

$$= 2.04\text{ mol } H_2O$$

2. ***Calculate solvent/solute mole ratios*** (needed to determine heats of solution).

$H_2SO_4(aq)$: $(900\text{ g } H_2O)/(18.0\text{ g/mol}) = 50.0\text{ mol } H_2O$
$(100\text{ g } H_2SO_4)/(98.1\text{ g/mol}) = 1.02\text{ mol } H_2SO_4$

$$\Downarrow$$

$$r = 50.0\text{ mol } H_2O/1.02\text{ mol } H_2SO_4 = 49.0\text{ mol } H_2O/\text{mol } H_2SO_4$$

$NaOH(aq)$: $[(0.800 \times 408)\text{g } H_2O]/(18.0\text{ g/mol}) = 18.1\text{ mol } H_2O$
$[(0.200 \times 408)\text{g NaOH}]/(40.0\text{ g/mol}) = 2.04\text{ mol NaOH}$

$$\Downarrow$$

$$r = 18.1\text{ mol } H_2O/2.04\text{ mol NaOH} = 8.90\text{ mol } H_2O/\text{mol NaOH}$$

$Na_2SO_4(aq)$: $(1263\text{ g } H_2O)/(18.0\text{ g/mol}) = 70.2\text{ mol } H_2O$
$(145\text{ g } Na_2SO_4)/(142\text{ g/mol}) = 1.02\text{ mol } Na_2SO_4$

$$\Downarrow$$

$$r = 70.2\text{ mol } H_2O/1.02\text{ mol } Na_2SO_4 = 68.8\text{ mol } H_2O/\text{mol } Na_2SO_4$$

3. ***Calculate extent of reaction.*** To calculate ξ, we note that 1.02 mol H_2SO_4 reacted. From Equation 9.1-3,

$$\xi = \frac{(n_{H_2SO_4})_{\text{reacted}}}{|\nu_{H_2SO_4}|} = \frac{1.02\text{ mol}}{1\text{ mol}} = 1.02$$

4. ***Calculate ΔH.*** This problem is made tricky by the fact that water is not just the solvent in the solutions involved but is also formed as a reaction product. We will take as references the reactant and product solutions at 25°C and evaluate ΔH using Equation 9.5-1a:

$$\Delta H = \xi\,\Delta H_r^\circ + \sum n_{\text{out}}\hat{H}_{\text{out}} - \sum n_{\text{in}}\hat{H}_{\text{in}}$$

It is convenient in solution chemistry calculations to tabulate the products $n\hat{H}$ rather than n and $\hat{H}$ separately. The completed enthalpy table is shown below, followed by the calculations that led to the entries.

References: H_2SO_4(aq, $r = 49$), NaOH(aq, $r = 8.9$), Na_2SO_4(aq, $r = 69$) at 25°C

Substance	$n_{\text{in}}\hat{H}_{\text{in}}$ (kJ)	$n_{\text{out}}\hat{H}_{\text{out}}$ (kJ)
H_2SO_4(aq)	57.5	—
NaOH(aq)	0	—
Na_2SO_4(aq)	—	58.9

$H_2SO_4(aq,\ r = 49,\ 40°C)$: From Table 2.174, p. 2-184 of *Perry's Chemical Engineers' Handbook* (see Footnote 2), the heat capacity of a sulfuric acid solution with the given composition is by interpolation, approximately 0.916 cal/(g·°C), or 3.83 J/(g·°C).

$$n\hat{H} = m\int_{25°C}^{40°C} C_p\,dT$$

$$= \frac{1000\text{ g}}{}\left|\frac{3.83\text{ J}}{\text{g}\cdot°\text{C}}\right|\frac{(40-25)°\text{C}}{}\left|\frac{1\text{ kJ}}{1000\text{ J}}\right. = 57.5\text{ kJ}$$

$NaOH(aq,\ r = 8.9,\ 25°C)$: $n\hat{H} = 0$

$Na_2SO_4(aq,\ r = 69,\ 35°C)$: In the absence of better information, we will assume that the heat capacity of the solution is that of pure water, 4.184 J/(g·°C).

$$n\hat{H} = m\int_{25°C}^{35°C} C_p\,dT$$

$$= \frac{1408\text{ g}}{}\left|\frac{4.184\text{ J}}{\text{g}\cdot°\text{C}}\right|\frac{(35-25)°\text{C}}{}\left|\frac{1\text{ kJ}}{1000\text{ J}}\right. = 58.9\text{ kJ}$$

The heats of formation of H_2SO_4(l) and NaOH(c) are given in Table B.1, and the heats of solution of these species are given in Table B.11. *Perry's Chemical Engineers' Handbook* (see Footnote 2) on p. 2-192 gives the standard heat of formation of Na_2SO_4(aq, $r = 1100$) as -330.82 kcal/mol $Na_2SO_4 = -1384$ kJ/mol Na_2SO_4. In the absence of heat of solution data, we will assume that this value also applies to the solution for which $r = 69$ moles of water per mole of solute. The standard heats of formation of the species involved in the reaction

$$H_2SO_4(\text{aq},\ r = 49) + 2\text{NaOH}(\text{aq},\ r = 8.9) \rightarrow Na_2SO_4(\text{aq}) + 2H_2O(\text{l})$$

are obtained from Equation 9.5-3 (heat of formation of the solution equals heat of formation of the solute plus heat of solution) as

$$\begin{aligned}
H_2SO_4(\text{aq}): &\quad \Delta\hat{H}_f^\circ = [(-811.3) + (-73.3)]\ \text{kJ/mol}\ H_2SO_4 = -884.6\ \text{kJ/mol}\ H_2SO_4 \\
\text{NaOH(aq)}: &\quad \Delta\hat{H}_f^\circ = [(-426.6) + (-41.5)]\ \text{kJ/mol NaOH} = -468.1\ \text{kJ/mol NaOH} \\
Na_2SO_4(\text{aq}): &\quad \Delta\hat{H}_f^\circ = -1384\ \text{kJ/mol}\ Na_2SO_4 \\
H_2O(\text{l}): &\quad \Delta\hat{H}_f^\circ = -285.84\ \text{kJ/mol}\ H_2O
\end{aligned}$$

and the standard heat of reaction is therefore

$$\begin{aligned}
\Delta H_r^\circ &= [(-1384)(1) + (-285.84)(2) - (-884.6)(1) - (-468.1)(2)]\ \text{kJ} \\
&= -134.9\ \text{kJ}
\end{aligned}$$

5. ***Energy balance.***

$$\begin{aligned}
Q = \Delta H &= \xi\,\Delta H_r^\circ + \sum n_{\text{out}}\hat{H}_{\text{out}} - \sum n_{\text{in}}\hat{H}_{\text{in}} \\
&= (1.02)(-134.9\ \text{kJ}) + (58.9 - 57.5)\ \text{kJ} = \boxed{-136\ \text{kJ}}
\end{aligned}$$

When a strong acid or base is dissolved in water, it dissociates into ionic species; for example, dissolved NaOH exists as Na^+ and OH^- in a dilute solution. **Heats of formation of ions** may be determined from heats of solutions of such substances and may be used to calculate heats of formation of dilute solutions of highly dissociated materials. A good discussion of this topic and a table of heats of formation of ions is given by Hougen, Watson, and Ragatz.[9]

Test Yourself

(Answers, p. 659)

The heat of formation of A(s) is $(\Delta\hat{H}_f^\circ)_A = -100$ kJ/mol; heats of solution of A in a solvent B are $\Delta\hat{H}_s^\circ(r = 50\ \text{mol B/mol A}) = -10$ kJ/mol and $\Delta\hat{H}_s^\circ(r \rightarrow \infty) = -15$ kJ/mol.

1. (a) What is the standard heat of formation of A(soln, $r = 50$) relative to B and the elements of A(s)?

(b) What is $\Delta\hat{H}_f^\circ$ for A(soln, $r \rightarrow \infty$) relative to the same references?

2. (a) What is the enthalpy (kJ/mol A) of a solution of A in B at 25°C for which $r = 50$, relative to B and the elements of A at 25°C?

(b) What is the enthalpy (kJ) of a solution containing 5 mol of A in 250 mol of B at 25°C, relative to A(s) and B(l) at 25°C? What is it relative to B(l) and the elements of A at 25°C?

9.6 FUELS AND COMBUSTION

The use of heat generated by a combustion reaction to produce steam, which drives turbines to produce electricity, may be the single most important commercial application of chemical reactions.

[9] O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles*, Part I, Wiley, New York, 1954, pp. 315–317.

The analysis of fuels and combustion reactions and reactors has always been an important activity for chemical engineers. In this section, we review the properties of the fuels most often used for power generation and outline techniques for energy balances on combustion reactors.

9.6a Fuels and Their Properties

Fuels burned in power-plant furnaces may be solids, liquids, or gases. Some of the more common fuels are:

Solid fuels: Principally coal (a mixture of carbon, water, noncombustible ash, hydrocarbons, and sulfur), coke (primarily carbon—the solid residue left after coal or petroleum is heated, driving off volatile substances and decomposing hydrocarbons), and to a small extent wood and solid waste (garbage).

Liquid fuels: Principally hydrocarbons obtained by distilling crude oil (petroleum); also coal tars and shale oil. There is also a strong worldwide interest in the use of alcohols obtained by fermenting grains and other forms of biomass.

Gaseous fuels: Principally natural gas (80% to 95% methane, the balance ethane, propane, and small quantities of other gases); also light hydrocarbons obtained from petroleum or coal treatment, acetylene, and hydrogen.

Coal contains primarily carbon and combustible hydrocarbons, but also has substantial amounts of noncombustible ash and as much as 5% sulfur by weight. These minor constituents often raise issues in the use of coal and stimulate the following questions.

1. What becomes of the sulfur when coal is burned? What about the ash? (Suggest two possibilities for the ash.)

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2. In view of the answer to the preceding question, why might coal be less desirable as a fuel than natural gas?

3. What might prompt a power company to use coal as its primary fuel despite its drawbacks relative to liquid or gaseous fuels?

The **heating value** of a combustible material is the negative of the standard heat of combustion. The **higher heating value** (or **total heating value** or **gross heating value**) is $-\Delta\hat{H}_c^\circ$ with $H_2O(l)$ as a combustion product, and the **lower heating value** (or **net heating value**) is the value based on $H_2O(v)$ as a product. Since $\Delta\hat{H}_c^\circ$ is always negative, the heating value is positive.

To calculate a lower heating value of a fuel from a higher heating value or vice versa, you must determine the moles of water produced when one mole of the fuel is burned. If this quantity is designated n, then

$$HHV = LHV + n\Delta\hat{H}_v(H_2O,\ 25°C) \tag{9.6-1}$$

(Try to prove this relationship from the definitions of *LHV* and *HHV* and Hess's law.) The heat of vaporization of water at 25°C is

$$\Delta\hat{H}_v(H_2O, 25°C) = 44.013\ \text{kJ/mol} \tag{9.6-2a}$$

$$= 18{,}934\ \text{Btu/lb-mole} \tag{9.6-2b}$$

If a fuel contains a mixture of combustible substances, its heating value (lower or higher) is

$$HV = \sum x_i(HV)_i \tag{9.6-3}$$

where $(HV)_i$ is the heating value of the ith combustible substance. If the heating values are expressed in units of (energy)/(mass), then the x_is are the mass fractions of the fuel components, while if the dimensions of the heating values are (energy)/(mole), then the x_is are mole fractions.

Example 9.6-1 Calculation of a Heating Value

A natural gas contains 85% methane and 15% ethane by volume. The heats of combustion of methane and ethane at 25°C and 1 atm with water *vapor* as the assumed product are given below:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(v): \quad \Delta\hat{H}_c^\circ = -802 \text{ kJ/mol}$$
$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \rightarrow 2CO_2(v) + 3H_2O(v): \quad \Delta\hat{H}_c^\circ = -1428 \text{kJ/mol}$$

Calculate the higher heating value (kJ/g) of the natural gas.

Solution Since the heating value per unit mass of the fuel is desired, we will first calculate the composition on a mass basis:

$$1 \text{ mol fuel} \Longrightarrow \begin{array}{l} 0.85 \text{ mol } CH_4 \Longrightarrow 13.6 \text{ g } CH_4 \\ 0.15 \text{ mol } C_2H_6 \Longrightarrow \underline{4.5 \text{ g } C_2H_6} \\ \qquad\qquad\qquad\quad 18.1 \text{ g total} \end{array}$$

Thus
$$x_{CH_4} = 13.6 \text{ g } CH_4/18.1 \text{ g} = 0.751 \text{ g } CH_4/\text{g fuel}$$
$$x_{C_2H_6} = 1 - x_{CH_4} = 0.249 \text{ g } C_2H_6/\text{g fuel}$$

The higher heating values of the components are calculated from the given heats of combustion (which are the negatives of the lower heating values) as follows:

$$(HHV)_{CH_4} = (LHV)_{CH_4} + n_{H_2O}(\Delta\hat{H}_v)_{H_2O}$$
$$= \left[802 \frac{\text{kJ}}{\text{mol } CH_4} + \frac{2 \text{ mol } H_2O}{\text{mol } CH_4}\left(44.013 \frac{\text{kJ}}{\text{mol } H_2O}\right)\right]\frac{1 \text{ mol}}{16.0 \text{ g } CH_4}$$
$$= 55.6 \text{ kJ/g}$$
$$(HHV)_{C_2H_6} = \left[1428 \frac{\text{kJ}}{\text{mol } C_2H_6} + \frac{3 \text{ mol } H_2O}{\text{mol } C_2H_6}\left(44.013 \frac{\text{kJ}}{\text{mol } H_2O}\right)\right]\frac{1 \text{ mol}}{30.0 \text{ g } C_2H_6}$$
$$= 52.0 \text{ kJ/g}$$

The higher heating value of the mixture is from Equation 9.6-3:

$$HHV = x_{CH_4}(HHV)_{CH_4} + x_{C_2H_6}(HHV)_{C_2H_6}$$
$$= [(0.751)(55.6) + (0.249)(52.0)] \text{ kJ/g} = \boxed{54.7 \text{ kJ/g}}$$

Higher heating values for several common solid, liquid, and gaseous fuels are given in Section 24 of *Perry's Chemical Engineers' Handbook* (see Footnote 2). Such values often depend upon the source and type of the particular fuel (e.g., hardwood vs. softwood, sub-bituminous vs. bituminous coal), and given values should only be used as estimates. Additional estimates of heating values for a variety of solid, liquid, and gaseous fuels can be found in the *Biomass Energy Data Book*,[10] from which the values in Table 9.6-1 have been excerpted.

Test Yourself

(Answers, p. 659)

1. The standard heat of the reaction

$$n\text{-}C_4H_{10}(v) + \tfrac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O(v)$$

is −2658 kJ/mol. What is the lower heating value per mol of *n*-butane vapor? The higher heating value?

2. A gas mixture contains 40.0 wt% H_2 (HHV = 143 kJ/g) and 60.0 wt% CH_4 (HHV = 55 kJ/g). Calculate the higher heating value of this mixture in kJ/g.

[10] *Biomass Energy Data Book*, U.S. Department of Energy, http://cta.ornl.gov/bedb/appendix_a.shtml.

TABLE 9.6-1 Typical Heating Values of Common Fuels (see Footnote 10)

	Higher Heating Value	
Fuel	kJ/g	Btu/lb_m
Natural gas	52	22,000
Hydrogen	142	61,000
Low-sulfur diesel	46	20,000
Crude oil	46	20,000
Coal (wet basis)	24	10,000
Bituminous coal (wet basis)	27	12,000
Corn stover (dry basis)	17	7,500
Forest residue (dry basis)	16	7,100

3. In 2008, the average cost of coal for utility plants was roughly \$41 per ton. What would natural gas have to cost (\$/ton) to be as economical as coal on a \$/Btu basis? (Use Table 9.6-1.)

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4. Another way to compare fuels is in terms of the greenhouse gases they generate upon combustion. Using the information in Table 9.6-1, estimate the ratio of CO_2 generated from natural gas (assume it's methane) to that generated from coal in the production of a fixed amount of heat.

9.6b Adiabatic Flame Temperature

When a fuel is burned, a considerable amount of energy is released. Some of this energy is transferred out of the reactor as heat, and the remainder raises the temperature of the reaction products; the less heat transferred, the higher the product temperature. The highest achievable temperature is reached if the reactor is adiabatic and all of the energy released by combustion goes to raise the temperature of the combustion products. This temperature is called the **adiabatic flame temperature**, T_{ad}.

Calculation of an adiabatic flame temperature follows the general procedure outlined in Section 9.5b. Unknown stream flow rates are first determined by material balances. Reference conditions are chosen, specific enthalpies of feed components are calculated, and specific enthalpies of product components are expressed in terms of the product temperature, T_{ad}. Finally, $\Delta\dot{H}(T_{ad})$ for the process is evaluated and substituted into the energy balance equation ($\Delta\dot{H} = 0$), which is solved for T_{ad}.

Suppose 1 mol of a fuel species with heat of combustion $\Delta\hat{H}_c^\circ$ is burned completely with pure oxygen or air in an adiabatic reactor, with the product stream emerging at a temperature T_{ad}. Recalling that tabulated heats of combustion presume a stoichiometric coefficient of 1 mol for the fuel, it is easy to show from Equation 9.1-3 that the extent of reaction $\xi = 1$ (Show it.) and, therefore, $\xi\Delta H_r^\circ = (1 \text{ mol of fuel}) \times \Delta\hat{H}_c^\circ$. If the reference conditions for calculating the enthalpies of the reactants and products are the molecular feed and product species at the conditions used in the definition of $\Delta\hat{H}_c^\circ$, Equation 9.5-1a written in terms of amounts instead of rates becomes

$$\Delta H = (1 \text{ mol of feed}) \times \Delta\hat{H}_c^\circ + \sum_{\text{out}} n_i \hat{H}_i(T_{ad}) - \sum_{\text{in}} n_i \hat{H}_i(T_{i0})$$

Since the reactor is adiabatic, $Q = 0$ in the energy balance. If shaft work and kinetic and potential energy changes (W_s, ΔE_k, ΔE_p) are negligible compared to each term in the above expression for ΔH, the energy balance simplifies to $\Delta H = 0$, which in turn leads to

$$\Delta \hat{H}_c^\circ + \sum_{\text{out}} n_i \hat{H}_i(T_{ad}) - \sum_{\text{in}} n_i \hat{H}_i(T_{i0}) = 0 \qquad \textbf{(9.6-4)}$$

In Equation 9.6-4, the values of n_i are the moles of oxygen, nitrogen (if the oxygen is part of an air feed stream), CO_2, and H_2O associated with the complete combustion of 1 mol of fuel, T_{i0} is the temperature of feed species i, and the reference conditions for the enthalpy calculations are those used to determine the value of $\Delta \hat{H}_c^\circ$.

If the third-order polynomial heat capacity formulas in Table B.2 are used to determine $\hat{H}_i(T_{ad})$ for each product species, Equation 9.6-4 becomes a fourth-order polynomial equation. Solving this equation for T_{ad} is easily accomplished with a spreadsheet or equation-solving program, and even more easily if APEx is used. The next example illustrates the procedure.

Example 9.6-2 Calculation of an Adiabatic Flame Temperature

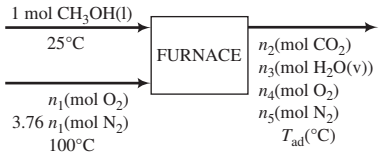
Liquid methanol is to be burned with 100% excess air. The engineer designing the furnace must calculate the highest temperature that the furnace walls will have to withstand so that an appropriate material of construction can be chosen. Perform this calculation, assuming that the methanol is fed at 25°C and the air enters at 100°C.

Solution

Basis: 1 mol CH_3OH Burned

Assume complete combustion. From Table B.1,

$$CH_3OH(l) + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O(l): \quad \Delta \hat{H}_c^\circ = -726.6 \text{ kJ/mol}$$



Calculate Component Amounts

$$(n_{O_2})_{\text{theoretical}} = 1.50 \text{ mol}$$

$$n_1 = (2)(1.50 \text{ mol}) = 3.00 \text{ mol } O_2 \text{ fed}$$

$$\Downarrow$$

$$(3.76 \text{ mol } N_2/\text{mol } O_2)(3.00 \text{ mol } O_2) = 11.28 \text{ mol } N_2 \text{ fed}$$

Material balances yield

$$n_2 = 1.00 \text{ mol } CO_2$$
$$n_3 = 2.00 \text{ mol } H_2O$$
$$n_4 = 1.50 \text{ mol } O_2$$
$$n_5 = 11.28 \text{ mol } N_2$$

The following spreadsheet illustrates the calculation of the adiabatic temperature from Equation 9.6-4. The values shown correspond to an initial guess of $T_{ad} = 200$°C. Formulas entered in cells are shown below the spreadsheet.

	A	B	C	D	E	F	G
1	**Solution to Example 9.6-2**						
2							
3	References: CH3OH(l), O2, N2, CO2, H2O(l) at 25C						
4	DeltaHc	−726.6					
5	Species	n(in)	H(in)	n(in)H(in)	n(out)	H(out)	n(out)H(out)
6	CH3OH	1	0	0	—	—	—
7	O2	3	2.235	6.704	1.5	5.305	7.957
8	N2	11.28	2.187	24.671	11.28	5.132	57.893
9	CO2	—	—	—	1	7.079	7.079
10	H2O(v)	—	—	—	2	50.023	100.046
11	Sum			31.375			172.975
12							
13	Tfuel	25					
14	Tair	100					
15	Tad	200					
16	DeltaH	−585.000					

[B4] =DeltaHcl("methanol") [$= \Delta\hat{H}_c^\circ$]
[C6] =Enthalpy("methanol",25,B13,,"l")
[C7] =Enthalpy("O2",25,B14)
[C8] =Enthalpy("N2",25,B14)
[D6] =B6*C6
[D7] =B7*C7
[D8] =B8*C8
[D11] =Sum(D6:D8) $\left[= \sum n_{in}\hat{H}_{in}\right]$
[B16] =B4 + G11 – D11 [$= \Delta H$]
[F7] =Enthalpy("O2",25,B$15)
[F8] =Enthalpy("N2",25,B$15)
[F9] =Enthalpy("CO2",25,B$15)
[F10] =44.013 + Enthalpy("H2O",25,B$15,,"g")
[G7] =E7*F7
[G8] =E8*F8
[G9] =E9*F9
[G10] =E10*F10
[G11] =Sum(G7:G10) $\left[= \sum n_{out}\hat{H}_{out}\right]$

In Cell F10, 44.013 is the heat of vaporization of water at 25°C and 1 atm (from Equation 9.6-2a). Once the spreadsheet has been set up as shown, Excel's Solver is used to set the value in Cell B16 equal to zero by varying the value in Cell B15. The value in Cell B15 immediately changes to the adiabatic temperature,

$$\boxed{T_{ad} = 1257°C}$$

The furnace walls will therefore never be exposed to a temperature greater than 1257°C as long as the feed and air properties remain the same.

Once the spreadsheet has been set up, the adiabatic temperature can be easily calculated for different fuel and air temperatures by varying the values in Cells B13 and B14 and repeating the calculations using Excel's Solver.

The adiabatic flame temperature is much greater when pure oxygen rather than air is fed to the reactor and is greatest when the fuel and oxygen are fed in stoichiometric proportion.

Test Yourself

(Answers, p. 660)

1. What is the adiabatic flame temperature of a fuel?
2. Suppose T_{ad} is the adiabatic flame temperature calculated for a given feed (fuel + air) to a furnace. Give two reasons why the actual furnace temperature might be less than T_{ad}.
3. Why should the adiabatic flame temperature be much higher for a pure oxygen feed than for an air feed?

9.6c Flammability and Ignition

In this section and the one that follows, we discuss qualitatively what happens during the rapid chemical reaction between a fuel and oxygen. Along the way, we provide answers to the following questions:

1. What is a flame? Why are some flames blue and some yellow?
2. If you light a match in a mixture of methane and air that contains 10% CH_4 by volume, the mixture will burn explosively, but if the mixture contains 20% CH_4 nothing will happen. Why?
3. What is an explosion? What is the loud noise you hear when something explodes?
4. Hydrogen and oxygen react explosively to form water, yet if you mix these two gases in a flask, nothing happens. Why not?

We have so far in this text only considered the initial and final conditions in a chemical reactor, and not how long it may have taken to get from one to the other. When you study **chemical reaction kinetics**, you will learn that the rate of a reaction depends strongly on the reaction temperature; for many reactions, a temperature rise of only 10°C is enough to double the rate.

Suppose a mixture of methane and air containing 10 mole% CH_4 is heated by a central heat source (e.g., an electrical coil) at atmospheric pressure, beginning at room temperature. Although methane reacts with oxygen

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

the reaction proceeds at an immeasurably low rate at room temperature, and to an observer nothing would seem to be happening in the reactor.

As the temperature increases, the rate of the oxidation reaction also increases, and measurable amounts of CO_2 and H_2O appear. However, if the heat source is turned off, the reactor temperature drops again—the rate at which heat is generated by the reaction alone is not enough to compensate for the rate at which heat is lost from the reaction zone.

However, if the temperature at any point in the reactor reaches about 640°C or higher, the rate of heat generation by the reaction exceeds the rate of heat loss from the reaction zone. The gas adjacent to this zone is then heated above 640°C, causing the zone of rapid reaction to spread. The temperature of the gas rapidly rises by several hundred or even a thousand degrees in a fraction of a second; even if the heating source is turned off, the rate of heat generation by the now rapidly occurring reaction is enough to maintain the system at its high temperature until the reactants are exhausted.

Combustion is defined as a rapid, high-temperature oxidation reaction. What happens in the reactor just described after the reaction rate accelerates dramatically is combustion, whereas the initial slow oxidation reaction between methane and oxygen to form CO_2 and H_2O and other reactions between these species, such as the formation reaction of formaldehyde

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$

are not classified as combustion reactions.

The rapid increase in the rate of an oxidation reaction when the reaction mixture exceeds a certain temperature is called **ignition**; the temperature at which this phenomenon occurs is called the **ignition temperature**, and the time between the instant when the mixture reaches the ignition temperature and the moment of ignition is the **ignition lag**. The ignition temperature and lag are shown here on a representative plot of the temperature of a fuel mixture that is being heated.

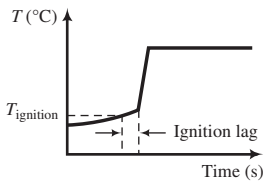


TABLE 9.6-2 Flammability Limits, Flash Points, and Autoignition Temperatures for Selected Species. Excerpted from Crowl and Louvar.[11]

	Flammability Limits		Temperatures (°C)	
Species	Lower	Upper	Flash Point	Autoignition
Paraffins				
Methane	5.3	15.0	−222.5	632
Ethane	3.0	12.5	−130.0	472
Propane	2.2	9.5	−104.4	493
Butane	1.9	8.5	−60.0	408
Olefins				
Ethylene	3.1	32.0	—	490
Propylene	2.4	10.3	−107.8	458
Aromatics				
Benzene	1.4	7.1	−11.1	740
Toluene	1.4	6.7	4.4	810
Alcohols				
Methanol	7.3	36.0	12.2	574
Ethanol	4.3	19.0	12.8	558
Ketones				
Acetone	3.0	13.0	−17.8	700
Methyl Ethyl Ketone	1.8	10.0	−4.4	514

The value of the ignition temperature depends on a number of things for a given fuel, including the fuel-to-air ratio, the total pressure in the reactor, and even the reactor geometry. For any given fuel, there is a lower limit to this quantity called the **autoignition temperature**. Representative values of this quantity for stoichiometric fuel–air mixtures at 1 atm are given in Table 9.6-2. Ignition lags are typically 0.1–10 s in duration and decrease with increasing temperature above the autoignition temperature.

We saw in Section 9.6b that the highest attainable temperature in a combustion reaction—the adiabatic flame temperature—depends on the fuel-to-air ratio, and we stated but did not prove that this upper temperature limit is a maximum when the fuel and oxygen are present in stoichiometric proportion. If the mixture is either **rich** (fuel in excess) or **lean** (O_2 in excess), the adiabatic flame temperature decreases.

SAFETY →

The terms *lower (or lean) flammability limit* and *upper (rich) flammability limit* were introduced in previous end-of-chapter problems. A fuel–air mixture whose composition falls outside these limits is incapable of igniting or exploding, even if exposed to a spark or flame. The range of compositions between the two flammability limits is known as the *explosive range* of the mixture, and the terms *lower and upper explosion limits* are used interchangeably with the corresponding flammability limits.

If a liquid (or a volatile solid) is exposed to air, the vapor given off could form a combustible mixture with the air adjacent to it, and a spark or match lit in the vicinity of the liquid could cause

[11] D. A. Crowl and J. F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2nd Edition, Prentice Hall, Upper Saddle River, 2002.

the mixture to ignite or explode. The **flash point** of a liquid is the temperature at which the liquid gives off enough vapor to form an ignitable mixture with the air above the liquid surface. The flash point of gasoline, for example, is roughly −43°C, and that of ethanol is 12.8°C, so that these liquids constitute fire hazards at room temperature, while the flash points of fuel oils vary from 38°C to 55°C, making the hazards associated with these materials considerably less. Table 9.6-2 includes flash points for a limited number of species.

Table 9.6-2 shows flammability limits for a limited number of species drawn from a list given by Crowl and Louvar. For example, Table 9.6-2 gives the lower and upper flammability limits of a mixture of methane in air as 5.3% and 15.0%. Thus, a CH_4–air mixture containing between 5.3% and 15.0% CH_4 must be considered a fire or explosion hazard, while a mixture containing 3% CH_4 or 18% CH_4 may be considered safe as long as the latter mixture is not diluted with additional air. Crowl and Louvar and *Perry's Chemical Engineers Handbook* (Footnote 2, pp. 2-515 to 2-517) give methods for estimating flammability limits when tabulated values cannot be found, and they also give methods for accounting for the effects of temperature and pressure on flammability limits.

Example 9.6-3 Ignition Temperature and Flammability Limits

Propane gas and air are to be mixed and fed to a combustion reactor. The combustion is to be initiated with a gas torch. Determine the minimum and maximum percentages of propane in the feed to the reactor and the minimum required temperature of the torch flame.

Solution From Table 9.6-2,

$$\text{Minimum mole\% } C_3H_8 \text{ for combustion} = 2.2\%$$
$$\text{Maximum mole\% } C_3H_8 \text{ for combustion} = 9.5\%$$

The torch flame temperature must be at least as high as the autoignition temperature of a propane–air mixture, which from Table 9.6-2 is $\boxed{493°C}$.

Test Yourself

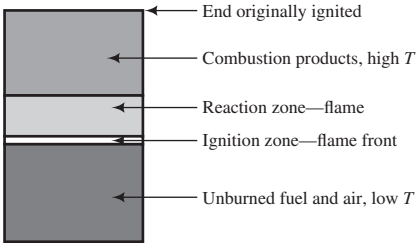
(Answers, p. 660)

1. Briefly define the following terms: (a) ignition, (b) autoignition temperature, (c) ignition lag, (d) flammability limits of a fuel–air mixture, and (e) flash point of a liquid.
2. Use Table 9.6-2 to answer the following questions:
   - **(a)** What would happen if a spark were struck in a methane–air mixture containing 10% CH_4? What about a mixture containing 20% CH_4?
   - **(b)** If a methane–air mixture containing 20% CH_4 were heated to 700°C, would the combustion reaction take place? What would happen if the heat source were turned off?
   - **(c)** Pure methane is clearly not within the explosive range of methane–air mixtures, yet if pure methane is blown out of a cylinder into a room and a match is lit nearby, a flame is observed that persists after the match is withdrawn. How is this possible?

9.6d Flames and Detonations

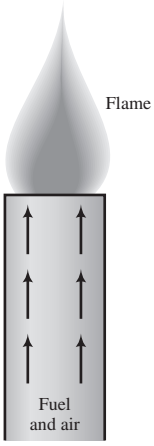
Suppose a combustible gas–air mixture is contained in an open-ended tube, and a match or another ignition source is applied to one end of the tube. The gas mixture at this end is heated and eventually ignites. The intense heat generated by the combustion reaction raises the chemical species formed during the reaction to high energy states. When these species return to lower energy states, some of the energy they lose is given off in the form of light. The result is a visible **flame** accompanying the combustion.

Initially the flame is located at the end of the tube that was ignited. However, the heat of combustion quickly raises the adjacent unburned gas to its ignition point, causing the flame to "travel" toward the other end of the tube. At some point, the tube appears as follows.



The flame front moves in the direction of the unburned gases at a velocity called the **flame velocity**, which typically has a value of 0.3 to 1 m/s. The exact value of the flame velocity depends on a number of things, including the type of fuel, fuel-to-air ratio, initial temperature and pressure of the unburned gases, and the geometry of the combustion chamber.

Suppose now that instead of being stationary in the tube, the combustion mixture is fed continuously into the bottom (as in a Bunsen burner), and the top is ignited. If the velocity with which the gases leave the tube equals the velocity with which the flame would travel down in a stationary gas, a **stationary flame** is achieved at the top. The wall of the tube lowers the flame velocity, so that the flame burns at the end but does not penetrate into the tube.



If the gas flow rate is increased, the flame size and rate of heat generation both increase, since a larger quantity of gas is being burned. However, once the flow rate reaches a critical value, the flame can no longer travel back as fast as the combustion region is transported away from the burner. The gases in the combustion region become increasingly diluted with air, until the region finally falls outside the flammability limits and the fire is literally blown out.

On the other hand, if the gas flow rate to the burner tube is decreased, the gas velocity in the tube may become lower than the flame propagation velocity in the tube. The result is **flashback**—the flame travels back through the tube toward the fuel source. Flashback is extremely dangerous, and any flow system involving combustible gases must be designed to guarantee that the flow rate stays above the flame propagation velocity.

When combustion of a well-mixed fuel–air mixture occurs, the fuel rapidly reacts with oxygen to form a number of unstable intermediate species (such as oxygen and hydrogen atoms, and OH and H_2O radicals), which then proceed through a complicated chain mechanism to form CO_2 and H_2O. Some of these species undergo transitions that cause them to emit radiation whose wavelength falls within the blue region of the visible spectrum. The result is that the flame appears blue.

On the other hand, when the fuel and air are not well mixed (such as when a pure hydrocarbon gas is burned as it emerges from a stack and mixes with atmospheric air), the combustion proceeds relatively slowly, and some of the hydrocarbon fuel decomposes to form elementary carbon and hydrogen before oxidation takes place. The heat of reaction is sufficient to raise the temperature to a point where the carbon particles glow incandescently. A yellow flame is the result.

Finally, suppose ignition of a gas takes place in a confined or partially confined space. The large temperature rise in the combustion region causes a rapid buildup of pressure in this region. If the combustion is fast enough and the heat of reaction is high enough, a **detonation** may result, wherein a sharply defined high-pressure front, or **shock wave**, travels through the gas at a velocity well in excess of the flame propagation velocity in the gas. The shock wave rapidly compresses and ignites the gas as it passes through, giving the appearance of an instantaneous combustion.

Even after the combustion reaction that gave rise to the detonation has consumed all the available fuel, the shock wave can persist for large distances, carrying with it considerable energy. The energy of even a small shock wave is sufficient to vibrate the eardrums of anyone near the site of the detonation, producing the bang that always accompanies an explosion. The energy of a large shock wave may be sufficient to demolish a city.

Test Yourself

(Answers, p. 660)

You are the guest lecturer at a junior high school science fair. The following questions are put to you. How would you answer them in terms an intelligent 14-year-old might understand?

1. What is a flame?
2. What is a yellow flame? A blue flame?
3. What is detonation? What is the loud noise you hear when something explodes? What is it that knocks buildings over when dynamite is set off? How does a gun work?
4. (This one is from one of the science teachers who thought they should have asked *him* to give the lecture.) You say that hydrogen and oxygen react explosively to form water. Why is it that I can mix hydrogen and oxygen in a flask and nothing will happen? (*Hint:* Reread the beginning of Section 9.6c.)

9.7 SUMMARY

Large internal energy and enthalpy changes are often associated with chemical reactions, leading to substantial heat transfer (heating or cooling) requirements for chemical reactors. This chapter outlines methods of calculating $\Delta \dot{H}$ for open reactive systems and ΔU and ΔH for closed systems. Once the appropriate quantity has been determined, it may be substituted into the energy balance to determine the required heat transfer.

- The **heat of reaction** (or **enthalpy of reaction**), $\Delta H_r\,(T, P)$, is the enthalpy change when stoichiometric quantities of reactants at temperature T and pressure P are consumed completely to form products at the same temperature and pressure. The **standard heat of reaction**, ΔH_r°, is the heat of reaction at a specified reference temperature and pressure, in this text 25°C and 1 atm. At low to moderate pressures, the heat of reaction is nearly independent of P.

  For example, the standard heat of reaction for the complete combustion of methane is

  $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l): \quad \Delta H_r^\circ = -890.3 \text{ kJ}$$

  which signifies that if 1 g-mole of gaseous methane and 2 g-moles of gaseous oxygen at 25°C and 1 atm react completely to form 1 g-mole of gaseous carbon dioxide and 2 g-moles of liquid water and the products are brought back to 25°C and 1 atm, the net enthalpy change would be $\Delta H = -890.3$ kJ. If the energy balance reduces to $Q = \Delta H$, 890.3 kJ of heat would have to be transferred away from the reactor to keep the products at 25°C.
- If $\Delta H_r\,(T, P) < 0$, the reaction is **exothermic** at T and P: less energy is required to break the bonds holding the reactant molecules together than is released when the product bonds form, resulting in a net release of energy as the reaction proceeds. This energy may be transferred from the reactor as heat or it may serve to raise the temperature of the reaction mixture.
- Similarly, if $\Delta H_r\,(T, P) > 0$, the reaction is **endothermic**: more energy is required to break the reactant bonds than is released when the product bonds form, leading to a net absorption of energy as the reaction proceeds. Unless this energy is supplied to the reactor as heat, the mixture temperature decreases.
- Provided that gaseous reactants and products behave ideally and the specific volumes of liquid and solid reactants and

products are negligible compared with the specific volumes of the gases, the **internal energy of reaction** may be calculated from Equation 9.1-5. (This quantity is required for energy balances on constant-volume batch reactors.)

- According to **Hess's law**, if a stoichiometric equation for a reaction can be obtained as a linear combination of the equations for other reactions (i.e., by adding and subtracting those equations), the heat of the first reaction can be calculated as the same linear combination of the heats of the other reactions.
- The **standard heat of formation** of a species, $\Delta\hat{H}^\circ_f$, is the heat of the reaction in which one mole of the species is formed from its constituent elemental species in their naturally occurring states at 25°C and 1 atm. Standard heats of formation of many species are listed in Table B.1.
- A consequence of Hess's law is that the standard heat of any reaction may be calculated as

$$\Delta H^\circ_r = \sum \nu_i \, \Delta\hat{H}^\circ_{fi}$$

where ν_i is the stoichiometric coefficient of reactant or product species i (positive for products, negative for reactants), and $\Delta\hat{H}^\circ_{fi}$ is the standard heat of formation of that species.

- The **standard heat of combustion** of a species, $\Delta\hat{H}^\circ_c$, is the heat of the reaction in which one mole of the species undergoes complete combustion to form products in specified states. Standard heats of combustion of many species are listed in Table B.1, with the presumed combustion products being CO_2, $H_2O(l)$, SO_2 for species containing sulfur, and N_2 for species containing nitrogen. A consequence of Hess's law is that the standard heat of any reaction involving only oxygen and combustible species may be calculated as

$$\Delta H^\circ_r = -\sum \nu_i \, \Delta\hat{H}^\circ_{ci}$$

As before, ν_i(moles of Species i) is the stoichiometric coefficient of species i.

- When performing energy balances on a reactive chemical process, two procedures may be followed in the calculation of $\Delta\dot{H}$ (or ΔH or ΔU) that differ in the choice of reference states for enthalpy or internal energy calculations. In the **heat of reaction method**, the references are the reactant and product species at 25°C and 1 atm in the phases (solid, liquid, or gas) for which the heat of reaction is known. In the **heat of formation method**, the references are the elemental species that constitute the reactant and product species [e.g., C(s), O_2(g), H_2(g), etc.] at 25°C and 1 atm. In both methods, reference states for nonreactive species may be chosen for convenience, as was done for the nonreactive processes of Chapters 7 and 8.
- The heat of reaction method may be slightly easier when only one reaction occurs and the heat of reaction is known. When this method is used, the specific enthalpy of each species in every feed or product stream is calculated by choosing a process path from the reference state to the process state, calculating $\Delta\hat{H}$ for each heating and cooling step and each phase change in the path, and summing the enthalpies for the steps. When specific enthalpies have been calculated for all species in all of their inlet and outlet states, $\Delta\dot{H}$ for a continuous process is calculated as

$$\Delta\dot{H} = \xi\Delta\dot{H}^\circ_r + \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

In this equation, ξ is the extent of reaction (determined from Equation 9.1-3); $\dot{n}_i$ and $\hat{H}_i$ are respectively the molar flow rate and specific enthalpy of a process species in an inlet or outlet stream; and the summations are taken over all species in all of their inlet and outlet states. Once calculated, $\Delta\dot{H}$ is substituted in the open-system energy balance, which is solved for $\dot{Q}$ or whichever other variable is unknown.[12]

- The heat of formation method is generally easier when there are multiple reactions. When this method is used, the specific enthalpy of a species in a feed or product stream is calculated by choosing a process path from the reference state (the elements at 25°C) to the process state, beginning with the formation of the species from the elements ($\Delta\hat{H} = \Delta\hat{H}^\circ_f$); evaluating $\Delta\hat{H}$ for each subsequent heating and cooling step and each phase change in the path; and summing the enthalpies for the steps (including the formation step). When specific enthalpies have been calculated for all species in all of their inlet and outlet states, $\Delta\dot{H}$ is calculated for an open system as

$$\Delta\dot{H} = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

As before, the summations are taken over all species in all of their inlet and outlet states. Once calculated, $\Delta\dot{H}$ is substituted in the open-system energy balance, which is solved for $\dot{Q}$ or whichever other variable is unknown (see Footnote 12).

- Sometimes the feed conditions and heat input to a reactor are specified (as in an adiabatic reactor) and the outlet temperature, T_{out}, is to be determined. The procedure is to derive expressions for the specific enthalpies of the reactor outlet species in terms of T_{out}; substitute these expressions into the summation $\sum(\dot{n}_i\hat{H}_i)_{out}$ in the expression for $\Delta\dot{H}$; substitute in turn for $\Delta\dot{H}(T_{out})$ in the energy balance, and solve the resulting equation for T_{out}.
- The **standard heat of formation of a liquid solution** is the sum of the standard heat of formation of the solute and the standard heat of solution calculated using the methods of Section 8.5. The standard heat of a reaction involving solutions may be determined as the weighted sum of the heats of formation of the reactants and products (including the solutions), with the weighting factors being the stoichiometric coefficients (positive for products, negative for reactants).

[12] If the system in question is a closed system at constant pressure or if it is continuous and an amount (and not a flow rate) is the basis of calculation, the dots over variables would be deleted in the above formulas. If the system is a closed system at constant volume, U would replace H.

An energy balance for a reactor in which solutions react or form may be written by taking the feed and product solutions at 25°C and 1 atm as references and using the heat of reaction method.

- **Combustion** is a rapid high-temperature reaction between a fuel and oxygen. The **higher heating value** of a fuel is the negative of the standard heat of combustion of the fuel ($-\Delta\hat{H}_c^\circ$) with H_2O(l) as a combustion product, and the **lower heating value** is the negative of the standard heat of combustion based on H_2O(v) as a product. The relationship between the two heating values is given by Equation 9.6-1.
- The **adiabatic flame temperature** of a fuel is the temperature that would be attained if the fuel were burned in an adiabatic combustion chamber and all of the energy released went into raising the temperature of the reaction products (as opposed to being absorbed by or transferred through the reactor wall).
- When the temperature of a combustible mixture exceeds a certain value, after a short time lag the rate of the reaction and the reaction temperature increase extremely rapidly. This phenomenon is called **ignition**, and the time interval after T_{ignition} is reached and before the temperature increases sharply is the **ignition lag**. The lowest temperature at which ignition may occur for a fuel is the **autoignition temperature** of the fuel.
- If the mole percentage of a fuel in a fuel-air mixture falls below a certain value (the **lower flammability limit**) or above another value (the **upper flammability limit**), the mixture will not ignite or explode, even if exposed to a flame or spark. The composition range between the flammability limits is called the **explosive range** of the mixture.

PROBLEMS

9.1. The standard heat of the reaction

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

is $\Delta H_r^\circ = -904.7$ kJ.

(a) Briefly explain what that means. Your explanation may take the form "When _____ (specify quantities of reactant species and their physical states) react to form _____ (quantities of product species and their physical state), the change in enthalpy is _____."

(b) Is the reaction exothermic or endothermic at 25°C? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically? What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(c) What is ΔH_r° for

$$2NH_3(g) + \tfrac{5}{2}O_2 \rightarrow 2NO(g) + 3H_2O(g)$$

(d) What is ΔH_r° for

$$NO(g) + \tfrac{3}{2}H_2O(g) \rightarrow NH_3(g) + \tfrac{5}{4}O_2$$

(e) Estimate the enthalpy change associated with the consumption of 340 g NH_3/s if the reactants and products are all at 25°C. (See Example 9.1-1.) What have you assumed about the reactor pressure? (You don't have to assume that it equals 1 atm.)

(f) The values of ΔH_r° given in this problem apply to water vapor at 25°C and 1 atm, and yet the normal boiling point of water is 100°C. Can water exist as a vapor at 25°C and a total pressure of 1 atm? Explain your answer.

9.2. The standard heat of combustion of liquid *n*-octane to form CO_2 and liquid water at 25°C and 1 atm is $\Delta\hat{H}_c^\circ = -5471$ kJ/mol.

(a) Briefly explain what that means. Your explanation may take the form "When _____ (specify quantities of reactant species and their physical states) react to form _____ (quantities of product species and their physical states), the change in enthalpy is _____."

(b) Is the reaction exothermic or endothermic at 25°C? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically?

What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(c) If 25.0 mol/s of liquid octane is consumed and the reactants and products are all at 25°C, estimate the required rate of heat input or output (state which) in kilowatts, assuming that $\dot{Q} = \Delta\dot{H}$ for the process. What have you also assumed about the reactor pressure in your calculation? (You don't have to assume that it equals 1 atm.)

(d) The standard heat of combustion of *n*-octane *vapor* is $\Delta\hat{H}_c^\circ = -5528$ kJ/mol. What is the physical significance of the 57 kJ/mol difference between this heat of combustion and the one given previously?

(e) The value of $\Delta\hat{H}_c^\circ$ given in Part (d) applies to *n*-octane vapor at 25°C and 1 atm, and yet the normal boiling point of *n*-octane is 125.5°C. Can *n*-octane exist as a vapor at 25°C and a total pressure of 1 atm? Explain your answer.

9.3. The standard heat of the combustion reaction of liquid *n*-hexane to form $CO_2(g)$ and $H_2O(l)$, with all reactants and products at 77°F and 1 atm, is $\Delta H_r^\circ = -1.791 \times 10^6$ Btu. The heat of vaporization of hexane at 77°F is 13,550 Btu/lb-mole and that of water is 18,934 Btu/lb-mole.

(a) Is the reaction exothermic or endothermic at 77°F? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically? What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(b) Use the given data to calculate ΔH_r° (Btu) for the combustion of *n*-hexane vapor to form $CO_2(g)$ and $H_2O(g)$.

(c) If $\dot{Q} = \Delta\dot{H}$, at what rate in Btu/s is heat absorbed or released (state which) if 120 lb_m/s of O_2 is consumed in the combustion of hexane vapor, water vapor is the product, and the reactants and products are all at 77°F?

(d) If the reaction were carried out in a real reactor, the actual value of $\dot{Q}$ would be greater (less negative) than the value calculated in Part (c). Explain why.

9.4. The standard heat of the reaction

$$CaC_2(s) + 5H_2O(l) \rightarrow CaO(s) + 2CO_2(g) + 5H_2(g)$$

is $\Delta H_r^\circ = +69.36$ kJ.

(a) Is the reaction exothermic or endothermic at 25°C? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically? What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(b) Calculate ΔU_r° for this reaction. (See Example 9.1-2.) Briefly explain the physical significance of your calculated value.

(c) Suppose you charge 150.0 g of CaC_2 and liquid water into a rigid container at 25°C, heat the container until the calcium carbide reacts completely, and cool the products back down to 25°C, condensing essentially all the unconsumed water. Write and simplify the energy balance equation for this closed constant-volume system and use it to determine the net amount of heat (kJ) that must be transferred to or from the reactor (state which).

(d) If in Part (c) the term "rigid container" were replaced with "container at a constant pressure of 1 atm," the calculated value of Q would be slightly in error. Explain why.

(e) If you placed 1 mol of solid calcium carbide and 5 mol of liquid water in a container at 25°C and left them there for several days, upon returning you would not find 1 mol of solid calcium oxide, 2 mol of carbon dioxide, and 5 mol of hydrogen gas. Explain why not.

9.5. Use Hess's law to calculate the standard heat of the water-gas shift reaction

$$CO(g) + H_2O(v) \rightarrow CO_2(g) + H_2(g)$$

from each of the two sets of data given here.

(a) $CO(g) + H_2O(l) \rightarrow CO_2(g) + H_2(g)$: $\Delta H_r^\circ = +1226$ Btu

$H_2O(l) \rightarrow H_2O(v)$: $\Delta\hat{H}_v = +18{,}935$ Btu/lb-mole

(b) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$: $\Delta H_r^\circ = -121{,}740$ Btu

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(v)$: $\Delta H_r^\circ = -104{,}040$ Btu

9.6. Formaldehyde may be produced in the reaction between methanol and oxygen:

$$2CH_3OH(l) + O_2(g) \rightarrow 2HCHO(g) + 2H_2O(l): \quad \Delta H_r^\circ = -326.2 \text{ kJ}$$

The standard heat of combustion of hydrogen is

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l): \quad \Delta \hat{H}_c^\circ = -285.8 \text{ kJ/mol}$$

(a) Use these heats of reaction and Hess's law to determine the standard heat of the direct decomposition of methanol to form formaldehyde:

$$CH_3OH(l) \rightarrow HCHO(g) + H_2(g)$$

(b) Explain why you would probably use the method of Part (a) to determine the heat of the methanol decomposition reaction experimentally rather than carrying out the decomposition reaction and measuring ΔH_r° directly.

9.7. Use tabulated heats of formation (Table B.1) to determine the standard heats of the following reactions in kJ/mol, letting the stoichiometric coefficient of the first reactant in each reaction equal one.

(a) Nitrogen + oxygen react to form nitrogen dioxide (NO_2).

(b) Gaseous *n*-butane + oxygen react to form carbon monoxide + liquid water.

(c) Liquid *n*-heptane + oxygen react to form carbon dioxide + water vapor. After doing the calculation, write the stoichiometric equations for the formation of the reactant and product species, then use Hess's law to derive the formula you used to calculate ΔH_r°.

(d) Liquid sodium sulfate + carbon monoxide react to form liquid sodium sulfide + carbon dioxide. (Note that Table B.1 only lists the heats of formation of the solid sodium salts. To estimate the required heat of reaction, you will also need to use tabulated heats of fusion.)

9.8. Trichloroethylene, a widely used degreasing solvent for machine parts, is produced in a two-step reaction sequence. Ethylene is first chlorinated to yield tetrachloroethane, which is dehydrochlorinated to form trichloroethylene.

$$C_2H_4(g) + 2Cl_2(g) \rightarrow C_2H_2Cl_4(l) + H_2(g): \quad \Delta H_r^\circ = -385.76 \text{ kJ}$$

$$C_2H_2Cl_4(l) \rightarrow C_2HCl_3(l) + HCl(g)$$

The standard heat of formation of liquid trichloroethylene is −276.2 kJ/mol.

(a) Use the given data and tabulated standard heats of formation of ethylene and hydrogen chloride to calculate the standard heat of formation of tetrachloroethane and the standard heat of the second reaction.

(b) Use Hess's law to calculate the standard heat of the reaction

$$C_2H_4(g) + 2Cl_2(g) \rightarrow C_2HCl_3(l) + H_2(g) + HCl(g)$$

(c) If 300 mol/h of $C_2HCl_3(l)$ is produced in the reaction of Part (b) and the reactants and products are all at 25°C and 1 atm, how much heat is evolved or absorbed in the process? (Assume $\dot{Q} = \Delta \dot{H}$.)

(d) If the reaction of Part (c) were carried out and the final temperature in the reactor were 40°C instead of 25°C, how would it affect the problem solution? Explain your answer.

9.9. The standard heat of combustion of gaseous ethane is listed in Table B.1 as −1559.9 kJ/mol.

(a) In your own words, briefly explain what that means. (Your explanation should mention the reference states used to define the tabulated heats of combustion.)

(b) Use tabulated heats of formation to verify the given value of $\Delta\hat{H}^\circ_c$.

(c) Calculate the standard heat of the reaction in which ethane is dehydrogenated to form acetylene and hydrogen

$$C_2H_6(g) \rightarrow C_2H_2(g) + 2H_2(g)$$

using (i) tabulated heats of formation and (ii) tabulated heats of combustion (Equation 9.4-1).

(d) Write the stoichiometric equations for the combustion reactions of acetylene, hydrogen, and ethane, and use Hess's law to derive the formula you used in Part (c-ii).

9.10. The standard heat of combustion ($\Delta\hat{H}^\circ_c$) of liquid 2,3,3-trimethylpentane [C_8H_{18}] is reported in a table of physical properties to be −4850 kJ/mol. A footnote indicates that the reference temperature for the reported value is 25°C and the presumed combustion products are $CO_2(g)$ and $H_2O(g)$.

(a) In your own words, briefly explain what all that means.

(b) There is some question about the accuracy of the reported value, and you have been asked to determine the heat of combustion experimentally. You burn 2.010 grams of the hydrocarbon with pure oxygen in a constant-volume calorimeter and find that the net heat released when the reactants and products [$CO_2(g)$ and $H_2O(g)$] are all at 25°C is sufficient to raise the temperature of 1.00 kg of liquid water by 21.34°C. Write an energy balance to show that the heat released in the calorimeter equals $n_{C_8H_{18}}\,\Delta\hat{U}^\circ_c$, and calculate $\Delta\hat{U}^\circ_c$ (kJ/mol). Then calculate $\Delta\hat{H}^\circ_c$. (See Example 9.1-2.) By what percentage of the measured value does the tabulated value differ from the measured one?

(c) Use the result of Part (b) to estimate $\Delta\hat{H}^\circ_f$ for 2,3,3-trimethylpentane. Why would the heat of formation of 2,3,3-trimethylpentane probably be determined this way rather than directly from the formation reaction?

BIOENGINEERING

9.11. A culture of the fungus *aspergillus niger* is used industrially in the manufacture of citric acid and other organic species. Cells of the fungus have an ultimate analysis of $CH_{1.79}N_{0.2}O_{0.5}$, and the heat of formation of this species is necessary to approximate the heat duty for the bioreactor in which citric acid is to be produced. You collect a dried sample of the fungus and determine its heat of combustion to be −550 kJ/mol. Estimate the heat of formation (kJ/mol) of the dried fungus cells.

9.12. *n*-Butane is converted to isobutane in a continuous isomerization reactor that operates isothermally at 149°C. The feed to the reactor contains 93 mole% *n*-butane, 5% isobutane, and 2% HCl at 149°C, and a 40% conversion of *n*-butane is achieved.

(a) Taking a basis of 1 mol of feed gas, calculate the moles of each component of the feed and product mixtures and the extent of reaction, ξ.

(b) Calculate the standard heat of the isomerization reaction (kJ). Then, taking the feed and product species at 25°C as references, prepare an inlet–outlet enthalpy table and calculate and fill in the component amounts (mol) and specific enthalpies (kJ/mol). (See Example 9.5-1.)

(c) Calculate the amount of heat transfer (kJ) to or from the reactor (state which it is). Then determine the required heat transfer rate (kW) for a reactor feed of 325 mol/h.

(d) Use your calculated results to estimate the heat of the isomerization reaction at 149°C, ΔH_r(149°C) (kJ). List the assumptions built into the estimation. (One has to do with pressure.)

MATERIALS

Equipment Encyclopedia
reactors—CVD

www.wiley.com/college/felder

9.13. In the production of many microelectronic devices, continuous **chemical vapor deposition** (CVD) processes are used to deposit thin and exceptionally uniform silicon dioxide films on silicon wafers. One CVD process involves the reaction between silane and oxygen at a very low pressure.

$$SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2H_2(g)$$

The feed gas, which contains oxygen and silane in a ratio 8.00 mol O_2/mol SiH_4, enters the reactor at 298 K and 3.00 torr absolute. The reaction products emerge at 1375 K and 3.00 torr absolute. Essentially all of the silane in the feed is consumed.

(a) Taking a basis of 1 m^3 of feed gas, calculate the moles of each component of the feed and product mixtures and the extent of reaction, ξ.

(b) Calculate the standard heat of the silane oxidation reaction (kJ). Then, taking the feed and product species at 298 K (25°C) as references, prepare an inlet–outlet enthalpy table and calculate and fill in the component amounts (mol) and specific enthalpies (kJ/mol). (See Example 9.5-1.)

Data

$$(\Delta\hat{H}^\circ_f)_{SiH_4(g)} = -61.9\ \text{kJ/mol}, \quad (\Delta\hat{H}^\circ_f)_{SiO_2(s)} = -851\ \text{kJ/mol}$$

$$(C_p)_{SiH_4(g)}[\text{kJ/(mol·K)}] = 0.01118 + 12.2\times10^{-5}T - 5.548\times10^{-8}T^2 + 6.84\times10^{-12}T^3$$

$$(C_p)_{SiO_2(s)}[\text{kJ/(mol·K)}] = 0.04548 + 3.646\times10^{-5}T - 1.009\times10^{3}/T^2$$

The temperatures in the formulas for C_p are in kelvins.

(c) Calculate the heat (kJ) that must be transferred to or from the reactor (state which it is). Then determine the required heat transfer rate (kW) required for a reactor feed of 27.5 m^3/h.

MATERIALS

9.14. The production of most of the steel manufactured in the United States begins with the reduction of hematite ore (mostly ferric oxide) with coke (carbon) in a blast furnace to obtain pig iron. The basic reaction is

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g): \quad \Delta H_r(77°F) = 2.111\times10^5\ \text{Btu}$$

Suppose that stoichiometric amounts of ferric oxide and carbon are fed at 77°F, the reaction is complete, the iron emerges as a liquid at 2800°F, and CO emerges at 570°F. Perform the following calculations for a basis of 1 ton of iron produced.

(a) Draw and label a flowchart and perform all the material balance calculations needed to determine the amounts (lb-mole) of each feed and product stream component.

(b) Taking the reactant and product species in their normal states at 77°F as references, prepare an inlet–outlet enthalpy table and calculate and fill in all unknown component specific enthalpies (Btu/lb-mole). Use the following physical property data for iron:

$$\text{Fe(s):} \quad C_p[\text{Btu/(lb-mole·°F)}] = 5.90 + 1.50\times10^{-3}\,T(°F)$$

$$T_m = 2794°F, \quad \Delta\hat{H}_m(T_m) = 6496\ \text{Btu/lb-mole}$$

$$\text{Fe(l):} \quad C_p[\text{Btu/(lb-mole·°F)}] = 8.15$$

(c) Estimate the furnace heat requirement (Btu/ton Fe produced).

(d) List the assumptions that make the value calculated in Part (c) only an approximate estimate of the furnace heat requirement. (One of the assumptions has something to do with the reactor pressure.)

9.15. Normal heptane is dehydrocyclicized to toluene and hydrogen in a continuous vapor-phase reaction:

$$C_7H_{16} \rightarrow C_6H_5CH_3 + 4H_2$$

Pure heptane at 400°C is fed to the reactor. The reactor operates isothermally at 400°C and the reaction goes to completion. *Data:* The average heat capacity of *n*-heptane beween 25°C and 400°C is 0.2427 kJ/(mol·°C).

(a) Taking a basis of 1 mol of heptane fed, draw and label a flowchart.

(b) Taking elemental species [C(s), H_2(g)] at 25°C as references, prepare and fill in an inlet–outlet enthalpy table. (See Example 9.5-2.)

(c) Calculate the required heat transfer to or from the reactor (state which it is) in kJ.

(d) What is the heat of the heptane dehydrocyclization reaction (ΔH_r) at 400°C and 1 atm?

(e) The calculation of Part (c) would clearly have been much simpler if you had just looked up the heat of reaction at 400°C instead of calculating it after the fact. Briefly explain why you probably could not have done it that way.

9.16. The thermal decomposition of dimethyl ether

$$(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$$

is to be carried out in an isothermal 2.00-liter laboratory reactor at 600°C. The reactor is charged with pure dimethyl ether at a pressure of 350 torr. After about two hours, the reactor pressure is 875 torr.

(a) Has the reaction proceeded to completion at the end of the two-hour period? If not, what percentage of the dimethyl ether has decomposed?

(b) Taking elemental species [C(s), H_2(g), O_2(g)] at 25°C as references, prepare and fill in an inlet–outlet enthalpy table. (See Example 9.5-2.) Use tabulated data for methane, hydrogen, and carbon monoxide, and the following data for dimethyl ether:

$$\Delta\hat{H}_f^\circ = -180.16 \text{ kJ/mol}$$

$$C_p[\text{J/(mol·K)}] = 26.86 + 0.1659T - 4.179 \times 10^{-5}T^2 \quad (T \text{ in kelvins})$$

(c) Calculate ΔH_r(600°C) and ΔU_r(600°C) for the dimethyl ether decomposition reaction.

(d) How much heat (kJ) was transferred to or from the reactor (state which it is) during the two-hour period of the reaction?

(e) Suppose the reaction were instead carried out in an expandable reactor at 600°C at a constant pressure of 350 torr, with the same final percentage decomposition of dimethyl ether. Calculate the final volume of the reactor and the required amount of heat transfer. (*Note:* These should both be quick calculations.) Explain why the values of Q calculated in Part (d) and in this part are different, even though the initial conditions and extents of reaction are the same.

9.17. Sulfur dioxide is oxidized to sulfur trioxide in a small pilot-plant reactor. SO_2 and 100% excess air are fed to the reactor at 450°C. The reaction proceeds to a 65% SO_2 conversion, and the products emerge from the reactor at 550°C. The production rate of SO_3 is 1.00×10^2 kg/min. The reactor is surrounded by a water jacket into which water at 25°C is fed.

(a) Calculate the feed rates (standard cubic meters per second) of the SO_2 and air feed streams and the extent of reaction, ξ.

(b) Calculate the standard heat of the SO_2 oxidation reaction, ΔH_r° (kJ). Then, taking molecular species at 25°C as references, prepare and fill in an inlet–outlet enthalpy table and write an energy balance to calculate the necessary rate of heat transfer (kW) from the reactor to the cooling water.

(c) Calculate the minimum flow rate of the cooling water if its temperature rise is to be kept below 15°C.

(d) Briefly state what would have been different in your calculations and results if you had taken elemental species as references in Part (b).

9.18. Carbon monoxide at 25°C and steam at 150°C are fed to a continuous water-gas shift reactor. The product gas, which contains 40.0 mole% H_2, 40.0% CO_2, and the balance H_2O(v), emerges at 500°C at a rate of 3.50 SCMH (standard cubic meters per hour) and goes to a condenser. The gas and liquid streams leaving the condenser are in equilibrium at 15°C and 1 atm. The liquid may be taken to be pure water (no dissolved gases).

(a) Calculate the percent excess steam fed to the reactor and the rate of condensation of the water (kg/h).

(b) Calculate the rate (kW) at which heat must be transferred from the condenser.

(c) Taking atomic species at 25°C as references, prepare and fill in an inlet–outlet enthalpy table and calculate the required rate of heat transfer (kW) to or from the reactor.

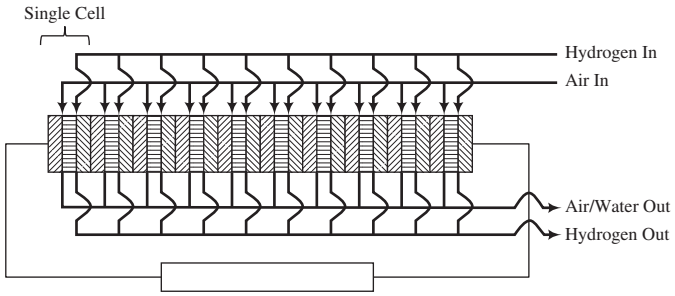
(d) It has been suggested that the carbon monoxide feed stream could pass through a heat exchanger prior to entering the reactor and the reactor product gas could pass through the same heat exchanger before entering the condenser. Sketch and label a flowchart of the heat exchanger and state economic benefits that might result from its use. (*Hint:* Heating and cooling operations are both expensive.)

ALTERNATIVE ENERGY

*__9.19.__ *Fuel cells* have been proposed as an alternative energy technology for use in stationary and transportation applications. A fuel cell is an electrochemical device in which hydrogen reacts with oxygen from the air to produce water and DC electricity. The most flexible fuel cell design is the proton exchange membrane fuel cell (PEMFC). A 1-W PEMFC could be used for portable applications such as cellular telephones, and a 100-kW PEMFC could be used to power an automobile.

A schematic of a 10-cell stack of fuel cells connected in series is shown on the next page. Each cell consists of an anode (left block with lines sloping up and to the right), electrolyte membrane (center block with horizontal lines), and cathode (right block with line sloping down and to the right). The hydrogen and air are fed in parallel to each cell. Also, the exiting gas flows are collected in parallel.

* Adapted from a problem contributed by Jason M. Keith of Mississippi State University.



The following reactions occur inside the PEMFC:

$$\text{Anode:} \quad H_2 \rightarrow 2H^+ + 2e^-$$
$$\text{Cathode:} \quad \tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$
$$\text{Overall:} \quad H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

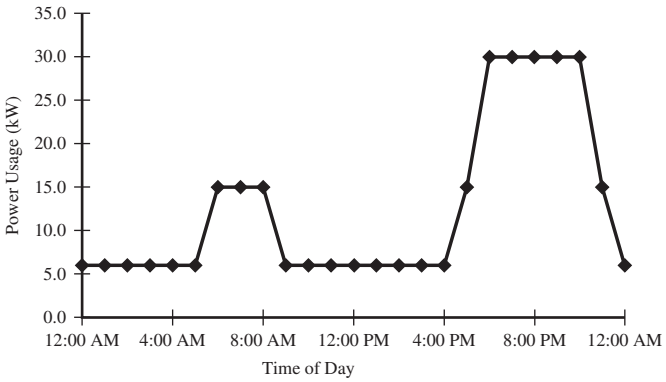
In this problem, we will analyze the flows of chemical species into and out of a PEMFC that could be used to produce electricity for an apartment complex. At full load, the fuel cell operates at a voltage of 26 volts and a current of 500 amps and has a maximum power of 13 kW. (*Note:* A single cell operates at 0.7 V.)

(a) According to the U.S. Energy Information Administration (www.eia.doe.gov), a typical household uses 936 kW·h in a month. Determine the average power usage (kW) per household and use the result to estimate the number of apartment units that could be powered with the 13 kW fuel cell.

(b) The hydrogen requirement for a PEMFC is given by $\left(n_{H_2}\right)_{\text{stoich}} = IN/2F$, where I is the current in A, N is the number of cells, and F is Faraday's constant, 96,485 coulombs of charge per mol of electrons. Note that in this expression, we use the constant 2 mol electrons per mol of fuel, which follows from the reaction at the anode. If the hydrogen is fed in 15% excess of this amount and the air is fed in 200% excess of the amount required to consume all the hydrogen, what are the flow rates of hydrogen and air required in mol/s and SLPM (standard liters per minute)?

(c) Determine the molar flow rate of hydrogen exiting from the anode and the molar composition of the cathode exit gas.

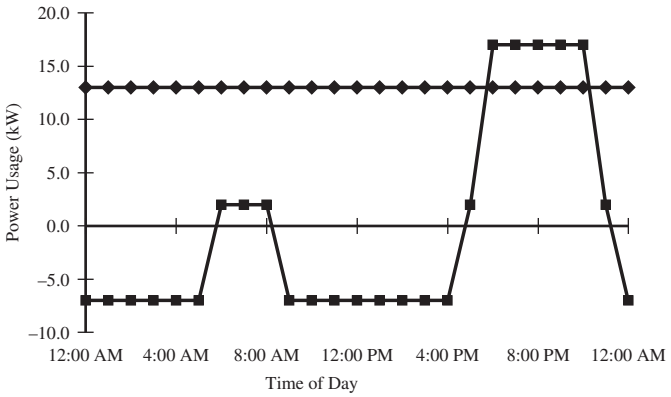
(d) The total electrical power demand in the 10 apartments is given in the plot below. Noting that fuel cells respond quickly to load changes but cannot exceed their rated capacity, calculate how many apartments could be safely powered with a 13 kW fuel cell? What is a disadvantage of this practice in terms of power usage?



(e) It has been suggested that a hybrid system with a fuel cell and a deep cycle battery should be used. The system works as follows:

- If the power demand exceeds the capacity of the fuel cell, the battery will be used to supply short-term power.
- If the power demand is below the fuel-cell capacity, the battery will be charged by the fuel cell.

The plot below shows the power usage from the fuel cell (diamonds) and the battery (squares) for the same power usage as the figure above. Determine the times when the battery is being charged and the minimum total energy capacity of the battery in kW·hr.

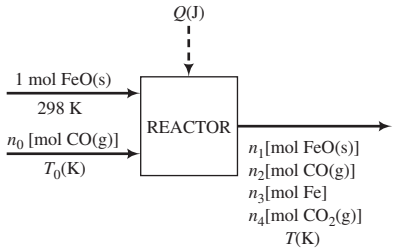


MATERIALS

9.20. Metallic iron is produced in the reaction between ferrous oxide and carbon monoxide:

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g), \quad \Delta H_r^\circ = -16.480\ \text{kJ}$$

The flowchart shown below depicts this process for a basis of 1 mol FeO fed at 298 K.



(a) We wish to explore the effects of the variables n_0 (the molar feed ratio of CO to FeO), T_0 (the feed temperature of the carbon monoxide), X (the fractional conversion of FeO), and T (the product temperature) on Q (the heat duty on the reactor). *Without doing any calculations*, sketch the shapes of the curves you would expect to obtain for the following plots:

- **(i)** Let $n_0 = 1$ mol CO fed/mol FeO fed, $T_0 = 400$ K, and $X = 1$. Vary T from 298 K to 1000 K, calculate Q for each T, and plot Q versus T.
- **(ii)** Let $n_0 = 1$ mol CO fed/mol FeO fed, $T = 700$ K, and $X = 1$. Vary T_0 from 298 K to 1000 K, calculate Q for each T_0, and plot Q versus T_0.
- **(iii)** Let $n_0 = 1$ mol CO fed/mol FeO fed, $T_0 = 400$ K, and $T = 500$ K. Vary X from 0 to 1, calculate Q for each X, and plot Q versus X.
- **(iv)** Let $X = 0.5$, $T_0 = 400$ K, and $T = 400$ K. Vary n_0 from 0.5 to 2 mol CO fed/mol FeO fed, calculate Q for each n_0, and plot Q versus n_0.

(b) Following is an inlet-outlet enthalpy table for the process:

References: FeO(s), CO(g), Fe(s), CO_2(g) at 25°C

Substance	n_{in} (mol)	$\hat{H}_{in}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{out}$ (kJ/mol)
FeO	1.00	0	n_1	$\hat{H}_1$
CO	n_0	$\hat{H}_0$	n_2	$\hat{H}_2$
Fe	—	—	n_3	$\hat{H}_3$
CO_2	—	—	n_4	$\hat{H}_4$

Write an expression for the heat duty on the reactor, Q(kJ), in terms of the ns and $\hat{H}$s in the table, the standard heat of the given reaction, and the extent of reaction, ξ. Then derive expressions for the quantities ξ, n_1, n_2, n_3, and n_4 in terms of the variables n_0 and X. Finally, derive expressions for $\hat{H}_0$ as a function of T_0 and for $\hat{H}_1, \hat{H}_2, \hat{H}_3$, and $\hat{H}_4$ as functions of T. In the latter derivations, use the following formulas for C_p[kJ/(mol·K)] in terms of T(K) adapted from Table 2-151 of *Perry's Chemical Engineers' Handbook* (see Footnote 2):

$$\begin{aligned}
\text{FeO(s):}\quad & C_p = 0.05280 + 6.243 \times 10^{-6} T - 3.188 \times 10^{2} T^{-2} \\
\text{Fe(s):}\quad & C_p = 0.01728 + 2.67 \times 10^{-5} T \\
\text{CO(g):}\quad & C_p = 0.02761 + 5.02 \times 10^{-6} T \\
\text{CO}_2\text{(g):}\quad & C_p = 0.04326 + 1.146 \times 10^{-5} T - 8.180 \times 10^{2} T^{-2}
\end{aligned}$$

(c) Calculate the heat duty, Q(kJ), for $n_0 = 2.0$ mol CO, $T_0 = 350$ K, $T = 550$ K, and $X = 0.700$ mol FeO reacted/mol FeO fed.

(d) Prepare a spreadsheet that has the following format (a partial solution is given for one set of process variables):

Problem 9.20														
	FeO + CO → Fe + CO2								DHr=	–16.480	kJ/mol			
n0	T0	X	T	Xi	n1	n2	n3	n4	H0	H1	H2	H3	H4	Q
(mol)	(K)		(K)	(mol)	(mol)	(mol)	(mol)	(mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ)
2	350	0.7	550	0.7	0.3	1.3	0.7	0.7	1.520	13.482	. . .	. . .	. . .	11.863

where DHr ($= \Delta H_r^\circ$) denotes the standard heat of the FeO reduction reaction and Xi (ξ) is the extent of reaction. Use the spreadsheet to generate the four plots described in Part (a). If the shapes of the plots do not match your predictions, explain why.

BIOENGINEERING

9.21. Ethyl alcohol (ethanol) can be produced by the fermentation of sugars derived from agricultural products such as sugarcane and corn. Some countries without large petroleum and natural gas reserves—such as Brazil—have found it profitable to convert a portion of their agricultural output to ethanol for fuel or for use as a feedstock in the synthesis of other chemicals.

In one such process, a portion of the starch in corn is converted to ethanol in two consecutive reactions. In a *saccharification* reaction, starch decomposes in the presence of certain enzymes (biological catalysts) to form an aqueous *mash* containing maltose ($C_{12}H_{22}O_{11}$, a sugar) and several other decomposition products. The mash is cooled and combined with additional water and a yeast culture in a batch fermentation tank (fermentor). In the fermentation reaction (actually a complex series of reactions), the yeast culture grows and in the process converts maltose to ethanol and carbon dioxide:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_2H_5OH + 4CO_2$$

The fermentor is a 550,000 gallon tank filled to 90% of its capacity with a suspension of mash and yeast in water. The mass of the yeast is negligible compared to the total mass of the tank contents. Thermal energy is released by the exothermic conversion of maltose to ethanol. In an adiabatic operating stage, the temperature of the tank contents increases from an initial value of 85°F to 95°F, and in a second stage the temperature is kept at 95°F by a reactor cooling system. The final reaction mixture contains carbon dioxide dissolved in a slurry containing 7.1 wt% ethanol, 6.9 wt% soluble and suspended solids, and the balance water. The mixture is pumped to a flash evaporator in which CO_2 is vaporized, and the ethanol product is then separated from the remaining mixture components in a series of distillation and stripping operations.

Data

- One bushel (56 lb_m) of corn yields 25 gallons of mash fed to the fermentor, which in turn yields 2.6 gallons of ethanol. Roughly 101 bushels of corn is harvested from an acre of land.

- A batch fermentation cycle (charging the fermentation tank, running the reaction, discharging the tank, and preparing the tank to receive the next load) takes eight hours. The process operates 24 hours per day, 330 days per year.
- The specific gravity of the fermentation reaction mixture is approximately constant at 1.05. The average heat capacity of the mixture is 0.95 Btu/(lb_m·°F).
- The standard heat of combustion of maltose to form CO_2(g) and H_2O(l) is $\Delta\hat{H}_c^\circ = -5649$ kJ/mol.

(a) Calculate (i) the quantity of ethanol (lb_m) produced per batch, (ii) the quantity of water (gal) that must be added to the mash and yeast in the fermentation tank, and (iii) the acres of land that must be harvested per year to keep the process running.

(b) Calculate the standard heat of the maltose conversion reaction, ΔH_r° (Btu).

(c) Estimate the total amount of heat (Btu) that must be transferred from the fermentor during the reaction period. Take only the maltose conversion into account in this calculation (i.e., neglect the yeast growth reaction and any other reactions that may occur in the fermentor), assume that the heat of reaction is independent of temperature in the range from 77°F (= 25°C) to 95°F, and neglect the heat of solution of carbon dioxide in water.

(d) Although Brazil and Venezuela are neighboring countries, producing ethanol from grain for use as a fuel is an important process in Brazil and an almost nonexistent one in Venezuela. What difference between the two countries probably accounts for this observation?

9.22. As described in Problem 9.21, the manufacture of ethanol from corn starch involves fermentation using a yeast that converts sugars from the starch to ethanol and carbon dioxide in a complicated series of reactions. Taking the sugars to be represented by maltose (molecular weight = 342.3 g/mol), the sum of the fermentation reactions can be written as

$$C_{12}H_{22}O_{11}(aq) + H_2O \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \qquad \textbf{(1)}$$

(a) The heat of combustion of solid maltose has been measured as −5649 kJ/mol. Estimate the standard heat of the fermentation reaction in Equation 1. State any assumptions.

(b) When the system is operated at 85°F, 0.8 kg of yeast is produced for every kg of ethanol formed. The yeast used in the process has a chemical formula $CH_{1.8}O_{0.5}N_{0.2}$ and a standard heat of combustion of −23.4 kJ/g. A modification of the fermentation reaction that accounts for the production of yeast and also shows the consumption of added ammonia is

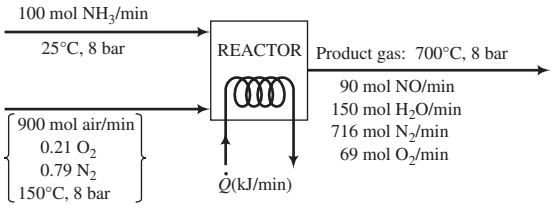
$$C_{12}H_{22}O_{11}(aq) + cNH_3(aq) \rightarrow dC_2H_5OH(aq) + eCO_2(g) + fCH_{1.8}O_{0.5}N_{0.2}(s) + gH_2O \qquad \textbf{(2)}$$

where c, d, e, f, and g are stoichiometric coefficients. Determine the values of the coefficients, estimate the heat of formation of the yeast, and include this result in obtaining a new value for the standard heat of the fermentation reaction of the yeast by Equation 2. State any assumptions.

9.23. Ammonia is oxidized with air to form nitric oxide in the first step of the production of nitric acid. Two principal gas-phase reactions occur:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O$$

All species in the following flowchart are gases.



(a) Taking elemental species [N_2(g), H_2(g), O_2(g)] at 25°C as references, prepare and fill in an inlet–outlet enthalpy table.
(b) Calculate the required rate of heat transfer to or from the reactor in kW.
(c) What would have been different in your calculations and results in Parts (a) and (b) if you had taken molecular species as references in Part (a)?

9.24. Synthetically produced ethanol is an important industrial commodity used for various purposes, including as a solvent (especially for substances intended for human contact or consumption); in coatings, inks, and personal-care products; for sterilization; and as a fuel. Industrial ethanol is a petrochemical synthesized by the hydrolysis of ethylene:

$$C_2H_4(g) + H_2O(v) \rightleftharpoons C_2H_5OH(v)$$

Some of the product is converted to diethyl ether in the undesired side reaction

$$2C_2H_5OH(v) \rightleftharpoons (C_2H_5)_2O(v) + H_2O(v)$$

The combined feed to the reactor contains 53.7 mole% C_2H_4, 36.7% H_2O and the balance nitrogen, and enters the reactor at 310°C. The reactor operates isothermally at 310°C. An ethylene conversion of 5% is achieved, and the yield of ethanol (moles ethanol produced/mole ethylene consumed) is 0.900.

Data for Diethyl Ether

$$\Delta\hat{H}_f^\circ = -271.2 \text{ kJ/mol } \textit{for the liquid}$$
$$\Delta\hat{H}_v = 26.05 \text{ kJ/mol} \quad \text{(assume independent of } T\text{)}$$
$$C_p[\text{kJ/(mol}\cdot\text{°C)}] = 0.08945 + 40.33 \times 10^{-5}T(\text{°C}) - 2.244 \times 10^{-7}T^2$$

(a) Calculate the reactor heating or cooling requirement in kJ/mol feed.
(b) Why would the reactor be designed to yield such a low conversion of ethylene? What processing step (or steps) would probably follow the reactor in a commercial implementation of this process?

9.25. Formaldehyde is produced commercially by the catalytic oxidation of methanol. In a side reaction, methanol is oxidized to CO_2.

$$CH_3OH + O_2 \rightarrow CH_2O + H_2O$$
$$CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$$

A mixture containing 55.6 mole% methanol and the balance oxygen enters a reactor at 350°C and 1 atm at a rate of 4.60×10^4 L/s. The reaction products emerge at the same temperature and pressure at a rate of 6.26×10^4 L/s. An analysis of the products yields a molar composition of 36.7% CH_2O, 4.1% CO_2, 14.3% O_2, and 44.9% H_2O. The required reactor cooling rate is calculated to be 1.05×10^5 kW.
(a) Is the calculated cooling rate correct for the given stream data?
(b) The stream data cannot be correct. Prove it.

9.26. Benzaldehyde is produced from toluene in the catalytic reaction

$$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CHO + H_2O$$

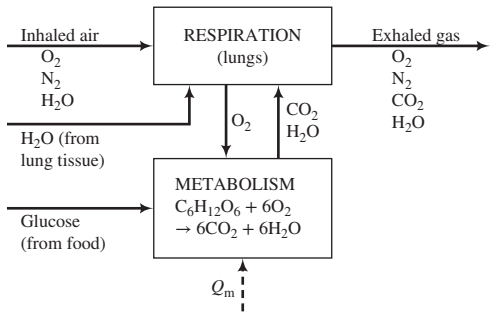
Dry air and toluene vapor are mixed and fed to the reactor at 350°F and 1 atm. Air is supplied in 100% excess. Of the toluene fed to the reactor, 13% reacts to form benzaldehyde and 0.5% reacts with oxygen to form CO_2 and H_2O. The product gases leave the reactor at 379°F and 1 atm. Water is circulated through a jacket surrounding the reactor, entering at 80°F and leaving at 105°F. During a four-hour test period, 29.3 lb_m of water is condensed from the product gases. (Total condensation may be assumed.) The standard heat of formation of benzaldehyde vapor is −17,200 Btu/lb-mole; the heat capacities of both toluene and benzaldehyde vapors are approximately 31 Btu/(lb-mole·°F); and that of liquid benzaldehyde is 46 Btu/(lb-mole·°F).
(a) Calculate the volumetric flow rates (ft^3/h) of the combined feed stream to the reactor and the product gas.
(b) Calculate the required rate of heat transfer from the reactor (Btu/h) and the flow rate of the cooling water (gal/min).
(c) Suppose the process proceeds as designed for several weeks, but one day the product gas and coolant streams emerge at higher temperatures, and the product contains significantly less

benzaldehyde. The coolant flow rate is increased, but the product gas temperature cannot be brought down to its prescribed value, so the process must be shut down for troubleshooting. List and briefly explain several possible causes of the problem.

BIOENGINEERING

*9.27. In respiration, air is inhaled into the lungs, which provide a large surface area for transport of oxygen, carbon dioxide, and water to or from the blood. The transported oxygen is delivered to body cells where it oxidizes glucose and fats from food to produce carbon dioxide, water, and thermal energy. The carbon dioxide and water are transported from the cells to the blood and back to the lungs, from which they are exhaled. The exhaled gas is at body temperature and saturated with water, some produced in the glucose and fat oxidation and some additionally drawn from moist lung tissue. Other water-containing streams—food, water, perspiration, and excreted waste streams—maintain the body's level of hydration.

Suppose an individual inhales air at 20°C and 20% relative humidity, and 25% of the inhaled oxygen is consumed in the glucose oxidation reaction. (Under certain conditions, it is reasonable to neglect the oxidation of fats.) A flowchart of the respiration–metabolism process is shown below. The water in the exhaled gas equals the inhaled water plus the water produced by glucose oxidation plus additional water drawn from the lungs. $\dot{Q}_m$ represents only the heat transferred to or from the body as a consequence of the phenomena just described; not shown are heat and work transferred due to other bodily processes.



(a) Assume a basis of 1 mol bone-dry air (plus the water that goes with it) inhaled at 20°C. Draw and fully label a flowchart of the metabolic process, considering only breathing and glucose oxidation as components of the process. You don't need to label the streams between the two units, since this problem will not require determining their masses or compositions. Do a degree-of-freedom analysis of the overall system.

(b) Suppose all of the water and CO_2 produced from the glucose oxidation are transported to the lungs and exhaled, and calculate the masses of all components of all labeled streams.

(c) If the individual inhales an average of 500 mL of air per breath and takes 12 breaths per minute, how much water (fluid ounces) must she drink per day to make up for the water she loses by breathing?

(d) Returning to the original basis, estimate the heat (kJ) transferred to or from the body as a consequence of breathing and glucose oxidation, assuming that the glucose is oxidized at 37°C and at that temperature $\Delta\hat{H}_c = -2816$ kJ/mol.

9.28. Lime (calcium oxide) is widely used in the production of cement, steel, medicines, insecticides, plant and animal food, soap, rubber, and many other familiar materials. It is usually produced by heating and decomposing limestone ($CaCO_3$), a cheap and abundant mineral, in a *calcination* process:

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

(a) Limestone at 25°C is fed to a continuous calcination reactor. The calcination is complete, and the products leave at 900°C. Taking 1 metric ton (1000 kg) of limestone as a basis and elemental species [Ca(s), C(s), O_2(g)] at 25°C as references for enthalpy calculations, prepare and fill in an inlet–outlet enthalpy table and prove that the required heat transfer to the reactor is 2.7×10^6 kJ.

* Adapted from a problem contributed by Stephanie Farrell of Rowan University.

(b) In a common variation of this process, hot combustion gases containing oxygen and carbon monoxide (among other components) are fed into the calcination reactor along with the limestone. The carbon monoxide is oxidized in the reaction

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)$$

Suppose

- the combustion gas fed to a calcination reactor contains 75 mole% N_2, 2.0% O_2, 9.0% CO, and 14% CO_2;
- the gas enters the reactor at 900°C in a feed ratio of 20 kmol gas/kmol limestone;
- the calcination is complete;
- all of the oxygen in the gas feed is consumed in the CO oxidation reaction;
- the reactor effluents are at 900°C.

Again taking a basis of 1 metric ton of limestone calcined, prepare and fill in an inlet–outlet enthalpy table for this process [don't recalculate enthalpies already calculated in Part (a)] and calculate the required heat transfer to the reactor.

(c) You should have found that the heat that must be transferred to the reactor is significantly lower with the combustion gas in the feed than it is without the gas. By what percentage is the heat requirement reduced? Give two reasons for the reduction. State another benefit of feeding the combustion gas, besides the reduction of the heating requirement.

9.29. A pair of gas-phase reactions with the following stoichiometric equations take place in a continuous reactor:

$$A + B \rightarrow C$$
$$2C \rightarrow D + B$$

The reactions of ethylene and water to form ethanol and of ethanol to form diethyl ether and water constitute such a reaction system. (See Problem 9.24.)

(a) Suppose the reactor feed contains A, B, and inerts (I), with mole fractions x_{A0}, x_{B0}, and x_{I0}, respectively. Letting f_A denote the fractional conversion of A (mol A consumed/mol A fed) and Y_C the yield of C based on consumption of A (mol C generated/mol A consumed), prove that for a basis of 1 mol of feed, the number of moles of each species at the outlet are as follows:

$$n_A = x_{A0}(1 - f_A)$$
$$n_C = x_{A0} f_A Y_C$$
$$n_D = \tfrac{1}{2}(x_{A0} f_A - n_C)$$
$$n_B = x_{B0} - x_{A0} f_A + n_D$$
$$n_I = x_{I0}$$

(b) Write a spreadsheet to perform material and energy balance calculations for a basis of 1.00 mol feed. The program should take as inputs

(i) the standard heats of formation (kJ/mol) of A(g), B(g), C(g), and D(g);
(ii) the coefficients (a, b, c, d) of the formulas $C_p = a + bT + cT^2 + dT^3$ for gaseous A, B, C, D, and I, where C_p has units of kJ/(mol·°C);
(iii) the feed and product temperatures, T_f(°C) and T_p(°C);
(iv) x_{A0}, x_{B0}, f_A, and Y_C.

It should generate an inlet–outlet enthalpy table based on elemental species at 25°C as references and then calculate the required heat transfer to or from the reactor, Q(kJ). The spreadsheet should be tested using the species and reactions of Problem 9.24 and should appear as shown below. (Some of the input data and calculated results are shown.)

Problem 9.29						
Species	Formula	DHf	a	b	c	d
A	C2H4(v)	52.28	0.04075	11.47e-5	−6.891e-8	17.66e-12
B	H2O(v)					
C	C2H5OH(v)					
D	(C4H10)O(v)	−246.8	0.08945	40.33e-5	−2.244e-7	
I	N2(g)					
Tf	Tp	xA0	xB0	xI0	fA	YC
310	310	0.537	0.367	0.096	0.05	0.90
	n(in)	H(in)	n(out)	H(out)		
Species	(mol)	(kJ/mol)	(mol)	(kJ/mol)		
A						
B						
C						
D						
I						
Q(kJ)=	−1.31					

where DHf [$= \Delta\hat{H}_f^\circ$(kJ/mol)] denotes the standard heat of formation.

(c) Use the program to calculate Q at the reactor conditions shown in the spreadsheet, then for a feed temperature of 175°C and all other input parameters the same. (The enthalpy table and the value of Q should automatically correct themselves as soon as you type in the new value of T_f.) Print out and turn in your program output for the second feed temperature.

(d) Run the program for several different values of T_p, f_A, and Y_C. Summarize the effects of each of these parameters on Q and briefly explain why your results make sense.

9.30. A gas mixture containing 85 mole% methane and the balance oxygen is to be charged into an evacuated well-insulated 20-liter reaction vessel at 25°C and 200 kPa. An electrical coil in the reactor, which delivers heat at a rate of 100 watts, will be turned on for 85 seconds and then turned off. Formaldehyde will be produced in the reaction

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$

The reaction products will be cooled and discharged from the reactor.

(a) Calculate the maximum pressure that the reactor is likely to have to withstand, assuming that there are no side reactions. If you were ordering the reactor, why would you specify an even greater pressure in your order? (Give several reasons.)

(b) Why would heat be added to the feed mixture rather than running the reactor adiabatically?

(c) Suppose the reaction is run as planned, the reaction products are analyzed chromatographically, and some CO_2 is found. Where did it come from? If you had taken it into account, would your calculated pressure in Part (a) have been larger, smaller, or can't you tell without doing the detailed calculations?

9.31. Ethylene oxide is produced by the catalytic oxidation of ethylene:

$$C_2H_4(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_4O(g)$$

An undesired competing reaction is the combustion of ethylene to CO_2.

The feed to a reactor contains 2 mol C_2H_4/mol O_2. The conversion and yield in the reactor are respectively 25% and 0.70 mol C_2H_4O produced/mol C_2H_4 consumed. A multiple-unit process separates the reactor outlet stream components: C_2H_4 and O_2 are recycled to the reactor, C_2H_4O is sold, and CO_2 and H_2O are discarded. The reactor inlet and outlet streams are each at 450°C, and the fresh feed and all species leaving the separation process are at 25°C. The combined fresh feed-recycle stream is preheated to 450°C.

(a) Taking a basis of 2 mol of ethylene entering the reactor, draw and label a flowchart of the complete process (show the separation process as a single unit) and calculate the molar amounts and compositions of all process streams.

(b) Calculate the heat requirement (kJ) for the entire process and that for the reactor alone.

Data for gaseous ethylene oxide

$$\Delta\hat{H}_f^\circ = -51.00\ \text{kJ/mol}$$
$$C_p[\text{J/(mol·K)}] = -4.69 + 0.2061T - 9.995 \times 10^{-5}T^2$$

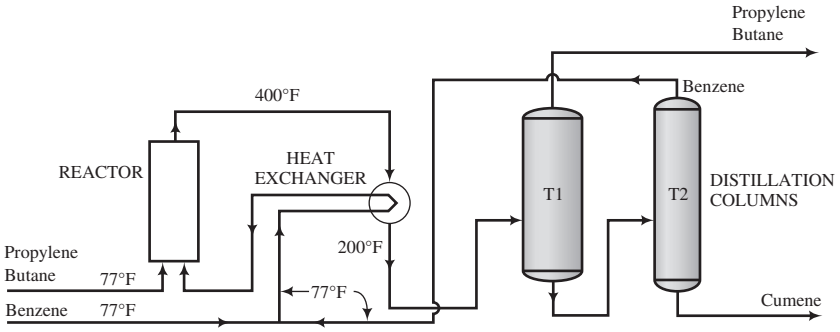
where T is in kelvins.

(c) Calculate the flow rate (kg/h) and composition of the fresh feed, the overall conversion of ethylene, and the overall process and reactor heat requirements (kW) for a production rate of 1500 kg C_2H_4O/day. Briefly explain the reasons for separating and recycling the ethylene–oxygen stream.

(d) One of the attributes of this process defined in the problem statement is extremely unrealistic. What is it?

Equipment Encyclopedia
reactor, heat exchanger, distillation column
www.wiley.com/college/felder

9.32. Cumene ($C_6H_5C_3H_7$) is produced by reacting benzene with propylene [$\Delta H_r^\circ(77°F) = -39{,}520$ Btu].



A liquid feed containing 75 mole% propylene and 25% *n*-butane and a second liquid stream containing essentially pure benzene are fed to the reactor. Fresh benzene and recycled benzene, both at 77°F, are mixed in a 1:3 ratio (1 mole fresh feed/3 moles recycle) and passed through a heat exchanger, where they are heated by the reactor effluent before being fed to the reactor. The reactor effluent enters the exchanger at 400°F and leaves at 200°F. The pressure in the reactor is sufficient to maintain the effluent stream as a liquid.

After being cooled in the heat exchanger, the reactor effluent is fed to a distillation column (T1). All of the butane and unreacted propylene are removed as overhead product from the column, and the cumene and unreacted benzene are removed as bottoms product and fed to a second distillation column (T2) where they are separated. The benzene leaving the top of the second column is the recycle that is mixed with the fresh benzene feed. Of the propylene fed to the process, 20% does not react and leaves in the overhead product from the first distillation column. The production rate of cumene is 1200 lb_m/h.

(a) Calculate the mass flow rates of the streams fed to the reactor, the molar flow rate and composition of the reactor effluent, and the molar flow rate and composition of the overhead product from the first distillation column, T1.

(b) Calculate the temperature of the benzene stream fed to the reactor and the required rate of heat addition to or removal from the reactor. Use the following approximate heat capacities in your calculations: C_p[Btu/(lb_m·°F)] = 0.57 for propylene, 0.55 for butane, 0.45 for benzene, and 0.40 for cumene.

(c) Most people unfamiliar with the chemical process industry imagine that chemical engineers are people who deal mainly with chemical reactions carried out on a large scale. In fact, in most industrial processes,

a visitor to the plant would have trouble finding the reactor in a maze of towers and tanks and pipes that were added to the process design to improve the profitability of the process. Briefly explain how the heat exchanger, the two distillation columns, and the recycle stream in the cumene process serve that function.

Equipment Encyclopedia
reactor, settler, distillation column, heat exchanger

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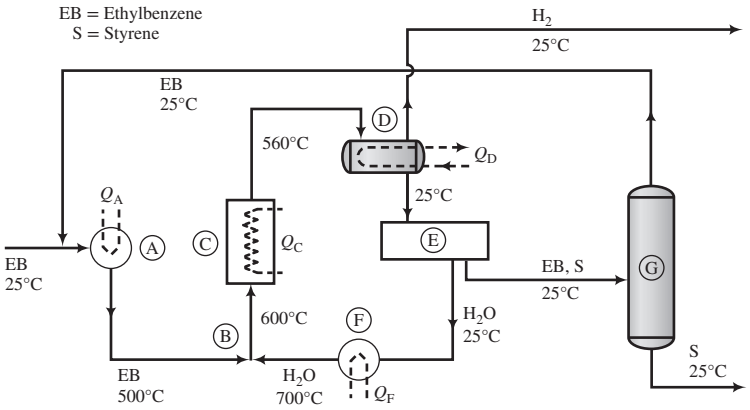
9.33. Ethylbenzene is converted to styrene in the catalytic dehydrogenation reaction

$$C_8H_{10}(g) \rightarrow C_8H_8(g) + H_2: \quad \Delta H_r^\circ(600°C) = +124.5\ \text{kJ}$$

A flowchart of a simplified version of the commercial process is shown here.



Fresh and recycled liquid ethylbenzene combine and are heated from 25°C to 500°C Ⓐ, and the heated ethylbenzene is mixed adiabatically with steam at 700°C Ⓑ to produce the feed to the reactor at 600°C. (The steam suppresses undesired side reactions and removes carbon deposited on the catalyst surface.) A once-through conversion of 35% is achieved in the reactor Ⓒ, and the products emerge at 560°C. The product stream is cooled to 25°C Ⓓ, condensing essentially all of the water, ethylbenzene, and styrene and allowing hydrogen to pass out as a recoverable by-product of the process.

The water and hydrocarbon liquids are immiscible and are separated in a settling tank decanter Ⓔ. The water is vaporized and heated Ⓕ to produce the steam that mixes with the ethylbenzene feed to the reactor. The hydrocarbon stream leaving the decanter is fed to a distillation tower Ⓖ (actually, a series of towers), which separates the mixture into essentially pure styrene and ethylbenzene, each at 25°C after cooling and condensation steps have been carried out. The ethylbenzene is recycled to the reactor preheater, and the styrene is taken off as a product.

(a) On a basis of 100 kg/h styrene produced, calculate the required fresh ethylbenzene feed rate, the flow rate of recycled ethylbenzene, and the circulation rate of water, all in mol/h. (Assume $P = 1$ atm.)

(b) Calculate the required rates of heat input or withdrawal in kJ/h for the ethylbenzene preheater Ⓐ, steam generator Ⓕ, and reactor Ⓒ.

(c) Suggest possible ways to improve the energy economy of this process.

Physical Property Data

Ethylbenzene:	$(C_p)_{\text{liquid}}$	$= 182\ \text{J/(mol}\cdot°\text{C)}$
	$(\Delta\hat{H}_v)$	$= 36.0\ \text{kJ/mol at } 136°\text{C}$
	$(C_p)_{\text{vapor}}[\text{J/(mol}\cdot°\text{C)}]$	$= 118 + 0.30T(°\text{C})$
Styrene:	$(C_p)_{\text{liquid}}$	$= 209\ \text{J/(mol}\cdot°\text{C)}$
	$(\Delta\hat{H}_v)$	$= 37.1\ \text{kJ/mol at } 145°\text{C}$
	$(C_p)_{\text{vapor}}[\text{J/(mol}\cdot°\text{C)}]$	$= 115 + 0.27T(°\text{C})$

Equipment Encyclopedia
reactor, boiler

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9.34. Formaldehyde is produced by decomposing methanol over a silver catalyst:

$$CH_3OH \rightarrow HCHO + H_2$$

To provide heat for this endothermic reaction, some oxygen is included in the feed to the reactor, leading to the partial combustion of the hydrogen produced in the methanol decomposition.

The feed to an adiabatic formaldehyde production reactor is obtained by bubbling a stream of air at 1 atm through liquid methanol. The air leaves the vaporizer saturated with methanol and contains 42%

methanol by volume. The stream then passes through a heater in which its temperature is raised to 145°C. To avoid deactivating the catalyst, the maximum temperature attained in the reactor must be limited to 600°C. For this purpose, saturated steam at 145°C is metered into the air–methanol stream, and the combined stream enters the reactor. A fractional methanol conversion of 70.0% is achieved in the reactor, and the product gas contains 5.00 mole% hydrogen. The product gas is cooled to 145°C in a waste heat boiler in which saturated steam at 3.1 bar is generated from liquid water at 30°C. Several absorption and distillation units follow the waste heat boiler, and formaldehyde is ultimately recovered in an aqueous solution containing 37.0 wt% HCHO. The plant is designed to produce 36 metric kilotons of this solution per year, operating 350 days/yr.

(a) Draw the process flowchart and label it completely. Show the absorption/distillation train as a single unit with the reactor product gas and additional water entering and the formaldehyde solution and a gas stream containing methanol, oxygen, nitrogen, and hydrogen leaving.

(b) Calculate the operating temperature of the methanol vaporizer.

(c) Calculate the required feed rate of steam to the reactor (kg/h) and the molar flow rate and composition of the product gas.

(d) Calculate the rate (kg/h) at which steam is generated in the waste heat boiler.

(e) Enough saturated steam was added to the feed to the reactor to keep the reactor outlet temperature at 600°C. Explain in your own words (i) why adding steam lowers the outlet temperature, and (ii) the economic drawbacks of higher and lower outlet temperatures.

Equipment Encyclopedia
reactor, condenser
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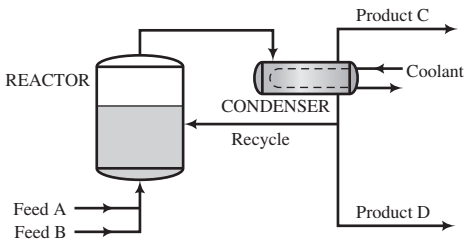
9.35. The synthesis of ethyl chloride is accomplished by reacting ethylene with hydrogen chloride in the presence of an aluminum chloride catalyst:

$$C_2H_4(g) + HCl(g) \xrightarrow{\text{catalyst}} C_2H_5Cl(g): \quad \Delta H_r(0°C) = -64.5\ \text{kJ}$$

Process data and a simplified schematic flowchart are given here.



Data

Reactor: adiabatic, outlet temperature = 50°C
Feed A: 100% HCl(g), 0°C
Feed B: 93 mole% C_2H_4, 7% C_2H_6, 0°C
Product C: Consists of 1.5% of the HCl, 1.5% of the C_2H_4, and all of the C_2H_6 that enter the reactor
Product D: 1600 kg $C_2H_5Cl(l)$/h, 0°C
Recycle to reactor: $C_2H_5Cl(l)$, 0°C
C_2H_5Cl: $\Delta\hat{H}_v = 24.7$ kJ/mol (assume independent of T)
$(C_p)_{C_2H_5Cl(v)}[\text{kJ/(mol}\cdot°C)] = 0.052 + 8.7 \times 10^{-5}T(°C)$

The reaction is exothermic, and if the heat of reaction is not removed in some way, the reactor temperature could increase to an undesirably high level. To avoid this occurrence, the reaction is carried out with the catalyst suspended in liquid ethyl chloride. As the reaction proceeds, most of the heat liberated goes to vaporize the liquid, making it possible to keep the reaction temperature at or below 50°C.

The stream leaving the reactor contains ethyl chloride formed by reaction and that vaporized in the reactor. This stream passes through a heat exchanger where it is cooled to 0°C, condensing essentially all of the ethyl chloride and leaving only unreacted C_2H_4, HCl, and C_2H_6 in the gas phase. A portion of the liquid condensate is recycled to the reactor at a rate equal to the rate at which ethyl chloride is

vaporized, and the rest is taken off as product. At the process conditions, heats of mixing and the influence of pressure on enthalpy may be neglected.

(a) At what rates (kmol/h) do the two feed streams enter the process?

(b) Calculate the composition (component mole fractions) and molar flow rate of product stream C.

(c) Write an energy balance around the reactor and use it to determine the rate at which ethyl chloride must be recycled.

(d) A number of simplifying assumptions were made in the process description and the analysis of this process system, so the results obtained using a more realistic simulation would differ considerably from those you should have obtained in Parts (a)–(c). List as many of these assumptions as you can think of.

BIOENGINEERING

ALTERNATIVE ENERGY

*__9.36.__ Biodiesel fuel—a sustainable alternative to petroleum diesel as a transportation fuel—is produced via the transesterification of triglyceride molecules derived from vegetable oils or animal fats. For every 9 kg of biodiesel produced in this process, 1 kg of glycerol, $C_3H_8O_3$, is produced as a byproduct. Finding a market for the glycerol is important for biodiesel manufacturing to be economically viable.

A process for converting glycerol to the industrially important specialty chemical intermediates acrolein, C_3H_4O, and hydroxyacetone (acetol), $C_3H_6O_2$, has been proposed.[13]

$$C_3H_8O_3 \rightarrow C_3H_4O + 2H_2O$$
$$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O$$

The reactions take place in the vapor phase at 325°C in a fixed bed reactor over an acid catalyst. The feed to the reactor is a vapor stream at 325°C containing 25 mol% glycerol, 25% water, and the balance nitrogen. All of the glycerol is consumed in the reactor, and the product stream contains acrolein and hydroxyacetone in a 9:1 mole ratio. Data for the process species are shown below.

Species	$\Delta\hat{H}_f^\circ$(kJ/mol)	C_p[kJ/(mol·°C)]
glycerol(v)	−620	0.1745
acrolein(v)	−65	0.0762
hydroxyacetone(v)	−372	0.1096
water(v)	−242	0.0340
nitrogen(g)	0	0.0291

(a) Assume a basis of 100 mol fed to the reactor, and draw and completely label a flowchart. Carry out a degree-of-freedom analysis assuming that you will use extents of reaction for the material balances. Then calculate the molar amounts of all product species.

(b) Calculate the total heat added or removed from the reactor (state which it is), using the constant heat capacities given in the above table.

(c) Assuming this process is implemented along with biodiesel production, how would you determine whether the biodiesel is an economically viable alternative to petroleum diesel?

(d) If you do a degree-of-freedom analysis based on atomic species balances, you are likely to count one more equation than you have unknowns, and yet you know the system has zero degrees of freedom. Guess what the problem is, and then prove it.

__9.37.__ Ammonia is oxidized in a well-insulated continuous reactor:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(v): \quad \Delta H_r^\circ = -904.7\ \text{kJ}$$

* Adapted from a problem contributed by Jeffrey Seay of the University of Kentucky.

[13] J. Seay and M. J. Eden, "Incorporating Environmental Impact Assessment into Conceptual Process Design," *J. Environmental Progress & Sustainable Energy*, **28**, 30 (2009).

The feed stream enters at 200°C and the products leave at temperature T_{out}(°C). The inlet–outlet enthalpy table for the reactor appears as follows:

References: NH_3(g), O_2(g), NO(g), H_2O(v) at 25°C, 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
NH_3(g)	4.00	$\hat{H}_1$	—	—
O_2(g)	6.00	$\hat{H}_2$	$\dot{n}_3$	$\hat{H}_3$
NO(g)	—	—	$\dot{n}_4$	$\hat{H}_4$
H_2O(v)	—	—	$\dot{n}_5$	$\hat{H}_5$

(a) Draw and label a process flowchart and calculate the molar amounts of the product stream components and the extent of reaction, ξ. Fill in the values of $\dot{n}_3$, $\dot{n}_4$, and $\dot{n}_5$ in the enthalpy table.

(b) The energy balance for this reactor reduces to $\Delta\dot{H} \approx 0$. Summarize the assumptions that must be made to obtain this result.

(c) Calculate the values of $\hat{H}_1$ and $\hat{H}_2$ and write expressions for $\hat{H}_3$, $\hat{H}_4$, and $\hat{H}_5$ in terms of the outlet temperature, T_{out}, and the heat capacity formulas in Table B.2. Then calculate T_{out} from the energy balance, using a spreadsheet. (See Example 9.5-3.)

(d) A design engineer obtained a preliminary estimate of the reactor outlet temperature using only the first terms of the heat capacity formulas in Table B.2. [For example, $(C_p)_{NH_3} \approx 0.03515$ kJ/(mol·°C).] What value did she calculate? Taking the result of Part (c) to be correct, determine the percentage error in T_{out} that results from using the one-term heat capacity formulas.

(e) The preliminary estimate of Part (d) of T_{out} was mistakenly used as the basis of the design and construction of the reactor. Was this a potentially dangerous error from the standpoint of reactor safety or did it in fact lower the hazard potential? Explain.

9.38. Coke can be converted into CO—a fuel gas—in the reaction

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

A coke that contains 84% carbon by mass and the balance noncombustible ash is fed to a reactor with a stoichiometric amount of CO_2. The coke is fed at 77°F, and the CO_2 enters at 400°F. Heat is transferred to the reactor in the amount of 5859 Btu/lb_m coke fed. The gaseous products and the solid reactor effluent (the ash and unburned carbon) leave the reactor at 1830°F. The heat capacity of the solid is 0.24 Btu/(lb_m·°F).

(a) Calculate the percentage conversion of the carbon in the coke.

(b) The carbon monoxide produced in this manner can be used as a fuel for residential home heating, as can the coke. Speculate on the advantages and disadvantages of using the gas. (There are several of each.)

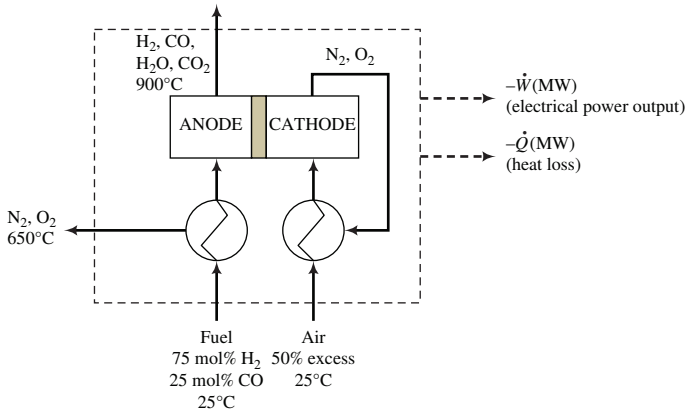
MATERIALS

ALTERNATIVE ENERGY

**9.39.* *Solid oxide fuel cells* (SOFC) have been proposed as an alternative energy technology for use in large stationary power applications (1 to 10 MW of electrical power). These devices have an ion-conducting ceramic material (such as yttria-stabilized zirconia) as the membrane that separates the anode from the cathode, and typically operate at 500–1000°C. There are two advantages to operating fuel cells at such high temperatures: They can be powered directly by fuels besides hydrogen, including carbon monoxide (which poisons the platinum catalyst in low-temperature fuel cells) and hydrocarbons, and the heat produced by fuel cell inefficiencies can be recovered and used elsewhere in the plant.

In the SOFC shown in the following figure, a mixture containing 75 mole% hydrogen and the balance carbon monoxide reacts with oxygen from air to produce water and carbon dioxide plus DC electricity. The overall process is shown in the following schematic diagram, and a device consisting of 10 single fuel cells stacked in series is shown in Problem 9.19.

* Adapted from a problem contributed by Jason M. Keith of Mississippi State University.



The process functions as follows:

- Hydrogen and carbon monoxide at 25°C are preheated and fed to the anode compartments of the single cells, where they combine with oxygen ions that have come through membranes that separate the electrodes and form water and carbon dioxide plus free electrons. The membranes are permeable to oxygen ions but impermeable to electrons. The fractional conversions of H_2 and CO are each 95.0%. The reaction products and unconsumed fuel are transported from the anode compartments to an incinerator.
- The electrons form at all but the last of the anodes of each cell and flow through a conducting plate to the cathode of the adjacent cell. The electrons from the last cell flow through an external circuit that delivers electricity to the devices being powered by the fuel cell and connects back to the cathode of the first cell.
- Fifty percent excess air at 25°C is preheated and fed to each cell cathode, where the oxygen in the air reacts with the electrons entering the cathode to produce the oxygen ions that permeate through the membrane to the cell anode. The exit streams from the cathodes are combined and pass through the air and fuel preheaters before being discharged to the atmosphere.

The following reactions occur in the SOFC:

$$\begin{aligned}
\text{Anode:} \quad & 2H_2 + 2O^{-2} \rightarrow 2H_2O + 4e^- \\
& 2CO + 2O^{-2} \rightarrow 2CO_2 + 4e^- \\
\text{Cathode:} \quad & O_2 + 4e^- \rightarrow 2O^{-2} \\
\text{Overall:} \quad & 2H_2 + O_2 \rightarrow 2H_2O \\
& 2CO + O_2 \rightarrow 2CO_2
\end{aligned}$$

A 1.00 MW (maximum) SOFC is used to power an office building that has the following average electrical energy demand for each tenant when the building is occupied.

Item	Units	Power (W)/unit
Lights	120	33
Computers	30	125
Monitors	30	80
Photocopier	1	800
Refrigerator	1	200

After normal business hours, an average of 5 computers, 5 monitors, and the refrigerator are left on by each tenant.

(a) Determine the total number of tenants in the office building whose offices can be powered by the 1.00 MW SOFC.

(b) Determine the heat loss from the fuel cell in kW when the cell is putting out its full power output of 1 MW, assuming a thermal efficiency of 60.0% (i.e., the electric power output is 60% of the total rate of enthalpy change for the unit).

(c) The fractional conversion of the CO and H_2 fed to the fuel cell are each 95%. Determine the required input molar flow rate of the fuel. (*Suggestion:* Start by taking a basis of 100 mol fuel, then scale the process to the specified 1.00 MW electrical power output. Don't forget that you know the thermal efficiency of the process.)

(d) Calculate the required fuel input molar flow rate after business hours.

9.40. The synthesis of methanol from carbon monoxide and hydrogen is carried out in a continuous vapor-phase reactor at 5.00 atm absolute. The feed contains CO and H_2 in stoichiometric proportion and enters the reactor at 25°C and 5.00 atm at a rate of 21.1 m^3/h. The product stream emerges from the reactor at 127°C. The rate of heat transfer from the reactor is 21.0 kW. Calculate the fractional conversion achieved and the volumetric flow rate (m^3/h) of the product stream. (See Example 9.5-4.)

Equipment Encyclopedia
reactor, heat exchanger
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9.41. Carbon disulfide, a key component in the manufacture of rayon fibers, is produced in the reaction between methane and sulfur vapor over a metal oxide catalyst:

$$CH_4(g) + 4S(v) \rightarrow CS_2(g) + 2H_2S(g)$$
$$\Delta H_r(700°C) = -274\ \text{kJ}$$

Methane and molten sulfur, each at 150°C, are fed to a heat exchanger in stoichiometric proportion. Heat is exchanged between the reactor feed and product streams, and the sulfur in the feed is vaporized. The gaseous methane and sulfur leave the exchanger and pass through a second preheater in which they are heated to 700°C, the temperature at which they enter the reactor. Heat is transferred from the reactor at a rate of 41.0 kJ/mol of feed. The reaction products emerge from the reactor at 800°C, pass through the heat exchanger, and emerge at 200°C with sulfur as a liquid. Use the following heat capacity data to perform the requested calculations: C_p[J/(mol·°C)] ≈ 29.4 for S(l), 36.4 for S(v), 71.4 for CH_4(g), 31.8 for CS_2(v), and 44.8 for H_2S(g).

(a) Estimate the fractional conversion achieved in the reactor. In enthalpy calculations, take the feed and product species at 700°C as references.

(b) Suppose the heat of reaction at 700°C had not been given. What would be different in your solution to Part (a)? (Be thorough in your explanation.) Sketch the process paths from the feed to the products built into both the calculation of Part (a) and your alternative calculation. Explain why the result would be the same regardless of which method you used.

(c) Suggest a method to improve the energy economy of the process.

9.42. The equilibrium constant for the ethane dehydrogenation reaction,

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

is defined as

$$K_p(\text{atm}) = \frac{y_{C_2H_4} y_{H_2}}{y_{C_2H_6}} P$$

where P(atm) is the total pressure and y_i is the mole fraction of the ith substance in an equilibrium mixture. The equilibrium constant has been found experimentally to vary with temperature according to the formula

$$K_p(T) = 7.28 \times 10^6 \exp[-17{,}000/T(\text{K})] \qquad \textbf{(1)}$$

The heat of reaction at 1273 K is +145.6 kJ, and the heat capacities of the reactive species may be approximated by the formulas

$$\left.\begin{aligned} (C_p)_{C_2H_4} &= 9.419 + 0.1147T(\text{K}) \\ (C_p)_{H_2} &= 26.90 + 4.167 \times 10^{-3} T(\text{K}) \\ (C_p)_{C_2H_6} &= 11.35 + 0.1392T(\text{K}) \end{aligned}\right\} \text{[J/(mol·K)]}$$

Suppose pure ethane is fed to a continuous constant-pressure adiabatic reactor at 1273 K and pressure P(atm), the products emerge at T_f(K) and P(atm), and the residence time of the reaction mixture in the reactor is large enough for the outlet stream to be considered an equilibrium mixture of ethane, ethylene, and hydrogen.

(a) Prove that the fractional conversion of ethane in the reactor is

$$f = \left(\frac{K_p}{P + K_p}\right)^{1/2} \tag{2}$$

(b) Write an energy balance on the reactor, and use it to prove that

$$f = \frac{1}{1 + \phi(T_f)} \tag{3}$$

where

$$\phi(T_f) = \frac{\Delta H_r(1273\text{ K}) - \displaystyle\int_{T_f}^{1273\text{K}} [(\nu C_p)_{C_2H_4} + (\nu C_p)_{H_2}]\, dT}{\displaystyle\int_{T_f}^{1273\text{K}} (\nu C_p)_{C_2H_6}\, dT} \tag{4}$$

Finally, substitute for ΔH_r and the heat capacities in Equation 4 to derive an explicit expression for $\phi(T_f)$.

(c) We now have two expressions for the fractional conversion f: Equation 2 and Equation 3. If these expressions are equated, K_p is replaced by the expression of Equation 1, and $\phi(T_f)$ is replaced by the expression derived in Part (b), the result is one equation in one unknown, T_f. Derive this equation, and transpose the right side to obtain an expression of the form

$$\psi(T_f) = 0 \tag{5}$$

(d) Prepare a spreadsheet to take P as input, solve Equation 5 for T_f (use Goal Seek or Solver), and determine the final fractional conversion, f. (*Suggestion:* Set up columns for P, T_f, f, K_p, ϕ, and ψ.) Run the program for P(atm) = 0.01, 0.05, 0.10, 0.50, 1.0, 5.0, and 10.0. Plot T_f versus P and f versus P, using a logarithmic coordinate scale for P.

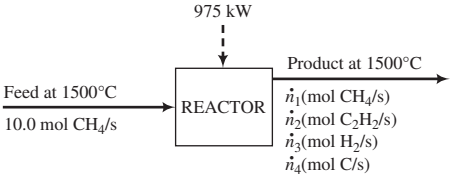
9.43. You are checking the performance of a reactor in which acetylene is produced from methane in the reaction

$$2CH_4(g) \rightarrow C_2H_2(g) + 3H_2(g)$$

An undesired side reaction is the decomposition of acetylene:

$$C_2H_2(g) \rightarrow 2C(s) + H_2(g)$$

Methane is fed to the reactor at 1500°C at a rate of 10.0 mol CH_4/s. Heat is transferred to the reactor at a rate of 975 kW. The product temperature is 1500°C and the fractional conversion of methane is 0.600. A flowchart of the process and an enthalpy table are shown below.



References: C(s), H_2(g), at 25°C, 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
CH_4	10.0	41.65	$\dot{n}_1$	$\hat{H}_1$
C_2H_2	—	—	$\dot{n}_2$	$\hat{H}_2$
H_2	—	—	$\dot{n}_3$	$\hat{H}_3$
C	—	—	$\dot{n}_4$	$\hat{H}_4$

(a) Using the heat capacities given below for enthalpy calculations, write and solve material balances and an energy balance to determine the product component flow rates and the yield of acetylene (mol C_2H_2 produced/mol CH_4 consumed).

$$\begin{aligned} CH_4(g): &\quad C_p \approx 0.079\ \text{kJ/(mol}\cdot\text{°C)} \\ C_2H_2(g): &\quad C_p \approx 0.052\ \text{kJ/(mol}\cdot\text{°C)} \\ H_2(g): &\quad C_p \approx 0.031\ \text{kJ/(mol}\cdot\text{°C)} \\ C(s): &\quad C_p \approx 0.022\ \text{kJ/(mol}\cdot\text{°C)} \end{aligned}$$

For example, the specific enthalpy of methane at 1500°C relative to methane at 25°C is $[0.079\ \text{kJ/(mol}\cdot\text{°C)}](1500\text{°C} - 25\text{°C}) = 116.5\ \text{kJ/mol}$.

(b) The reactor efficiency may be defined as the ratio (actual acetylene yield/acetylene yield with no side reaction). What is the reactor efficiency for this process?

(c) The *mean residence time* in the reactor [τ(s)] is the average time gas molecules spend in the reactor in going from inlet to outlet. The more τ increases, the greater the extent of reaction for every reaction occurring in the process. For a given feed rate, τ is proportional to the reactor volume and inversely proportional to the feed stream flow rate.

(i) If the mean residence time increases to infinity, what would you expect to find in the product stream? Explain.

(ii) Someone proposes running the process with a much greater feed rate than the one used in Part (a), separating the products from the unconsumed reactants, and recycling the reactants. Why would you expect that process design to increase the reactor efficiency? What else would you need to know to determine whether the new design would be cost-effective?

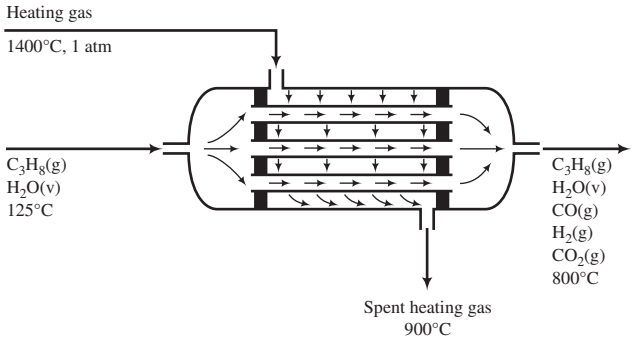
9.44. Hydrogen is produced in the steam reforming of propane:

$$C_3H_8(g) + 3H_2O(v) \rightarrow 3CO(g) + 7H_2(g)$$

The water–gas shift reaction also takes place in the reactor, leading to the formation of additional hydrogen:

$$CO(g) + H_2O(v) \rightarrow CO_2(g) + H_2(g)$$

The reaction is carried out over a nickel catalyst in the tubes of a shell-and-tube reactor. The feed to the reactor contains steam and propane in a 6:1 molar ratio at 125°C, and the products emerge at 800°C. The excess steam in the feed assures essentially complete consumption of the propane. Heat is added to the reaction mixture by passing the exhaust gas from a nearby boiler over the outside of the tubes that contain the catalyst. The gas is fed at 4.94 m^3/mol C_3H_8, entering the unit at 1400°C and 1 atm and leaving at 900°C. The unit may be considered adiabatic.



(a) Calculate the molar composition of the product gas, assuming that the heat capacity of the heating gas is 0.040 kJ/(mol·°C).

(b) Is the reaction process exothermic or endothermic? Explain how you know. Then explain how running the reaction in a reactor–heat exchanger improves the process economy.

9.45. In a **coal gasification** process, carbon (the primary constituent of coal) reacts with steam to produce carbon monoxide and hydrogen (*synthesis gas*). The gas may either be burned or subjected to further processing to produce any of a variety of chemicals.

A coal contains 10.5 wt% moisture (water) and 22.6 wt% noncombustible ash. The remaining fraction of the coal contains 81.2 wt% C, 13.4% O, and 5.4% H. A coal slurry containing 2.00 kg coal/kg water is fed at 25°C to an adiabatic gasification reactor along with a stream of pure oxygen at the same temperature. The following reactions take place in the reactor:

$$C(s) + H_2O(v) \rightarrow CO(g) + H_2(g): \quad \Delta H_r^\circ = +131.3\ \text{kJ} \tag{1}$$

$$C(s) + O_2(g) \rightarrow CO_2(g): \quad \Delta H_r^\circ = -393.5\ \text{kJ} \tag{2}$$

$$2H(\text{in coal}) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(v): \quad \Delta H_r^\circ \approx -242\ \text{kJ} \tag{3}$$

Gas and slag (molten ash) leave the reactor at 2500°C. The gas contains CO, H_2, CO_2, and H_2O.[14]

(a) Feeding oxygen to the reactor lowers the yield of synthesis gas, but no gasifier ever operates without supplementary oxygen. Why does the oxygen lower the yield? Why it is nevertheless always supplied. (*Hint:* All the necessary information is contained in the first two stoichiometric equations and associated heats of reaction shown above.)

(b) Suppose the oxygen gas fed to the reactor and the oxygen in the coal combine with all the hydrogen in the coal (Reaction 3) and with some of the carbon (Reaction 2), and the remainder of the carbon is consumed in Reaction 1. Taking a basis of 1.00 kg coal fed to the reactor and letting n_0 equal the moles of O_2 fed, draw and label a flowchart. Then derive expressions for the molar flow rates of the four outlet gas species in terms of n_0. [Partial solution: $n_{H_2} = (51.3 - n_0)$ mol H_2.]

(c) The standard heat of combustion of the coal has been determined to be −21,400 kJ/kg, taking $CO_2(g)$ and $H_2O(l)$ to be the combustion products. Use this value and the given elemental composition of the coal to prove that the standard heat of formation of the coal is −1510 kJ/kg. Then use an energy balance to calculate n_0, using the following approximate heat capacities in your calculation:

Species	O_2	CO	H_2	CO_2	H_2O(v)	Slag(l)
C_p[kJ/(mol·°C)]	0.0336	0.0332	0.0300	0.0508	0.0395	—
C_p[kJ/(kg·°C)]	—	—	—	—	—	1.4

Take the heat of fusion of ash (the heat required to convert ash to slag) to be 710 kJ/kg.

9.46. Five cubic meters of a 1.00-molar aqueous sulfuric acid solution (SG = 1.064) is stored at 25°C. Use data in Tables B.1 and B.11 to calculate the standard heat of formation of the solution in kJ/mol H_2SO_4 relative to the solute elements and water, and the total enthalpy of the solution relative to the same reference conditions.

9.47. Calculate the standard heat (kJ/mol) of the neutralization reaction between dilute hydrochloric acid and dilute sodium hydroxide solutions, taking the heat of solution of NaCl to be +4.87 kJ/mol. Then calculate the standard heat of the reaction between hydrogen chloride gas and solid sodium hydroxide to form solid sodium chloride and liquid water. What is the physical significance of the difference between the two calculated values?

9.48. A 10.0 mole% aqueous sulfuric acid solution (SG = 1.27) is to be titrated to neutrality at 25°C with a 3.00-molar caustic soda (sodium hydroxide) solution (SG = 1.13):

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

(a) Calculate the required volume ratio (cm^3 caustic solution/cm^3 acid solution).

(b) Calculate the standard heats of formation (kJ/mol solute) of each of the three solutions involved in this process, and the heat released (kJ/cm^3 acid solution neutralized) if the reactants and products are all at 25°C. The heat of solution of sodium sulfate is −1.17 kJ/mol. Assume that $Q = \Delta H$ for the process. (See Example 9.5-5.)

[14] In a real coal gasification reactor, sulfur in the coal would form hydrogen sulfide in the product gas, nitrogen in the coal would form N_2, some of the carbon monoxide formed in the first reaction would react with steam to form carbon dioxide and more hydrogen, and some of the carbon in the coal would react with hydrogen to form methane. For simplicity, we are ignoring these reactions.

9.49. Most of the world's chlorine and sodium hydroxide are obtained through the electrolysis of brine:

$$NaCl(aq) + H_2O(l) \rightarrow \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) + NaOH(aq)$$

(a) Determine the standard heats of formation of NaCl(aq) and NaOH(aq) and then the standard heat of the brine electrolysis reaction. The standard heat of solution of NaCl is $\Delta\hat{H}_s(r = \infty) = +4.87$ kJ/mol NaCl.

(b) Several years ago, the annual production of chlorine in the United States was roughly 8800 metric kilotons. Calculate the energy requirement in MW·h/yr corresponding to this production rate, assuming that all of the chlorine is produced by electrolysis at 25°C and the required energy input equals ΔH for the process.

9.50. Calcium chloride is a salt used in a number of food and medicinal applications and in brine for refrigeration systems. Its most distinctive property is its affinity for water: in its anhydrous form it efficiently absorbs water vapor from gases, and from aqueous liquid solutions it can form (at different conditions) calcium chloride hydrate ($CaCl_2 \cdot H_2O$), dihydrate ($CaCl_2 \cdot 2H_2O$), tetrahydrate ($CaCl_2 \cdot 4H_2O$), and hexahydrate ($CaCl_2 \cdot 6H_2O$).

You have been given the task of determining the standard heat of the reaction in which calcium chloride hexahydrate is formed from anhydrous calcium chloride:

$$CaCl_2(s) + 6H_2O(l) \rightarrow CaCl_2 \cdot 6H_2O(s): \quad \Delta H_r^\circ\,(\text{kJ}) = ?$$

By definition, the desired quantity is the *heat of hydration* of calcium chloride hexahydrate. You cannot carry out the hydration reaction directly, so you resort to an indirect method. You first dissolve 1.00 mol of anhydrous $CaCl_2$ in 10.0 mol of water in a calorimeter and determine that 64.85 kJ of heat must be transferred away from the calorimeter to keep the solution temperature at 25°C. You next dissolve 1.00 mol of the hexahydrate salt in 4.00 mol of water and find that 32.1 kJ of heat must be transferred *to* the calorimeter to keep the temperature at 25°C.

(a) Use these results to calculate the desired heat of reaction. (*Suggestion:* Begin by writing out the stoichiometric equations for the two dissolution processes.)

(b) Calculate the standard heat of reaction in kJ for Ca(s), Cl_2(g) and H_2O reacting to form $CaCl_2$ (aq, $r = 10$).

(c) Speculate about why the standard heat of reaction in forming calcium chloride hexahydrate cannot be measured directly by reacting the anhydrous salt with water in a calorimeter.

9.51. A dilute aqueous solution of sulfuric acid at 25°C is used to absorb ammonia in a continuous reactor, thereby producing ammonium sulfate, a fertilizer:

$$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

(a) If the ammonia enters the absorber at 75°C, the sulfuric acid enters at 25°C, and the product solution emerges at 25°C, how much heat must be withdrawn from the unit per mol of $(NH_4)_2SO_4$ produced? (All needed physical property data may be found in Appendix B.)

(b) Estimate the final temperature if the reactor of Part (a) is adiabatic and the product of the solution contains 1.00 mole% ammonium sulfate. Take the heat capacity of the solution to be that of pure liquid water [4.184 kJ/(kg·°C)].

(c) In a real (imperfectly insulated) reactor, would the final solution temperature be less than, equal to, or greater than the value calculated in Part (b), or is there no way to tell without more information? Briefly explain your answer.

9.52. A 2.00 mole% sulfuric acid solution is neutralized with a 5.00 mole% sodium hydroxide solution in a continuous reactor. All reactants enter at 25°C. The standard heat of solution of sodium sulfate is −1.17 kJ/mol Na_2SO_4, and the heat capacities of all solutions may be taken to be that of pure liquid water [4.184 kJ/(kg·°C)].

(a) How much heat (kJ/kg acid solution fed) must be transferred to or from the reactor contents (state which it is) if the product solution emerges at 40°C?

(b) Estimate the product solution temperature if the reactor is adiabatic, neglecting heat transferred between the reactor contents and the reactor wall.

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9.53. A 12.0-molar solution of sodium hydroxide (SG = 1.37) is neutralized with 75.0 mL of a 4.0 molar solution of sulfuric acid (SG = 1.23) in a well-insulated container.

(a) Estimate the volume of the sodium hydroxide solution and the final solution temperature if both feed solutions are at 25°C. The heat capacity of the product solution may be taken to be that of pure liquid water, the standard heat of solution of sodium sulfate is −1.17 kJ/mol, and the energy balance reduces to $Q = \Delta H$ for this constant-pressure batch process.

(b) List several additional assumptions you made to arrive at your estimated volume and temperature.

BIOENGINEERING

*__9.54.__ Citric acid ($C_6H_8O_7$) is used in the preparation of many foods, pharmaceuticals, soft drinks, and personal-care products. Although it can be recovered by concentration and crystallization from citrus juices, especially lemons, modern commercial production involves synthesis by fermentation of molasses or other carbohydrates such as glucose or fructose by the fungus *Aspergillus niger* (*A. niger*). The process involves addition of the fungus to a fermenter along with glucose, nutrients, water, and air that is bubbled through the fermentation broth. After the desired conversion, the resulting liquor is processed first by filtration of the cell mass and other solids from the liquid and then recovery and purification of the citric acid by crystallization.

As part of the evaluation of a proposed continuous fermentation process, you have been asked to estimate the heating or cooling requirement associated with a fermenter that is to produce 10.0 kg of citric acid per hour. Feed to the unit includes (1) an aqueous solution that is 20.0 wt% glucose ($C_6H_{12}O_6$), 0.4% ammonia, and the remainder water; and (2) air at 1.2 atm, saturated with water, providing a molar flow rate of oxygen twice that of the glucose. Leaving the fermenter are (3) a gas stream at 1 atm containing N_2, unreacted O_2, and CO_2 formed by fermentation, and saturated with water, and (4) a liquid stream containing cell mass produced in the fermenter, water, citric acid, and unreacted ammonia and glucose. All streams may be assumed to be at 25°C, as are the contents of the well-mixed fermenter. The stoichiometry of the fermentation reaction is given by

$$C_6H_{12}O_6(aq) + aNH_3(aq) + bO_2(g) \rightarrow cCH_{1.79}N_{0.2}O_{0.5}(s) + dCO_2(g) + eH_2O(l) + fC_6H_8O_7(aq)$$

where the coefficients of the species $(a, b, \ldots)$ are to be determined. Experiments on the fermentation reaction have found that 70% of the glucose consumed is converted to citric acid and that the *respiratory quotient* (RQ) is 0.45 (RQ = moles of CO_2 produced per mole of O_2 consumed).

The following table gives data for selected process species. Information on other species may be found in Table B.1.

Species	MW(g/mol)	$\Delta\hat{H}_f^\circ$(kJ/mol)	$\Delta\hat{H}_s$(kJ/mol)
glucose(s)	180	−1006.8	9.9
citric acid(s)	192	−1543.8	22.6
ammonia(g)	17	−46.19	−35
cellular material(s)	24.6	−59.9	—

(a) Use elemental species balances to determine the coefficients in the stoichiometric equation.

(b) The system is sized so that 90% of the limiting reactant is consumed. For a citric acid production rate of 10 kg/h, estimate all stream and constituent flow rates in both kg/h and mol/h. What are the volumetric flow rates of air entering the fermenter and of the off-gas stream?

(c) The heats of formation for glucose and citric acid given in the above process description are for the species as solids, while the heat of formation of ammonia is for a gas. However, the fermentation reaction involves aqueous solutions of all three species. Show how Hess's law can be used in estimating heat of formation in an aqueous solution from a heat of formation of either gaseous or solid species. (*Note:* Heats of solution may be assumed constant.)

(d) Determine the rate at which heat must be added to or removed from (state which) the fermenter.

* This problem is adapted from A. Saterbak, L. V. McIntire, K.-Y. San, *Bioengineering Fundamentals*, Pearson Prentice Hall, 2007.

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(e) Various strains of *A. niger* exist, with some being useful in the production of specific chemicals, such as citric acid, and some being harmful. Provide a brief description of how it is to be cultured for the application in this problem.

SAFETY

(f) Identify safety issues associated with use of *A. niger* in the production of citric acid. Pick one of these issues and suggest means for mitigating risks in the process under consideration.

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9.55. Ammonia scrubbing is one of many processes for removing sulfur dioxide from flue gases. The gases are bubbled through an aqueous solution of ammonium sulfite, and the SO_2 reacts to form ammonium bisulfite:

$$(NH_4)_2SO_3(aq) + SO_2(g) + H_2O(l) \rightarrow 2NH_4HSO_3(aq)$$

Subsequent process steps yield concentrated SO_2 and regenerate ammonium sulfite, which is recycled to the scrubber. The sulfur dioxide is either oxidized and absorbed in water to form sulfuric acid or reduced to elemental sulfur.

Flue gas from a power-plant boiler containing 0.30% SO_2 by volume enters a scrubber at a rate of 50,000 mol/h at 50°C. The gas is bubbled through an aqueous solution containing 10.0 mole% ammonium sulfite that enters the scrubber at 25°C. The gas and liquid effluents from the scrubber both emerge at 35°C. The scrubber removes 90% of the SO_2 entering with the flue gas. The effluent liquid is analyzed and is found to contain 1.5 moles $(NH_4)_2SO_3$ per mole of NH_4HSO_3. The heat of formation of $(NH_4)_2SO_3(aq)$ at 25°C is −890.0 kJ/mol, and that of $NH_4HSO_3(aq)$ is −760 kJ/mol. The heat capacities of all liquid solutions may be taken to be 4.0 J/(g·°C) and that of the flue gas may be taken to be that of nitrogen. Evaporation of water may be neglected. Calculate the required rate of heat transfer to or from the scrubber (kW).

9.56. Various uses for nitric acid are given in Problem 6.43, along with information about how this important chemical is synthesized industrially. The key reactions are oxidations of ammonia to nitric oxide and of nitric oxide to nitrogen dioxide, followed by dissolution of NO_2 in water:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(v)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

Nitric oxide generated on dissolution of NO_2 in water is oxidized to produce additional NO_2, which is then combined with water to form more HNO_3. In this problem we neglect side reactions that would lower the product yield.

Ammonia vapor at 275°C and 8 atm is mixed with air, also at 275°C and 8 atm, and the combined stream is fed to a converter. Fresh air entering the system at 30°C and 1 atm with a relative humidity of 50% is compressed to 100°C and 8 atm, and the compressed air then exchanges heat with the product gas leaving the converter. The quantity of oxygen in the feed to the converter is 20% in excess of the amount theoretically required to convert all of the ammonia to HNO_3. The entire process after the compressor may be taken to operate at a constant pressure of 8 atm.

In the converter, the ammonia is completely oxidized, with a negligible amount of NO_2 formed. The product gas leaves the converter at 850°C, and, as described in the preceding paragraph, exchanges heat with the air entering the system. The product gas then is fed to a waste-heat boiler that produces superheated steam at 200°C and 10 bar from liquid water at 35°C. The product gas leaving the waste-heat boiler is cooled further to 35°C and fed to an absorption column in which the NO is completely oxidized to NO_2, which in turn combines with water (some of which is present in the product gas). Water is fed to the absorber at 25°C, at a rate sufficient to form a 55 wt% aqueous nitric acid solution. The NO formed in the reaction of NO_2 to produce HNO_3 is oxidized, and the NO_2 produced is hydrated to form still more HNO_3. The off-gas from the process may be taken to contain only N_2 and O_2.

(a) Construct a flowchart showing all process streams, including input and output from the process and the following equipment: converter, air compressor, exchanger recovering heat from the converter product, waste-heat boiler producing superheated steam, exchanger cooling the product gas before it is fed to the absorber, and absorber.

(b) Taking a basis of 100 kmol of ammonia fed to the process, develop spreadsheets (preferably incorporating the use of APEx) to determine the following:

(i) Molar amounts (kmol) of oxygen, nitrogen, and water vapor in the air fed to the process, cubic meters of air fed to the process, and kmol of water fed to the absorber.

(ii) Molar amounts, molar composition, and volume of the off-gas leaving the absorber.
(iii) Mass (kg) of product nitric acid solution.
(iv) Molar amounts and composition of the gas leaving the converter.
(v) Heat removed from or added to (state which) the converter.
(vi) Temperature of the product gas after it has exchanged heat with the air, assuming no heat is transferred between the heat exchanger and the surroundings.
(vii) Production rate of superheated steam if the gas temperature leaving the boiler is 205°C. Before performing this calculation, determine if condensation of water occurs when the gas is cooled to 205°C. Since the superheated steam temperature is 200°C, explain why the selected temperature of the product gas is reasonable.
(viii) Heat removed from the product gas before it is fed to the absorber (*Hint:* Check the condition of the gas at 35°C) and mass of cooling water required to remove that heat if the water temperature can only be increased by 5°C. Assume no heat is transferred between the heat exchanger and the surroundings.
(ix) Heat removed from or added to the absorber. Assume the heat capacity of the nitric acid solution is approximately the same as that of liquid water and the outlet temperatures of the off-gas and product streams are 25°C and 35°C, respectively.

(c) Scale up the results calculated in Part (b) to determine all stream flow rates and heat transfer rates for a production rate of 5.0×10^3 kg/h of the product solution.

9.57. A natural gas is analyzed and found to consist of 85.5% v/v (volume percent) methane, 8.5% ethane, 2.5% propane, and 3.5% N_2 (noncombustible).
(a) Calculate the higher and lower heating values of this fuel in kJ/mol, using the heats of combustion in Table B.1.
(b) Calculate the lower heating value of the fuel in kJ/kg.
(c) State in your own words the meaning of the quantity calculated in Part (b).

9.58. An **ultimate analysis** of a coal is a series of operations that yields the percentages by mass of carbon, hydrogen, nitrogen, oxygen, and sulfur in the coal. The heating value of a coal is best determined in a calorimeter, but it may be estimated with reasonable accuracy from the ultimate analysis using the **Dulong formula**:

$$HHV(\text{kJ/kg}) = 33{,}801(\text{C}) + 144{,}158[(\text{H}) - 0.125(\text{O})] + 9413(\text{S})$$

where (C), (H), (O), and (S) are the mass fractions of the corresponding elements. The 0.125(O) term accounts for the hydrogen bound in the water contained in the coal.
(a) Derive an expression for the higher heating value (*HHV*) of a coal in terms of C, H, O, and S, and compare your result with the Dulong formula. Suggest a reason for the difference.
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(b) A coal with an ultimate analysis of 75.8 wt% C, 5.1% H, 8.2% O, 1.5% N, 1.6% S, and 7.8% ash (noncombustible) is burned in a power-plant boiler furnace. All of the sulfur in the coal forms SO_2. The gas leaving the furnace is fed through a tall stack and discharged to the atmosphere. The ratio ϕ (kg SO_2 in the stack gas/kJ heating value of the fuel) must be below a specified value for the power plant to be in compliance with Environmental Protection Agency regulations regarding sulfur emissions. Estimate ϕ, using the Dulong formula for the heating value of the coal.
(c) An earlier version of the EPA regulation specified that the mole fraction of SO_2 in the stack gas must be less than a specified amount to avoid a costly fine and the required installation of an expensive stack gas scrubbing unit. When this regulation was in force, a few unethical plant operators blew clear air into the base of the stack while the furnace was operating. Briefly explain why they did so and why they stopped this practice when the new regulation was introduced.

9.59. A fuel gas is known to contain methane, ethane, and carbon monoxide. A sample of the gas is charged into an initially evacuated 2.000-liter vessel at 25°C and 2323 mm Hg absolute. The vessel is weighed before and after being charged, and the mass difference is found to be 4.929 g. Next, the higher heating value of the gas is determined in a calorimeter to be 841.9 kJ/mol.
(a) Calculate the molar composition of the fuel gas.
(b) Calculate the lower heating value of the gas. State in your own words the physical significance of the calculated value.

9.60. A fuel gas containing 85.0 mole% methane and the balance ethane is burned completely with pure oxygen at 25°C, and the products are cooled to 25°C.

(a) Suppose the reactor is continuous. Take a basis of calculation of 1 mol/s of the fuel gas, assume some value for the percent excess oxygen fed to the reactor (the value you choose will not affect the results), and calculate $-\dot{Q}$(kW), the rate at which heat must be transferred from the reactor.

(b) Now suppose the combustion takes place in a constant-volume batch reactor. Take a basis of calculation of 1 mol of the fuel gas charged into the reactor, assume any percent excess oxygen, and calculate $-Q$(kJ). (*Hint:* Recall Equation 9.1-5.)

(c) Briefly explain why the results in Parts (a) and (b) do not depend on the percent excess O_2 and why they would not change if air rather than pure oxygen were fed to the reactor.

9.61. A mixture of air and a fine spray of gasoline at ambient (outside air) temperature is fed to a set of piston-fitted cylinders in an automobile engine. Sparks ignite the combustible mixtures in one cylinder after another, and the consequent rapid increase in temperature in the cylinders causes the combustion products to expand and drive the pistons. The back-and-forth motion of the pistons is converted to rotary motion of a crank shaft, motion that in turn is transmitted through a system of shafts and gears to propel the car.

Consider a car driving on a day when the ambient temperature is 298 K and suppose that the rate of heat loss from the engine to the outside air is given by the formula

$$-\dot{Q}_l\left(\frac{\text{kJ}}{\text{h}}\right) \approx \frac{15 \times 10^6}{T_a(\text{K})}$$

where T_a is the ambient temperature.

(a) Take gasoline to be a liquid with a specific gravity of 0.70 and a higher heating value of 49.0 kJ/g, assume complete combustion and that the combustion products leaving the engine are at 298 K, and calculate the minimum feed rate of gasoline (gal/h) required to produce 100 hp of shaft work.

(b) If the exhaust gases are well above 298 K (which they are), is the work delivered by the pistons more or less than the value determined in Part (a)? Explain.

(c) If the ambient temperature is much lower than 298 K, the work delivered by the pistons would decrease. Give two reasons.

9.62. The heating value of a fuel oil is to be measured in a constant-volume bomb calorimeter. The bomb is charged with oxygen and 0.00215 lb_m of the fuel and is then sealed and immersed in an insulated container of water. The initial temperature of the system is 77.00°F. The fuel–oxygen mixture is ignited, and the fuel is completely consumed. The combustion products are CO_2(g) and H_2O(v). The final calorimeter temperature is 89.06°F. The mass of the calorimeter, including the bomb and its contents, is 4.62 lb_m, and the average heat capacity of the system (C_v) is 0.900 Btu/(lb_m·°F).

(a) Calculate $\Delta\hat{U}_c^\circ$ (Btu/lb_m oil) for the combustion of the fuel oil at 77°F. Briefly explain your calculation.

(b) What more would you need to know to determine the higher heating value of the oil?

9.63. Methanol vapor is burned with excess air in a catalytic combustion chamber. Liquid methanol initially at 25°C is vaporized at 1.1 atm and heated to 100°C; the vapor is mixed with air that has been preheated to 100°C, and the combined stream is fed to the reactor at 100°C and 1 atm. The reactor effluent emerges at 300°C and 1 atm. Analysis of the product gas yields a dry-basis composition of 4.8% CO_2, 14.3% O_2, and 80.9% N_2.

(a) Calculate the percentage excess air supplied and the dew point of the product gas.

(b) Taking a basis of 1 g-mole of methanol burned, calculate the heat (kJ) needed to vaporize and heat the methanol feed, and the heat (kJ) that must be transferred from the reactor.

(c) Suggest how the energy economy of this process could be improved. Then suggest why the company might choose not to implement your redesign.

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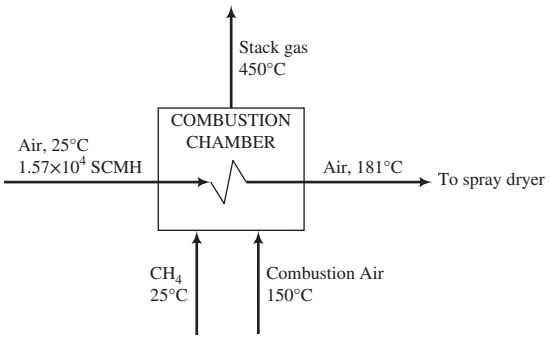
9.64. Methane at 25°C is burned in a boiler furnace with 10.0% excess air preheated to 100°C. Ninety percent of the methane fed is consumed, the product gas contains 10.0 mol CO_2/mol CO, and the combustion products leave the furnace at 400°C.

(a) Calculate the heat transferred from the furnace, $-\dot{Q}$(kW), for a basis of 100 mol CH_4 fed/s. (The greater the value of $-\dot{Q}$, the more steam is produced in the boiler.)

(b) Would the following changes increase or decrease the rate of steam production? (Assume the fuel feed rate and fractional conversion of methane remain constant.) Briefly explain your answers. (i) Increasing the temperature of the inlet air; (ii) increasing the percent excess air for a given stack gas temperature; (iii) increasing the selectivity of CO_2 to CO formation in the furnace; and (iv) increasing the stack gas temperature.

*__9.65.__ Methane is burned completely with 40% excess air. The methane enters the combustion chamber at 25°C, the combustion air enters at 150°C, and the stack gas [CO_2, H_2O(v), O_2, N_2] exits at 450°C. The chamber functions as a preheater for an air stream flowing in a pipe through the chamber to a spray dryer. The air enters the chamber at 25°C at a rate of 1.57×10^4 m^3(STP)/h and is heated to 181°C. All of the heat generated by combustion is used to heat the combustion products and the air going to the spray dryer (i.e., the combustion chamber may be considered adiabatic).



(a) Draw and completely label the process flow diagram and perform a degree-of-freedom analysis.
(b) Calculate the required molar flow rates of methane and combustion air (kmol/h) and the volumetric flow rates (m^3/h) of the two effluent streams. State all assumptions you make.
(c) When the system goes on line for the first time, environmental monitoring of the stack gas reveals a considerable quantity of CO, suggesting a problem with either the design or the operation of the combustion chamber. What changes from your calculated values would you expect to see in the temperatures and volumetric flow rates of the effluent streams [increase, decrease, cannot tell without doing the calculations]?

9.66. A gaseous fuel containing methane and ethane is burned with excess air. The fuel enters the furnace at 25°C and 1 atm, and the air enters at 200°C and 1 atm. The stack gas leaves the furnace at 800°C and 1 atm and contains 5.32 mole% CO_2, 1.60% CO, 7.32% O_2, 12.24% H_2O, and the balance N_2.
(a) Calculate the molar percentages of methane and ethane in the fuel gas and the percentage excess air fed to the reactor.
(b) Calculate the heat (kJ) transferred from the reactor per cubic meter of fuel gas fed.
(c) A proposal has been made to lower the feed rate of air to the furnace. State advantages and a drawback of doing so.

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9.67. A coal contains 73.0 wt% C, 4.7% H (not including the hydrogen in the coal moisture), 3.7% S, 6.8% H_2O, and 11.8% ash. The coal is burned at a rate of 50,000 lb_m/h in a power-plant boiler with air 50% in excess of that needed to oxidize all the carbon in the coal to CO_2. The air and coal are both fed at 77°F and 1 atm. The solid residue from the furnace is analyzed and is found to contain 28.7 wt% C, 1.6% S, and the balance ash. The sulfur oxidized in the furnace is converted to SO_2(g). Of the ash in the coal, 30% emerges in the solid residue and the balance is emitted with the stack gases as fly ash. The stack gas and solid residue emerge from the furnace at 600°F. The higher heating value of the coal is 18,000 Btu/lb_m.
(a) Calculate the mass flow rates of all components in the stack gas and the volumetric flow rate of this gas. (Ignore the contribution of the fly ash in the latter calculation, and assume that the stack gas contains a negligible amount of CO.)
(b) Assume that the heat capacity of the solid furnace residue is 0.22 Btu/(lb_m·°F), that of the stack gas is the heat capacity per unit mass of nitrogen, and 35% of the heat generated in the furnace is used to produce electricity. At what rate in MW is electricity produced?

* Adapted from a problem contributed by Jeffrey Seay of the University of Kentucky.

(c) Calculate the ratio (heat transferred from the furnace)/(heating value of the fuel). Why is this ratio less than one?

(d) Suppose the air fed to the furnace were preheated rather than being fed at ambient temperature, but that everything else (feed rates, outlet temperatures, and fractional coal conversion) were the same. What effect would this change have on the ratio calculated in Part (c)? Explain. Suggest an economical way in which this preheating might be accomplished.

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(e) At least three components of the stack gas from the power plant raise significant environmental concerns. Identify the components, explain why they are considered problems, and describe how the problems can be addressed in a modern coal-fired power plant.

(f) Several minor constituents of coal were not mentioned in the problem statement, and yet they may be part of the stack gas. Identify one such species and, as in Part (e), explain why it is a problem and how the problem either is or could be addressed in a modern coal-fired power plant.

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9.68. A mixture of methane, ethane, and argon at 25°C is burned with excess air in a power-plant boiler. The hydrocarbons in the fuel are completely consumed. The following variable definitions will be used throughout this problem:

$$\begin{aligned} x_M &= \text{mole fraction of methane in the fuel} \\ x_A &= \text{mole fraction of argon in the fuel} \\ P_{xs}(\%) &= \text{percent excess air fed to the furnace} \\ T_a(°C) &= \text{temperature of the entering air} \\ T_s(°C) &= \text{stack gas temperature} \\ r &= \text{ratio of } CO_2 \text{ to CO in the stack gas (mol } CO_2\text{/mol CO)} \\ \dot{Q}(\text{kW}) &= \text{rate of heat transfer from the furnace to the boiler tubes} \end{aligned}$$

(a) Without doing any calculations, sketch the shapes of the plots you would expect to obtain for plots of $\dot{Q}$ versus (i) x_M, (ii) x_A, (iii) P_{xs}, (iv) T_a, (v) T_s, and (vi) r, assuming in each case that the other variables are held constant. Briefly state your reasoning for each plot.

(b) Take a basis of 1.00 mol/s of fuel gas, draw and label a flowchart, and derive expressions for the molar flow rates of the stack gas components in terms of x_M, x_A, P_{xs}, and r. Then take as references the elements at 25°C, prepare and fill in an inlet–outlet enthalpy table for the furnace, and derive expressions for the specific molar enthalpies of the feed and stack gas components in terms of T_a and T_s.

(c) Calculate $\dot{Q}$(kW) for $x_M = 0.85$ mol CH_4/mol, $x_A = 0.05$ mol Ar/mol, $P_{xs} = 5\%$, $r = 10.0$ mol CO_2/mol CO, $T_a = 150°C$, and $T_s = 700°C$ (*Solution:* $\dot{Q} = -655$ kW.)

(d) Prepare a spreadsheet that has columns for x_M, x_A, P_{xs}, T_a, r, T_s, and $\dot{Q}$, plus columns for any other variables you might need for the calculation of $\dot{Q}$ from given values of the preceding six variables (e.g., component molar flow rates and specific enthalpies). Use the spreadsheet to generate plots of $\dot{Q}$ versus each of the following variables over the specified ranges:

$$\begin{aligned} x_M &= 0.00-0.85 \text{ mol } CH_4\text{/mol} \\ x_A &= 0.01-0.05 \text{ mol Ar/mol} \\ P_{xs} &= 0\%-100\% \\ T_a &= 25°C-250°C \\ r &= 1-100 \text{ mol } CO_2\text{/mol CO (make the } r \text{ axis logarithmic)} \\ T_s &= 500°C-1000°C \end{aligned}$$

When generating each plot, use the variable values given in Part (c) as base values. (For example, generate a plot of $\dot{Q}$ versus x_M for $x_A = 0.05$, $P_{xs} = 5\%$, and so on, with x_M varying from 0.00 to 0.85 on the horizontal axis.) If possible, include the plots on the same spreadsheet as the data.

Equipment Encyclopedia
condenser, boiler

www.wiley.com/college/felder

9.69. A gas stream consisting of *n*-hexane in methane is fed to a condenser at 60°C and 1.2 atm. The dew point of the gas (considering hexane as the only condensable component) is 55°C. The gas is cooled to 5°C in the condenser, recovering pure hexane as a liquid. The effluent gas leaves the condenser

saturated with hexane at 5°C and 1.1 atm and is fed to a boiler furnace at a rate of 207.4 L/s, where it is burned with 100% excess air that enters the furnace at 200°C. The stack gas emerges at 400°C and 1 atm and contains no carbon monoxide or unburned hydrocarbons. The heat transferred from the furnace is used to generate saturated steam at 10 bar from liquid water at 25°C.

(a) Calculate the mole fractions of hexane in the condenser feed and product gas streams and the rate of hexane condensation (liters condensate/s).

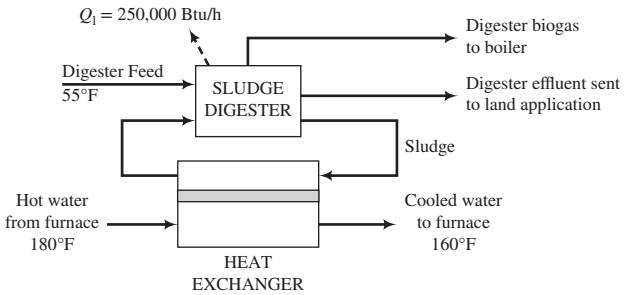
(b) Calculate the rate at which heat must be transferred from the condenser (kW) and the rate of generation of steam in the boiler (kg/s).

ENVIRONMENTAL

BIOENGINEERING

***9.70.** A city with a population of 200,000 people operates a 20.0×10^6 gal/day wastewater treatment plant. For every million gallons of wastewater treated, 1875 lb_m of solids are generated, with 75% of the solids being classified as "volatile" (meaning they are converted to gases during digestion).

Solids generated in the treatment plant are fed to an anaerobic digester in which microorganisms break down biodegradable material in the absence of oxygen. The feed to the digester contains 45,000 mg solids/L at 55°F and has a density approximately that of water. The digester operates at 95°F, converts 50% of the volatile solids to a biogas containing 65 vol% CH_4 and 35% CO_2 at a rate of 15 SCF (standard cubic feet) gas per lb_m of solids converted, and loses approximately 250,000 Btu/h of heat to the surroundings. To supply the heat needed to raise the feed temperature from 55°F to 95°F and to make up for the heat loss, a stream of sludge is pumped from the digester through a heat exchanger in which it comes into thermal contact with a stream of hot water. The heated sludge is returned to the digester. The digester biogas is fed to a furnace in which a fraction of it is burned to heat the water for the heat exchanger from 160°F to 180°F. A schematic of part of the process is shown below.



(a) Calculate the rate (SCF/h) at which biogas is produced in the digester and the total heating value (Btu/h) of the gas (= fuel flow rate × lower heating value).

(b) Calculate the rate of heat transfer (Btu/h) between the hot water and sludge and the volumetric flow rate (ft^3/h) of the water passing through the heat exchanger. Assume the heat of reaction of the anaerobic digestion process is negligible.

(c) If the biogas is burned in a boiler with 80% efficiency (that is, 80% of the heating value of the fuel goes to produce hot water for the heat exchanger), what fraction of the digester gas must be burned to heat the water from 160°F to 180°F? What happens to the other 20% of the heating value?

(d) If there is excess digester gas available after meeting the process–water heating demand, what are its potential uses?

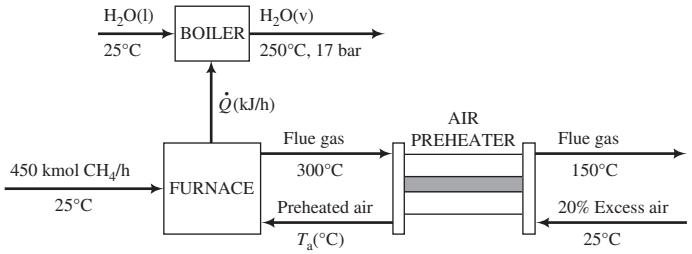
Equipment Encyclopedia
boiler, heat exchanger, furnace
www.wiley.com/college/felder

9.71. In the preliminary design of a furnace for industrial boiler, methane at 25°C is burned completely with 20% excess air, also at 25°C. The feed rate of methane is 450 kmol/h. The hot combustion gases leave the furnace at 300°C and are discharged to the atmosphere. The heat transferred from the furnace ($\dot{Q}$) is used to convert boiler feedwater at 25°C into superheated steam at 17 bar and 250°C.

(a) Draw and label a flowchart of this process [the chart should look like the one shown in Part (b) without the preheater] and calculate the composition of the gas leaving the furnace. Then, calculate $\dot{Q}$(kJ/h) and the rate of steam production in the boiler (kg/h).

* Adapted from a problem contributed by C. Michael Bullard of Hazen and Sawyer Engineers.

(b) In the actual boiler design, the air feed at 25°C and the combustion gas leaving the furnace at 300°C pass through a heat exchanger (the *air preheater*). The combustion (flue) gas is cooled to 150°C in the preheater and is then discharged to the atmosphere, and the heated air is fed to the furnace.



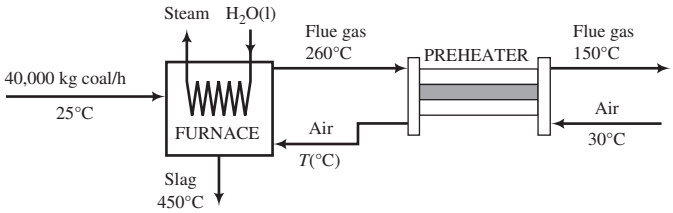
Calculate the temperature of the air entering the furnace (a computer solution is required) and the rate of steam production (kg/h).

(c) Explain why preheating the air increases the rate of steam production. (*Suggestion:* Use the energy balance on the furnace in your explanation.) Why does it make sense economically to use the combustion gas as the heating medium?

Equipment Encyclopedia
heat exchanger, furnace

www.wiley.com/college/felder

9.72. A bituminous coal is burned with air in a boiler furnace. The coal is fed at a rate of 40,000 kg/h and has an ultimate analysis of 76 wt% C, 5% H, 8% O, negligible amounts of N and S, and 11% noncombustible ash (see Problem 9.58), and a higher heating value of 25,700 kJ/kg. Air enters a preheater at 30°C and 1 atm with a relative humidity of 30%, exchanges heat with the hot flue gas leaving the furnace, and enters the furnace at temperature T_a(°C). The flue gas contains 7.71 mole% CO_2 and 1.29 mole% CO *on a dry basis*, and the balance is a mixture of O_2, N_2, and H_2O. It emerges from the furnace at 260°C and is cooled to 150°C in the preheater. Noncombustible residue (*slag*) leaves the furnace at 450°C and has a heat capacity of 0.97 kJ/(kg·°C).



(a) Prove that the air-to-fuel ratio is 16.1 standard cubic meters/kg coal and that the flue gas contains 4.6% H_2O by volume.

(b) Calculate the rate of cooling required to cool the flue gas from 260°C to 150°C and the temperature to which the air is preheated. (*Note:* A trial-and-error calculation is required.)

(c) If 60% of the heat transferred from the furnace ($-\dot{Q}$) goes into producing saturated steam at 30 bar from liquid boiler feedwater at 50°C, at what rate (kg/h) is steam generated?

9.73. Carbon monoxide is burned with excess air at 1 atm in an adiabatic reactor. The reactants are fed at 25°C and the final temperature (i.e., the adiabatic flame temperature) is 1500°C.

(a) Calculate the percentage excess air fed to the reactor.

(b) If the percentage excess air were increased, how would the adiabatic flame temperature change and why would it change in this manner?

Equipment Encyclopedia
boiler

www.wiley.com/college/felder

9.74. A natural gas containing 82.0 mole% CH_4 and the balance C_2H_6 is burned with 20% excess air in a boiler furnace. The fuel gas enters the furnace at 298 K, and the air is preheated to 423 K. The heat capacities of the stack-gas components may be assumed to have the following constant values:

$$\begin{aligned} CO_2: &\quad C_p = 50.0\ \text{J/(mol·K)} \\ H_2O(v): &\quad C_p = 38.5\ \text{J/(mol·K)} \\ O_2: &\quad C_p = 33.1\ \text{J/(mol·K)} \\ N_2: &\quad C_p = 31.3\ \text{J/(mol·K)} \end{aligned}$$

(a) Assuming complete combustion of the fuel, calculate the adiabatic flame temperature.
(b) How would the flame temperature change if the percent excess air were increased? How would it change if the percentage of methane in the fuel increased? Briefly explain both of your answers.

ENVIRONMENTAL

9.75. In a surface-coating operation, a polymer (plastic) dissolved in liquid acetone is sprayed on a solid surface and a stream of hot air is then blown over the surface, vaporizing the acetone and leaving a residual polymer film of uniform thickness. Because environmental standards do not allow discharging acetone into the atmosphere, a proposal to incinerate the stream is to be evaluated.

The proposed process uses two parallel columns containing beds of solid particles. The air-acetone stream, which contains acetone and oxygen in stoichiometric proportion, enters one of the beds at 1500 mm Hg absolute at a rate of 1410 standard cubic meters per minute. The particles in the bed have been preheated and transfer heat to the gas. The mixture ignites when its temperature reaches 562°C, and combustion takes place rapidly and adiabatically. The combustion products then pass through and heat the particles in the second bed, cooling down to 350°C in the process. Periodically the flow is switched so that the heated outlet bed becomes the feed gas preheater/combustion reactor and vice versa.

Use the following average values for C_p[kJ/(mol·°C)] in solving the problems to be given: 0.126 for C_3H_6O, 0.033 for O_2, 0.032 for N_2, 0.052 for CO_2, and 0.040 for H_2O(v).

(a) If the relative saturation of acetone in the feed stream is 12.2%, what is the stream temperature?
(b) Determine the composition of the gas after combustion, assuming that all of the acetone is converted to CO_2 and H_2O, and estimate the temperature of this stream.
(c) Estimate the rates (kW) at which heat is transferred from the inlet bed particles to the feed gas prior to combustion and from the combustion gases to the outlet bed particles. Suggest an alternative to the two-bed feed switching arrangement that would achieve the same purpose.

9.76. Liquid *n*-pentane at 25°C is burned with 30% excess oxygen (not air) fed at 75°C. The adiabatic flame temperature is T_{ad}(°C).

(a) Take as a basis of calculation 1.00 mol C_5H_{12}(l) burned and use an energy balance on the adiabatic reactor to derive an equation of the form $f(T_{ad}) = 0$, where $f(T_{ad})$ is a fourth-order polynomial $[f(T_{ad}) = c_0 + c_1T_{ad} + c_2T_{ad}^2 + c_3T_{ad}^3 + c_4T_{ad}^4]$. If your derivation is correct, the ratio c_0/c_4 should equal -6.892×10^{14}. Use a spreadsheet program to determine T_{ad}.
(b) Repeat the calculation of Part (a) using successively the first two terms, the first three terms, and the first four terms of the fourth-order polynomial equation. If the solution of Part (a) is taken to be exact, what percentage errors are associated with the linear (two-term), quadratic (three-term), and cubic (four-term) approximations?
(c) Why is the fourth-order solution at best an approximation and quite possibly a poor one? (*Hint:* Examine the conditions of applicability of the heat capacity formulas in Table B.2.)

9.77. Methane is burned with 25% excess air in a continuous adiabatic reactor. The methane enters the reactor at 25°C and 1.10 atm at a rate of 550 L/s, and the entering air is at 150°C and 1.1 atm. Combustion in the reactor is complete, and the reactor effluent gas emerges at 1.05 atm.

(a) Calculate the temperature and the degrees of superheat of the reactor effluent. (Consider water to be the only condensable species in the effluent.)
(b) Suppose only 15% excess air is supplied. Without doing any additional calculations, state how the temperature and degrees of superheat of the reactor effluent would be affected [increase, decrease, remain the same, cannot tell without more information] and explain your reasoning. What risk is involved in lowering the percent excess air?

SAFETY

*__9.78.__ Methane and 30% excess air are to be fed to a combustion reactor. An inexperienced technician mistakes his instructions and charges the gases together in the required proportion into an evacuated closed tank. (The gases were supposed to be fed directly into the reactor.) The contents of the charged tank are at 25°C and 4.00 atm absolute.

(a) Calculate the standard internal energy of combustion of the methane combustion reaction, $\Delta\hat{U}_c^\circ$(kJ/mol), taking CO_2(g) and H_2O(v) as the presumed products. Then prove that if the constant-pressure heat capacity of an ideal-gas species is independent of temperature, the

* Modified version of a problem in D. A. Crowl, D. W. Hubbard, and R. M. Felder, *Problem Set: Stoichiometry*, AIChE Center for Chemical Process Safety, New York, 1993.

specific internal energy of that species at temperature T(°C) relative to the same species at 25°C is given by the expression

$$\hat{U} = (C_p - R)(T - 25°\text{C})$$

where R is the gas constant. Use this formula in the next part of the problem.

(b) You wish to calculate the maximum temperature, $T_{\max}$(°C), and corresponding pressure, $P_{\max}$(atm), that the tank would have to withstand if the mixture it contains were to be accidentally ignited. Taking molecular species at 25°C as references and treating all species as ideal gases, prepare an inlet–outlet internal energy table for the closed system combustion process. In deriving expressions for each $\hat{U}_i$ at the final reactor condition ($T_{\max}$, $P_{\max}$), use the following approximate values for C_{pi}[kJ/(mol·°C)]: 0.033 for O_2, 0.032 for N_2, 0.052 for CO_2, and 0.040 for H_2O(v). Then use an energy balance and the ideal-gas equation of state to perform the required calculations.

(c) Why would the actual temperature and pressure attained in a real tank be less than the values calculated in Part (a)? (State several reasons.)

(d) Think of ways that the tank contents might be accidentally ignited. The list should suggest why accepted plant safety regulations prohibit the storage of combustible vapor mixtures.

9.79. A methanol-synthesis reactor is fed with a gas stream at 220°C consisting of 5.0 mole% methane, 25.0% CO, 5.0% CO_2, and the remainder hydrogen. The reactor and feed stream are at 7.5 MPa. The primary reaction occurring in the reactor and its associated equilibrium constant are

$$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$$

$$K = \frac{y_{\text{CH}_3\text{OH}} y_{\text{H}_2}}{y_{\text{CO}} y_{H_2}^2 P^2} = \exp\left(\begin{array}{l} 21.225 + \dfrac{9143.6}{T} - 7.492 \ln T \\ \quad + 4.076 \times 10^{-3} T - 7.161 \times 10^{-8} T^2 \end{array} \right)$$

where T is in kelvins. The product stream may be assumed to reach equilibrium at 250°C.

(a) Determine the composition (mole fractions) of the product stream and the percentage conversions of CO and H_2.

(b) Neglecting the effect of pressure on enthalpies, estimate the amount of heat (kJ/mol feed gas) that must be added to or removed from (state which) the reactor.

(c) Calculate the extent of reaction and heat removal rate (kJ/mol feed) for reactor temperatures between 200°C and 400°C in 50°C increments. Use these results to obtain an estimate of the adiabatic reaction temperature.

(d) Determine the effect of pressure on the reaction by evaluating extent of conversion and rate of heat transfer at 1 MPa and 15 MPa.

(e) Considering the results of your calculations in Parts (c) and (d), propose an explanation for selection of the initial reaction conditions of 250°C and 7.5 MPa.

9.80. In Problem 9.79, the synthesis of methanol from carbon monoxide and hydrogen was described. Further analysis, however, reveals that three reactions can take place:

$$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$$
$$\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$$
$$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$$

(a) Show that only two of these reactions are independent.

(b) The equilibrium constants for the first and third reactions are

$$K_{(1)} = \frac{y_{\text{CH}_3\text{OH}} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2}^2 P^2} = \exp\left(\begin{array}{l} 21.225 + \dfrac{9143.6}{T} - 7.492 \ln T \\ \quad + 4.076 \times 10^{-3} T - 7.161 \times 10^{-8} T^2 \end{array} \right)$$

$$K_{(3)} = \frac{y_{\text{CO}} y_{\text{H}_2\text{O}}}{y_{\text{CO}_2} y_{\text{H}_2}} = \exp\left(\begin{array}{l} 13.148 - \dfrac{5639.5}{T} - 1.077 \ln T \\ \quad - 5.44 \times 10^{-4} T + 1.125 \times 10^{-7} T^2 + \dfrac{49170}{T^2} \end{array} \right)$$

As in Problem 9.79, the feed composition is 5.0 mole% methane, 25.0% CO, 5.0% CO_2, and the remainder hydrogen. The temperature and pressure of the equilibrated product stream are 250°C and 7.5 MPa. Determine the composition (mole fractions) of the product stream and the percentage conversions of CO and H_2.

9.81. Natural gas that contains methane, ethane, and propane is to be burned with humid air. The adiabatic flame temperature is to be calculated from specified values of the following quantities:

$$\begin{aligned} y_{CH_4}, y_{C_2H_6}, y_{C_3H_8} &= \text{mole fractions of fuel components} \\ T_f, T_a &= \text{inlet temperatures of fuel and air; °C} \\ P_{xs} &= \text{percent excess air} \\ y_{W0} &= \text{mole fraction of water in the inlet air} \end{aligned}$$

(a) Without doing any calculations, predict the direction of change (increase, decrease, no change) in the adiabatic flame temperature you would expect for an increase in (i) y_{CH_4} with $y_{C_3H_8}$ held constant, (ii) T_f, (iii) T_a, (iv) P_{xs}, and (v) y_{W0}. Briefly state your reasoning for each variable.

(b) For a basis of 1 g-mole of natural gas, calculate the gram-moles of each molecular species in the feed and product streams, assuming complete combustion and negligible CO formation. The answer should be expressed in terms of the variables given above.

(c) Given below are expressions for the specific enthalpies of the feed and product components, relative to their elements at 25°C.

$$\hat{H}_i(\text{kJ/mol}) = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^4, \quad T \text{ in °C}$$

Substance (i)	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^8$	$e \times 10^{12}$
(1) CH_4	−75.72	3.431	2.734	0.122	−2.75
(2) C_2H_6	−85.95	4.937	6.96	−1.939	1.82
(3) C_3H_8	−105.6	6.803	11.30	−4.37	7.928
(4) N_2	−0.7276	2.900	0.110	0.191	−0.7178
(5) O_2	−0.7311	2.910	0.579	−0.2025	0.3278
(6) H_2O(v)	−242.7	3.346	0.344	0.2535	−0.8982
(7) CO_2	−394.4	3.611	2.117	−0.9623	1.866

Derive the given expression for the specific enthalpy of methane from the heat capacity data in Table B.2. Then show that ΔH for the reactor is given by an expression of the form

$$\Delta H = \alpha_0 + \alpha_1 T + \alpha_2 T^2 + \alpha_3 T^3 + \alpha_4 T^4$$

where T is the product temperature, and

$$\alpha_0 = \sum_{i=4}^{7} (n_i)_{out} a_i - \sum_{i=1}^{3} (n_i)_{in} \hat{H}_i(T_f) - \sum_{i=4}^{6} (n_i)_{in} \hat{H}_i(T_a)$$

$$\alpha_1 = \sum_{i=4}^{7} (n_i)_{out} b_i \qquad \alpha_3 = \sum_{i=4}^{7} (n_i)_{out} d_i$$

$$\alpha_2 = \sum_{i=4}^{7} (n_i)_{out} c_i \qquad \alpha_4 = \sum_{i=4}^{7} (n_i)_{out} e_i$$

(d) Write a spreadsheet program to take as input values of y_{CH_4}, $y_{C_3H_8}$, T_f, T_a, P_{xs}, and y_{W0}, and to solve the energy balance equation $[\Delta H(T) = 0]$ to determine the adiabatic flame temperature. Run the program for the following sets of input variable values:

Variable	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
y_{CH_4}	0.75	0.86	0.75	0.75	0.75	0.75
$y_{C_3H_8}$	0.04	0.04	0.04	0.04	0.04	0.04
T_f(°C)	40	40	150	40	40	40
T_a(°C)	150	150	150	250	150	150
P_{xs}	25%	25%	25%	25%	100%	25%
y_{W0}	0.0306	0.0306	0.0306	0.0306	0.0306	0.10

Suggestion: Near the top of the spreadsheet, enter the values of a, b, c, d, and e for each species. Starting several rows below the last of these entries, list in Column A labels for the input variables and all calculated variables (component molar flow rates, specific enthalpies, $T_{ad}, \alpha_0, \alpha_1, \ldots, \alpha_4, \Delta H$), and enter in adjacent columns the corresponding values or formulas for these variables in successive runs. (*Solution for Run 1:* $T_{ad} = 1743.1°C$.)

Equipment Encyclopedia
reactor, absorption column, stripper
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9.82. Acetylene is produced by pyrolyzing—decomposing at high temperature—natural gas (predominantly methane):

$$2CH_4(g) \rightarrow C_2H_2(g) + 3H_2$$

The heat required to sustain this endothermic reaction is provided by feeding oxygen to the reactor and burning a portion of the methane to form primarily CO and some CO_2.

A simplified version of the process is as follows. A stream of natural gas, which for the purposes of this problem may be considered pure methane, and a stream containing 96.0 mole% oxygen and the balance nitrogen are each preheated from 25°C to 650°C. The streams are combined and fed into an adiabatic converter, in which most of the methane and all of the oxygen are consumed, and the product gas is rapidly quenched to 38°C as soon as it emerges from the converter. The residence time in the converter is less than 0.01 s, low enough to prevent most but not all of the methane from decomposing to form hydrogen and solid carbon particles (soot). Of the carbon in the feed, 5.67% emerges as soot.

The cooled effluent passes through a carbon filter in which the soot is removed. The clean gas is then compressed and fed to an absorption column, where it is contacted with a recycled liquid solvent, dimethylformamide, or DMF (MW = 73.09). The off-gas leaving the absorber contains all of the hydrogen and nitrogen, 98.8% of the CO, and 95% of the methane in the gas fed to the column. The "lean" solvent fed to the absorber is essentially pure DMF; the "rich" solvent leaving the column contains all of the water and CO_2 and 99.4% of the acetylene in the gas feed. This solvent is analyzed and found to contain 1.55 mole% C_2H_2, 0.68% CO_2, 0.055% CO, 0.055% CH_4, 5.96% H_2O, and 91.7% DMF.

The rich solvent goes to a multiple-unit separation process from which three streams emerge. One—the *product gas*—contains 99.1 mole% C_2H_2, 0.059% H_2O, and the balance CO_2; the second—the *stripper off-gas*—contains methane, carbon monoxide, carbon dioxide, and water; and the third—the *regenerated solvent*—is the liquid DMF fed to the absorber.

A plant is designed to produce 5.00 metric tons per day of product gas. Your assignment is to calculate (i) the required flow rates (SCMH) of the methane and oxygen feed streams; (ii) the molar flow rates (kmol/h) and compositions of the gas fed to the absorber, the absorber off-gas, and the stripper off-gas; (iii) the DMF circulation rate: (iv) the overall product yield (mol C_2H_2 in the product gas/mol CH_4 in feed to reactor) and the fraction that this quantity represents of its theoretical maximum value; (v) the total heating requirements (kW) for the methane and oxygen feed preheaters; (vi) the temperature attained in the converter.

(a) Draw and label a flowchart of the process. Determine the degrees of freedom for the overall system, each individual process unit, and the feed-stream mixing point.

(b) Write and number a full set of equations for the quantities specified as (i)–(iv), identifying each one (e.g., C balance on converter, CH_4 balance on absorber, ideal-gas equation of state for feed streams, etc.). You should end with as many equations as unknown variables.

(c) Solve the equations of Part (b).

(d) Calculate quantities (v) and (vi).

(e) Speculate on what additional processing step(s) the absorber and stripper off-gases might be subjected to, and state your reasoning.

ENVIRONMENTAL

Equipment Encyclopedia
boiler, dryer
www.wiley.com/college/felder

**9.83.* The wastewater treatment plant at the Ossabaw Paper Company paper mill generates about 24 tonnes of sludge per day. The *consistency* of the sludge is 35%, meaning that the sludge contains 35 wt% solids and the balance liquids. The mill currently spends $40/tonne to dispose of the sludge in a landfill. The plant environmental engineer has determined that if the sludge consistency could be increased to 75%, the sludge could be incinerated (burned) to generate useful energy and to eliminate the environmental problems associated with landfill disposal.

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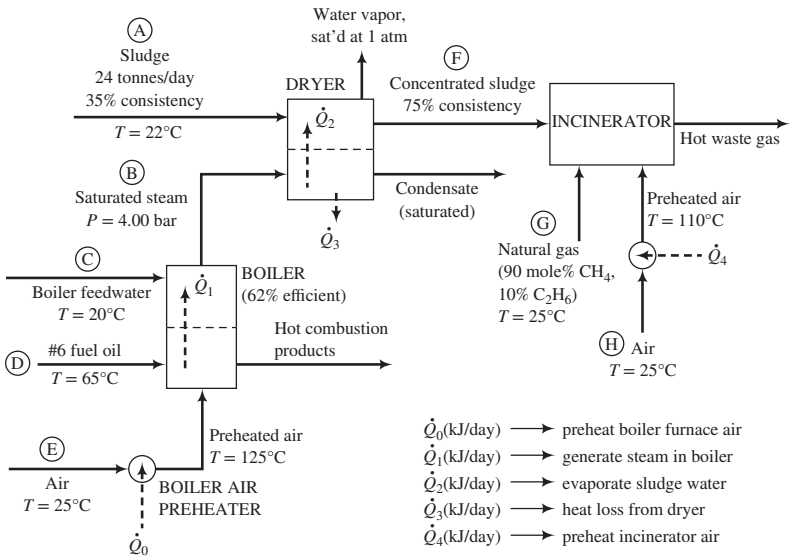
* Problem based on material contributed by Joseph Lemanski, formerly of the Kimberly-Clark Corporation, and Morton Barlaz of North Carolina State University.

A flowchart for a preliminary design of the proposed sludge-treatment process follows. For simplicity, we will assume that the liquid in the sludge is just water.



Process description: The sludge from the wastewater treatment plant (Stream Ⓐ) passes through a dryer where a portion of the water in the sludge is vaporized. The heat required for the vaporization comes from condensing saturated steam at 4.00 bar (Stream Ⓑ). The steam fed to the dryer is produced in the plant's oil-fired boiler from feedwater at 20°C (Stream Ⓒ). The heat required to produce the steam is transferred from the boiler furnace, where fuel oil (Stream Ⓓ) is burned with 25% excess air (Stream Ⓔ). The concentrated sludge coming from the dryer (Stream Ⓕ), which has a consistency of 75%, is fed to an incinerator. The heating value of the sludge is insufficient to keep the incinerator temperature high enough for complete combustion, so natural gas (Stream Ⓖ) is used as a supplementary fuel. A stream of outside air at 25°C (Stream Ⓗ) is heated to 110°C and fed to the incinerator along with the concentrated sludge and natural gas. The waste gas from the incinerator is discharged to the atmosphere.

Fuel oil: The oil is a low-sulfur No. 6 fuel oil. Its ultimate (elemental) analysis on a weight basis is 87% C, 10% H, 0.84% S, and the balance oxygen, nitrogen, and nonvolatile ash. The higher heating value of the oil is 3.75×10^4 kJ/kg and the heat capacity is $C_p = 1.8$ kJ/(kg·°C).

Boiler: The boiler has an efficiency of 62%, meaning that 62% of the heating value of the fuel oil burned is used to produce saturated steam at 4.00 bar from boiler feedwater at 20°C. Fuel oil at 65°C and dry air at 125°C are fed to the boiler furnace. The air feed rate is 25% in excess of the amount theoretically required for complete consumption of the fuel.

Sludge: The sludge from the wastewater treatment plant contains 35% w/w solids (S) and the balance liquids (which for the purposes of this problem may be treated as only water) and enters the dryer at 22°C. The sludge includes a number of volatile organic species, some of which may be toxic, and has a terrible odor. The heat capacity of the solids is approximately constant at 2.5 kJ/(kg·°C).

Dryer: The dryer has an efficiency of 55%, meaning that the heat transferred to the sludge, $\dot{Q}_2$, is 55% of the total heat lost by the condensing steam, and the remainder, $\dot{Q}_3$, is lost to the surroundings. The dryer operates at 1 atm, and the water vapor and concentrated sludge emerge at the corresponding saturation temperature. The steam condensate leaves the dryer as a liquid saturated at 4.00 bar.

Incinerator: The concentrated sludge has a heating value of 19,000 kJ/kg dry solids. For a feed sludge of 75% consistency, the incinerator requires 195 SCM natural gas/tonne wet sludge [1 SCM = 1 m^3(STP)]. The theoretical air requirement for the sludge is 2.5 SCM air/10,000 kJ of heating value. Air is fed in 100% excess of the amount theoretically required to burn the sludge and the natural gas.

(a) Use material and energy balances to calculate the mass flow rates (tonnes/day) of Streams Ⓑ, Ⓒ, Ⓓ, Ⓔ, Ⓕ, Ⓖ and Ⓗ, and heat flows $\dot{Q}_0, \dot{Q}_1, \ldots, \dot{Q}_4$(kJ/day). Take the molecular weight of air to be 29.0. (*Caution:* Before you start doing lengthy and unnecessary energy balance calculations on the boiler furnace, remember the given furnace efficiency.)

Exploratory Exercises—Research and Discover

(b) The money saved by implementing this process will be the current cost of disposing of the wastewater plant sludge in a landfill. Two major costs of implementing the process are the installed costs of the new dryer and incinerator. What other costs must be taken into account when determining the economic feasibility of the process? Why might management decide to go ahead with the project even if it proves to be unprofitable?

(c) What opportunities exist for improving the energy economy of the process? (*Hint:* Think about the need to preheat the fuel oil and the boiler and incinerator air streams and consider heat exchange possibilities.)

(d) The driving force for the introduction of this process is to eliminate the environmental cost of sludge disposal. What is that cost—that is, what environmental penalties and risks are associated with using landfills for hazardous waste disposal? What environmental problems might incineration introduce?

CHAPTER 10 Balances on Transient Processes

A system is said to be in a *transient* (or *unsteady-state*) condition if the value of any system variable changes with time. Batch and semibatch process systems are always transient: in a batch system, if nothing is changing with time then nothing is happening, and in a semibatch system (which has an input stream but no output stream or vice versa) at least the mass of the system contents must vary with time. Continuous systems are always transient when they are started up and shut down, and they become transient at other times due to planned or unexpected changes in operating conditions.[1]

The procedures for deriving balances on transient systems are essentially those developed in Chapters 4 (material balances) and 7 (energy balances). The main difference is that transient balances have nonzero accumulation terms that are derivatives, so that instead of algebraic equations the balances are differential equations.

10.0 LEARNING OBJECTIVES

After completing this chapter, you should be able to do the following:

- Derive material balance equations and provide initial conditions for well-mixed transient single-unit processes, and derive energy balance equations and provide initial conditions for well-mixed transient single-unit nonreactive processes.
- Predict transient system behavior by inspecting balance equations. For example, given an equation that has the form $[dC_A/dt = 4 - 2C_A,\ C_A(0) = 0]$, sketch the expected plot of C_A versus t without integrating the equation.
- Obtain analytical solutions to problems that involve single separable first-order differential balance equations.
- Derive balance equations for systems that involve several dependent variables [e.g., $y_1 = C_A(t)$, $y_2 = C_B(t)$, $y_3 = T(t)$] and express the equations in a form suitable for solution using equation-solving software $[dy_i/dt = f_i(y_1, y_2, \ldots, y_n, t), i = 1, 2, \ldots, n]$.

10.1 THE GENERAL BALANCE EQUATION . . . AGAIN

In Section 4.2, the general balance equation (4.2-1) was given as

$$\text{accumulation} = \text{input} + \text{generation} - \text{output} - \text{consumption}$$

Two forms of this equation were discussed: differential balances, which relate instantaneous rates of change at a moment in time, and integral balances, which relate changes that occur over a finite time period. We examine in this section the nature of the relationship between these two types of balances; in doing so, we belatedly show why they are called differential and integral.

[1] In reality, the concept of a true steady state is fiction, since there are *always* process variable fluctuations in real systems. When you assume steady-state operation, you are assuming that these fluctuations are small enough to be neglected without causing serious errors in calculated values.

10.1a Differential Balances

Suppose a species A is involved in a process. Let $\dot{m}_{in}$(kg/s) and $\dot{m}_{out}$(kg/s) be the rates at which A enters and leaves the process by crossing the boundaries, and let $\dot{r}_{gen}$(kg/s) and $\dot{r}_{cons}$(kg/s) be the rates of generation and consumption of A within the system by chemical reaction. Any or all of the variables $\dot{m}_{in}$, $\dot{m}_{out}$, $\dot{r}_{gen}$, and $\dot{r}_{cons}$ may vary with time.

Let us now write a balance on A for a period of time from t to $t + \Delta t$, supposing that Δt is small enough for the quantities $\dot{m}_{in}$, $\dot{m}_{out}$, $\dot{r}_{gen}$, and $\dot{r}_{cons}$ to be considered constant. (Since we will eventually let Δt approach 0, this assumption is not restrictive.) The terms of a balance on A are easily calculated.

$$\begin{aligned} \text{input(kg)} &= \dot{m}_{in}(\text{kg/s})\Delta t(\text{s}) \\ \text{output} &= \dot{m}_{out}\Delta t \\ \text{generation} &= \dot{r}_{gen}\Delta t \\ \text{consumption} &= \dot{r}_{cons}\Delta t \end{aligned}$$

We also suppose that the mass of A in the system changes by an amount ΔM(kg) during this small time interval. By definition, ΔM is the accumulation of A in the system. From the balance equation, (4.2-1),

$$\Delta M = (\dot{m}_{in} + \dot{r}_{gen} - \dot{m}_{out} - \dot{r}_{cons})\Delta t \qquad \textbf{(10.1-1)}$$

If now we divide by Δt and then let Δt approach 0, the ratio $\Delta M/\Delta t$ becomes the derivative of M with respect to $t(dM/dt)$, and the balance equation becomes

$$\boxed{\frac{dM}{dt} = \dot{m}_{in} + \dot{r}_{gen} - \dot{m}_{out} - \dot{r}_{cons}} \qquad \textbf{(10.1-2)}$$

This is the general differential balance equation: M is the amount of the balanced quantity in the system, and the four terms on the right side are rates that may vary with time.

If Equation 10.1-2 is applied to a continuous system at steady state, the quantity M must be a constant, its time derivative therefore equals zero, and the equation reduces to the familiar equation introduced in Chapter 4:

$$\text{input} + \text{generation} = \text{output} + \text{consumption}$$

However, as long as any term varies with time, the derivative on the left side of Equation 10.1-2 remains part of the equation. We conclude that *the balance equation for an unsteady-state system at an instant of time is a differential equation* (hence the term differential balance).

Equation 10.1-2 is an ordinary first-order differential equation. Before it can be solved to yield an expression for $M(t)$, a **boundary condition** must be provided—a specified value of the dependent variable (M) at some value of the independent variable (t). Frequently, the value of M at time $t = 0$ (an "initial condition") is specified. The complete balance equation would be Equation 10.1-2 followed by

$$t = 0, M = \ldots$$

or simply

$$M(0) = \ldots$$

When you analyze a transient system, your analysis is not complete unless every differential equation you derive is accompanied by a boundary condition similar to one of those just given.

The procedure for deriving a differential balance on an unsteady-state system normally begins with three steps: (1) Delete terms from the general balance equation that are either zero or negligible; (2) write an expression for the total amount of the balanced quantity (mass, particles, moles of a species, energy, etc.) in the system; and (3) differentiate the expression with respect to time to determine the accumulation term. Thereafter, substitute expressions for the nonzero terms in the equation, cancel variables if possible, and formulate a boundary condition (or an initial condition at $t = 0$). The next example gives two illustrations of this procedure.

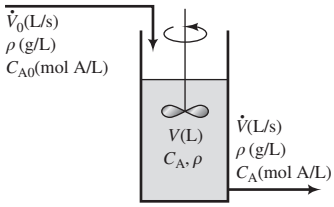
Example 10.1-1 Differential Balances on a Chemical Reactor

Equipment Encyclopedia
reactors-CSTR

www.wiley.com/college/felder

A continuous stirred-tank reactor is used to produce a compound R in the liquid-phase reaction A → R. Feed enters the reactor at a rate of $\dot{V}_0$(L/s); the concentration of the reactant in the feed is C_{A0}(mol A/L); and the volume of the tank contents is V(L). The vessel may be considered perfectly mixed, so that the concentration of A in the product stream equals that in the tank. For this process the rate of consumption of A equals kC_A[mol/(s·L of reaction volume)]. All fluids (the feed, the tank contents, and the product) may be taken to have the same density, ρ(g/L).

Write differential balances on total mass and on moles of A, expressing the balances in terms of the variables shown on the following diagram:



Solution Basis: Given Quantities

Total Mass Balance (generation = 0, consumption = 0)

$$\text{accumulation} = \text{input} - \text{output}$$

$$\text{Mass in reactor:} \quad M(\text{g}) = V(L)\rho(g/L)$$

$$\Downarrow$$

$$\text{accumulation(g/s)} = \frac{dM}{dt} = \frac{d(V\rho)}{dt} = \rho\frac{dV}{dt} \text{ (since } \rho \text{ is constant)}$$

$$\text{input(g/s)} = \dot{V}_0(\text{L/s})\rho(\text{g/L})$$

$$\text{output(g/s)} = \dot{V}(\text{L/s})\rho(\text{g/L})$$

$$\Downarrow$$

$$\rho\frac{dV}{dt} = \dot{V}_0\rho - \dot{V}\rho$$

$$\Downarrow \text{ cancel } \rho$$

$$\boxed{\begin{aligned} &dV/dt = \dot{V}_0 - \dot{V} \\ &t = 0, \quad V = V_0 \end{aligned}}$$

where V_0 is the initial volume of the tank contents.

Question: If $\dot{V}_0 = \dot{V}$ what does the mass balance tell you?

Balance on A

$$\text{accumulation} = \text{input} - \text{output} - \text{consumption}$$

$$\text{Moles of A in the reactor} = V(\text{L})C_\text{A}(\text{mol/L})$$

$$\Downarrow$$

$$\text{accumulation (mol A/s)} = \frac{d(VC_\text{A})}{dt}$$

$$\text{input (mol A/s)} = \dot{V}_0(\text{L/s})C_{\text{A0}}(\text{mol A/L})$$

$$\text{output (mol A/s)} = \dot{V}(\text{L/s})C_\text{A}(\text{mol A/L})$$

$$\text{consumption (molA/s)} = kC_\text{A}[\text{mol A/(s}\cdot\text{L)}]V(\text{L})$$

$$\Downarrow$$

$$\boxed{\begin{gathered}\frac{d(VC_\text{A})}{dt} = \dot{V}_0C_{\text{A0}} - \dot{V}C_\text{A} - kC_\text{A}V \\ t = 0, \quad C_\text{A} = C_\text{A}(0)\end{gathered}}$$

where $C_\text{A}(0)$ is the concentration of A in the initial tank contents. How you would solve this equation for the output concentration $C_\text{A}(t)$ depends on how the quantities $\dot{V}_0$, $\dot{V}$, and C_{A0} vary with time.

The procedure to follow when solving a problem involving a transient balance is to derive the differential balance equation, integrate it between initial and final times, and solve for the desired quantity or function of time.

Example 10.1-2 Water Balance on a City Reservoir

The water level in a municipal reservoir has been decreasing steadily during a dry spell, and local meteorologists predict that the drought could continue for another 60 days. The water company estimates that the consumption rate in the city is approximately 10^7 L/day. The State Conservation Service estimates that rainfall and stream drainage into the reservoir coupled with evaporation from the reservoir should yield a net water input rate of $10^6 \exp(-t/100)$ L/day, where t is the time in days from the beginning of the drought, at which time the reservoir contained an estimated 10^9 liters of water.

(a) Write a differential balance on the water in the reservoir.

(b) Integrate the balance to calculate the reservoir volume at the end of the 60 days of continued drought.

Solution

(a) We will write a balance on the mass of water in the reservoir, M(kg), but express the equation in terms of volumes to make use of the given data, using the relationship $M(\text{kg}) = \rho(\text{kg/L})V(\text{L})$. Since water is neither generated nor consumed by chemical reactions in the reservoir (more precisely, we assume that its rates of generation and consumption are negligible), the differential balance equation is

$$\text{accumulation} = \text{input} - \text{output}$$

$$\frac{dM}{dt} = \dot{m}_\text{in} + \dot{r}_\text{gen} - \dot{m}_\text{out} - r_\text{cons} \quad \text{(each term in kg/day)}$$

$$\Downarrow$$

$$\frac{dM}{dt} = \frac{d}{dt}(\rho V) = \rho(\text{kg/L})\frac{dV}{dt}(\text{L/day}) \quad (\text{since } \rho \text{ is constant})$$

$$\dot{m}_\text{in} = \rho(\text{kg/L})[10^6 e^{-t/100}(\text{L/day})]$$

$$\dot{m}_\text{out} = \rho(\text{kg/L})(10^7\ \text{L/day})$$

$$\dot{r}_\text{gen} = \dot{r}_\text{cons} = 0 \quad (\text{water is not produced or consumed in the reservoir})$$

$$\Downarrow \text{Cancel } \rho$$

$$\boxed{\begin{gathered}\frac{dV(t)}{dt} = 10^6 \exp(-t/100) - 10^7 \\ t = 0, \quad V = 10^9\ \text{L}\end{gathered}}$$

(b) We now separate variables and integrate the differential balance equation from $t = 0$ to $t = 60$ days:

$$\int_{V(0)}^{V(60)} dV = \int_0^{60\text{ d}} [10^6 \exp(-t/100) - 10^7]\, dt$$

$$\Downarrow$$

$$V(60\text{ days}) - V(0) = \int_0^{60\text{ d}} 10^6 e^{-t/100} dt - \int_0^{60\text{ d}} 10^7 dt$$

$$\Downarrow \quad V(0) = 10^9 \text{ liters}$$

$$V(60\text{ days}) = 10^9 - 10^6(10^2)e^{-t/100}\Big]_0^{60\text{ d}} - 10^7 t\Big]_0^{60\text{ d}}$$

$$= \boxed{4.45 \times 10^8 \text{ L}} \quad (verify)$$

10.1b A Brief Look Back at Integral Balances

Let us reconsider the form of the differential balance given in Equation 10.1-3.

$$\frac{dM}{dt} = \dot{m}_{\text{in}} + \dot{r}_{\text{gen}} - \dot{m}_{\text{out}} - \dot{r}_{\text{cons}} \qquad \textbf{(10.1-3)}$$

The equation may be rewritten as

$$dM = \dot{m}_{\text{in}} dt + \dot{r}_{\text{gen}} dt - \dot{m}_{\text{out}} dt - \dot{r}_{\text{cons}} dt$$

and integrated from an initial time t_0 to a later time t_f, to obtain

$$\int_{t_0}^{t_f} dM = M(t_f) - M(t_0) = \int_{t_0}^{t_f} \dot{m}_{\text{in}} dt + \int_{t_0}^{t_f} \dot{r}_{\text{gen}} dt - \int_{t_0}^{t_f} \dot{m}_{\text{out}} dt - \int_{t_0}^{t_f} \dot{r}_{\text{cons}} dt \qquad \textbf{(10.1-4)}$$

This is the integral balance equation. The left side is the accumulation of the balanced quantity in the system between t_0 and t_f. The term $(\dot{m}_{\text{in}} dt)$ is the amount of the balanced quantity that enters the system in the infinitesimal interval from t to $t + dt$, so that the integral

$$\int_{t_0}^{t_f} \dot{m}_{\text{in}} dt$$

is the total amount that enters between t_0 and t_f. Similar reasoning can be applied to the other terms, leading to the conclusion that Equation 10.1-4 is simply another statement of the general balance equation

$$\text{accumulation} = \text{input} + \text{generation} - \text{output} - \text{consumption} \qquad \textbf{(10.1-5)}$$

only now each term represents an amount of the balanced quantity rather than a rate. For a closed (batch) system, if the balanced quantity is mass (as opposed to energy), $\dot{m}_{\text{in}} = \dot{m}_{\text{out}} = 0$, and the equation may be written

$$M_{\text{initial}} + \int_{t_0}^{t_f} \dot{r}_{\text{generation}} dt = M_{\text{final}} + \int_{t_0}^{t_f} \dot{r}_{\text{consumption}} dt$$

or

$$\text{initial input} + \text{generation} = \text{final output} + \text{consumption}$$

This is the form of the integral balance equation given in Chapter 4 for a closed system.

Test Yourself

(Answers, p. 660)

A liquid, A, is poured at a rate of 10 kg/h into a tank that initially contains 350 kg of a second liquid, B. A reaction A → 2B takes place. Liquid is withdrawn from the reaction vessel at a rate of 10 kg/h.

1. Which terms of the general balance equation

$$\text{accumulation} = \text{input} + \text{generation} - \text{output} - \text{consumption}$$

do *not* equal zero in each of the following balances on the reaction vessel?
(a) Total mass. **(b)** Moles of A. **(c)** Moles of B.
2. Write and solve a differential mass balance on the system, letting $m(t)$ be the total mass of the system contents.

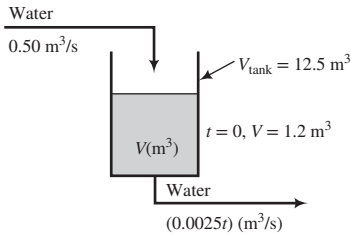
10.2 MATERIAL BALANCES

10.2a Total Mass Balances

A total mass balance necessarily has the form [accumulation = input − output], since mass can neither be generated nor consumed.[2] The accumulation term is always dM/dt, where $M(t)$ is the mass of the system contents. Once you have determined $M(t)$ by solving the differential balance equation, you may have to verify that the mathematical solution remains within the bounds of physical reality—that it does not become negative, for example, or that it does not exceed the total capacity of the system.

Example 10.2-1 Mass Balance on a Water Storage Tank

A 12.5-m^3 tank is being filled with water at a rate of 0.050 m^3/s. At a moment when the tank contains 1.20 m^3 of water, a leak develops in the bottom of the tank and gets progressively worse with time. The rate of leakage (m^3/s) can be approximated as $0.0025t$, where t(s) is the time from the moment the leak begins.



1. Write a mass balance on the tank and use it to obtain an expression for dV/dt, where V is the volume of water in the tank at any time. Provide an initial condition for the differential equation.
2. Solve the balance equation to obtain an expression for $V(t)$ and draw a plot of V versus t.

Solution

1. The total mass of the tank contents is $M(\text{kg}) = \rho(\text{kg/m}^3)V(\text{m}^3)$, where $\rho = 1000$ kg/m^3 is the density of liquid water. Then

$$\text{accumulation (kg/s)} = \frac{d(\rho V)}{dt} = \rho\frac{dV}{dt}$$

[2] We are excluding nuclear reactions from consideration.

(The second step follows from the fact that the density of the liquid water in the tank is independent of time and so may be taken out of the derivative.)

$$\text{input (kg/s)} = \rho(\text{kg/m}^3)(0.05\ \text{m}^3/\text{s}) = 0.05\rho$$

$$\text{output (kg/s)} = \rho(\text{kg/m}^3)[0.0025t(\text{m}^3/\text{s})] = 0.0025\rho t$$

Substituting these terms into the water balance equation (accumulation = input − output) and canceling ρ yields the differential equation

$$\boxed{\begin{aligned} \frac{dV}{dt} &= 0.050\ \text{m}^3/\text{s} - 0.0025t \\ t &= 0, \quad V = 1.2\ \text{m}^3 \end{aligned}}$$

Verify that each term in the equation (including dV/dt) has units of m^3/s.

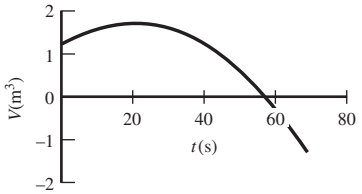
2. To solve the equation, we separate variables (bring dt to the right-hand side) and integrate from the initial condition ($t = 0$, $V = 1.2\ \text{m}^3$) to an arbitrary time, t, and corresponding volume, V.

$$\begin{aligned} dV(\text{m}^3) = (0.050 - 0.0025t)dt &\implies \int_{1.2\ \text{m}^3}^{V} dV = \int_0^t (0.050 - 0.0025t)dt \\ &\implies V\Big]_{1.2\ \text{m}^3}^{V} = \left(0.050t - 0.0025\frac{t^2}{2}\right)\Big]_0^t \\ &\implies V(\text{m}^3) = 1.2\ \text{m}^3 + 0.050t - 0.00125t^2 \end{aligned}$$

Check 1: When $t = 0$, $V = 1.2\ \text{m}^3$ (confirming the given initial condition). ✔

Check 2: $dV/dt = 0.050 - 0.0025t$ [differentiating $V(t)$ yields the original equation for dV/dt]. ✔

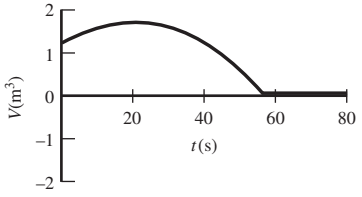
A plot of the derived expression for $V(t)$ is as follows:



Initially, the filling causes the volume of the tank contents to increase, but as the leak gets larger the tank begins to drain. The maximum volume is $1.7\ \text{m}^3$, well below the tank capacity of $12.5\ \text{m}^3$. At about $t = 57$ s the contents drain completely. The mathematical formula for V predicts negative volumes after this time, but physically the volume must remain at zero (the liquid discharges as fast as it is poured in). The actual solution of the balance equation is therefore

$$\boxed{\begin{aligned} V(\text{m}^3) &= 1.2 + 0.050t - 0.00125t^2 \quad 0 \le t \le 57\ \text{s} \\ &= 0 \qquad\qquad\qquad\qquad\quad t > 57\ \text{s} \end{aligned}}$$

The plot shown above should be changed in the range $t > 57$ s to a line coincident with the t axis.



10.2b A Brief Look Back at Calculus

As you will see, balances on transient systems often lead to differential equations that look like this:

$$\frac{d(VC_A)}{dt} = 1.50 \text{ mol/s} - 0.200VC_A \tag{10.2-1}$$

$$C_A(0) = 2.00 \text{ mol/L}$$

In this equation, 1.50 mol/s would be the sum of the input and generation terms in the balance on species A and $0.200VC_A$ would be the sum of the output and consumption terms. The goal would be to solve the differential balance to determine the concentration C_A(mol/L) as a function of time t(s), either as an analytical function or in the form of a table or plot.

This section reviews some calculus rules and procedures for solving differential equations like Equation 10.2-1. In what follows, x is an independent variable, $y(x)$ is a dependent variable, and a is a constant.

Rule 1*: *Derivative of a constant times a function

$$\frac{d(ay)}{dx} = a\frac{dy}{dx} \tag{10.2-2}$$

If the system volume in Equation 10.2-1 is constant, the equation would become

$$V\frac{dC_A}{dt} = 1.50 \text{ mol/s} - 0.200VC_A$$

We will shortly review how to solve this equation.

Rule 2*: *Product rule for differentiation

$$\frac{d(y_1y_2)}{dx} = y_1\frac{dy_2}{dx} + y_2\frac{dy_1}{dx} \tag{10.2-3}$$

If the system volume in Equation 10.2-1 changes with time (e.g., because the tank is being filled or discharged, or the reactor is a cylinder with a moving piston), the product rule yields

$$\frac{d(VC_A)}{dt} = V\frac{dC_A}{dt} + C_A\frac{dV}{dt} = 1.50 \text{ mol/s} - 0.200C_A$$

or

$$\frac{dC_A}{dt} = \frac{1}{V}[1.50 \text{ mol/s} - 0.200C_A] - \frac{C_A}{V}\left(\frac{dV}{dt}\right)$$

If V is constant, this equation reduces to the one given following Rule 1 (convince yourself). If it isn't, to solve for $C_A(t)$ you would have to obtain an independent expression for dV/dt and solve both equations simultaneously. We will discuss problems of this type in Section 10.5.

Rule 3*: *Solution of separable first-order differential equations

The general form of a first-order differential equation is

$$\frac{dy}{dx} = f(x, y)$$

Consider a specific example:

$$\frac{dy}{dx} = 3xy$$

Novice calculus students are often tempted to solve this equation by doing something like

$$y = \int (3xy)dx$$

which is correct but useless, since you cannot evaluate that integral without first substituting for $y(x)$, the function you are trying to determine.

A *separable* first-order differential equation is one that can be written in the form

$$\frac{dy}{dx} = f_1(x)f_2(y)$$
$$x = 0, \quad y = y(0)$$

The procedure for solving a separable equation is to bring all terms involving y (including dy) to one side of the equation and all terms involving x (including dx) to the other side, and then to integrate each side over its respective variable from the initial value [0 for x, $y(0)$ for y] to an arbitrary value:

$$\frac{dy}{dx} = f_1(x)f_2(y) \xrightarrow{\text{separate}} \frac{dy}{f_2(y)} = f_1(x)dx \xrightarrow{\text{integrate}} \int_{y(0)}^{y} \frac{dy}{f_2(y)} = \int_0^x f_1(x)dx \qquad \textbf{(10.2-4)}$$
$$x = 0, \quad y = y(0)$$

Each integral involves a function of only the variable of integration (y on the left, x on the right), and so both integrals can be evaluated to obtain an expression relating x and y.

Reconsider Equation 10.2-1 once more, letting the system volume V equal 1.00 liter.

$$\left\{ \begin{array}{l} \dfrac{dC_A}{dt} = 1.50 \text{ mol/s} - (0.200 \text{ L/s})C_A \\ t = 0, \quad C_A = 2.00 \text{ mol/L} \end{array} \right\}$$

$$\xrightarrow{\text{separate}} \frac{dC_A}{1.50 - 0.200C_A} = dt \xrightarrow{\text{integrate}} \int_{2.00}^{C_A} \frac{dC_A}{1.50 - 0.200C_A} = \int_0^t dt$$

$$\Longrightarrow -\frac{1}{0.200} \ln(1.50 - 0.200C_A)\Big]_{2.00}^{C_A} = t \Longrightarrow \ln\left(\frac{1.50 - 0.200C_A}{1.50 - 0.400}\right) = -0.200t$$

$$\Longrightarrow \frac{1.50 - 0.200C_A}{1.10} = e^{-0.200t} \Longrightarrow \boxed{C_A(\text{mol/L}) = \frac{1}{0.200}\left(1.50 - 1.10e^{-0.200t(\text{s})}\right)}$$

The last step is to check the solution. There are several ways to do it, which we will discuss later in the chapter, but the easiest one is to verify that the initial condition is satisfied. In this case, it is. If you substitute $t = 0$ into the expression for C_A, you should quickly find that $C_A = 2.0$.

Try to reproduce this procedure without looking back at it. The same procedure will be used to solve almost every balance equation in the remainder of this chapter.

Test Yourself

(Answers, p. 660)

Separate variables for each of the following equations to obtain integrals of the form of Equation 10.2-4. Then proceed as far as you can to obtain expressions for $y(t)$.

1. $(dy/dt) = 2 - t$, $y(0) = 1$.
2. $(dy/dt) = 2 - y$, $y(0) = 1$.
3. $(dy/dt) = (2 - t)(2 - y)$, $y(0) = 1$.

10.2c Balances on Single Well-Mixed Process Units

Here is the general procedure for writing and solving a transient material balance equation:

1. *Eliminate terms in the general balance equation that equal zero* (input and output for batch systems, generation and consumption for balances on total mass and nonreactive species).
2. *Write an expression for the total amount of the balanced species in the system* [$V(\text{m}^3)\rho(\text{kg/m}^3)$ for total mass, $V(\text{m}^3)C_\text{A}(\text{mol A/m}^3)$ or $n_\text{total}(\text{mol})x_\text{A}(\text{mol A/mol})$ for species A]. *Differentiate the expression with respect to time to obtain the accumulation term in the balance equation.*
3. *Substitute system variables into the remaining terms* (input, generation, output, consumption) *in the balance equation*. Make sure that all terms have the same units (kg/s, lb-mole/h, etc.).
4. *If $y(t)$ is the dependent variable to be determined* (e.g., the mass of the system contents, the concentration of species A, the mole fraction of methane), *rewrite the equation to obtain an explicit expression for dy/dt. Supply a boundary condition*—the value of the dependent variable at a specified time (usually $t = 0$). This condition may be expressed as $[t = 0, y = y_0]$ or simply $[y(0) = y_0]$, where y_0 is a number.
5. *Solve the equation—analytically if possible, otherwise numerically*. In the processes to be analyzed in this chapter, you will generally be able to use separation of variables to obtain the solution analytically.
6. *Check the solution.* You can do so using any (and preferably all) of these methods:
   - **(a)** Substitute $t = 0$ and verify that the known initial condition $[y(0) = y_0]$ is obtained.
   - **(b)** Find the long-time asymptotic (steady-state) value of the dependent variable by setting dy/dt equal to 0 in the original balance equation and solving the resulting algebraic equation for y_ss, and then verify that if you let $t \to \infty$ in your solution, $y \to y_\text{ss}$. (The equation may not have a steady-state solution, in which case this method will not work.)
   - **(c)** Differentiate your solution to obtain an expression for dy/dt, substitute for y and dy/dt in the original differential equation, and verify that the equation is satisfied.
7. *Use your solution to generate a plot or table of y versus t.*

The next example illustrates this procedure.

Example 10.2-2 Transient Behavior of a Stirred-Tank Reactor

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reactor-CSTR

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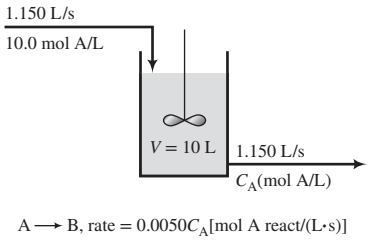
A liquid-phase reaction with stoichiometry A → B takes place in a continuous well-mixed 10.0-liter stirred-tank reactor. A schematic diagram of the process is shown below.



The reactor may be considered perfectly mixed, so that the contents are uniform and the concentration of A in the product stream equals that inside the tank. The tank is initially filled with a solution that contains 2.00 mol A/L, and the inlet and outlet flows then begin.

1. Write a balance on species A in the tank and provide an initial condition.
2. Calculate C_{AS}, the steady-state concentration of A in the tank (the value approached as $t \to \infty$).
3. Sketch the shape expected for a plot of C_A versus t.
4. Solve the balance equation for $C_A(t)$, check the solution, and draw the actual plot of C_A versus t.

Solution Compare what follows with the general procedure given prior to this example.

1. The total moles of A in the reactor at any time equals $(10.0\,\text{L})[C_A(\text{mol A/L})] = 10.0C_A\,(\text{mol A})$. Therefore,

$$\begin{aligned}
&\textit{Accumulation:} && \frac{d(10.0C_A)}{dt} = 10.0\,\frac{dC_A}{dt}\left(\frac{\text{mol A}}{\text{s}}\right)\\
&\textit{Input:} && (0.150\,\text{L/s})(10.0\,\text{mol A/L}) = 1.50\,\text{mol A/s}\\
&\textit{Output:} && (0.150\,\text{L/s})[C_A(\text{mol A/L})] = 0.150C_A(\text{mol A/s})\\
&\textit{Generation:} && 0\,\text{mol A/s (A is not a reaction product)}\\
&\textit{Consumption:} && (10.0\,\text{L})[0.0050C_A(\text{mol A/(L}\cdot\text{s)})] = 0.050C_A\,(\text{mol A/s})
\end{aligned}$$

   These terms are substituted into the balance equation on A (accumulation = input − output − consumption), which is then divided by 10.0 to obtain an expression for dC_A/dt. The result along with the initial condition for the equation $[C_A(0) = 2.00\,\text{mol A/L}]$ is

$$\boxed{\begin{gathered}\frac{dC_A}{dt} = 0.150\,\text{mol A/s} - (0.0200\,\text{L/s})C_A\\ t = 0, \quad C_A = 2.00\,\text{mol A/L}\end{gathered}}$$

2. At steady state nothing varies with time, so that the derivative of C_A (and of every other system variable) with respect to time must equal zero. Setting $dC_A/dt = 0$ in the balance equation and letting $C_A = C_{AS}$ (steady state) in the resulting equation yields

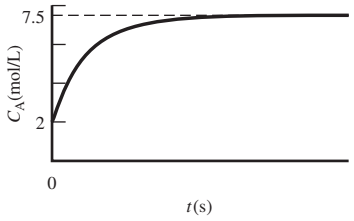
$$0 = 0.150\,\text{mol/s} - 0.0200C_{AS} \Longrightarrow \boxed{C_{AS} = 7.50\,\text{mol A/L}}$$

   If C_{AS} had not had an asymptotic (steady-state) limit, the equation would not have had a finite solution.

3. We can now deduce quite a lot about the plot of C_A versus t, even though we have not yet solved the differential balance equation. We know a point at $t = 0$ (the initial condition) and the asymptotic value as $t \to \infty$ (the steady-state solution), and we also have an expression for the slope of the plot at any time (dC_A/dt) as a function of the concentration (slope $= 0.150 - 0.0200C_A$). Let us summarize what we can deduce:
   - The plot originates at ($t = 0$, $C_A = 2.00$ mol/L).
   - At $t = 0$, the slope of the plot is $[0.150 - 0.0200](2.00\,\text{mol/s}) = 0.110$ mol/s. Since it is positive, C_A must increase as t increases.
   - As t continues to increase and C_A also increases, the slope of the curve $(0.150 - 0.0200C_A)$ gets progressively less positive. The curve must therefore be concave down.

   - After a long time, the plot asymptotes to $C_A = 7.50$ mol/L.

Combining all these observations leads to the following sketch:



4. We may now solve the differential balance to determine the values of C_A at specific values of t or vice versa. Reconsider the equation

$$\frac{dC_A}{dt} = 0.150 - 0.0200C_A$$
$$t = 0, \quad C_A = 2.00$$

Separating variables and integrating as in Equation 10.2-4 yields

$$\frac{dC_A}{0.150 - 0.0200C_A} = dt \Longrightarrow \int_{2.00}^{C_A} \frac{dC_A}{0.150 - 0.0200C_A} = \int_0^t dt = t$$

$$\Longrightarrow -\frac{1}{0.0200}\ln(0.150 - 0.0200C_A)\Big]_{2.00}^{C_A} = t \Longrightarrow \ln\left[\frac{0.150 - 0.0200C_A}{0.150 - 0.0200(2.00)}\right] = -0.0200t$$

$$\Longrightarrow \frac{0.150 - 0.0200C_A}{0.110} = e^{-0.0200t} \Longrightarrow \boxed{C_A(\text{mol/L}) = 7.50 - 5.50e^{-0.0200t}}$$

(Verify each step.)

We next check the solution.

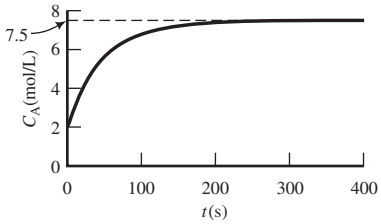
Check 1: Substitute $t = 0$ into the solution $\Longrightarrow C_A(0) = 2.00$ mol/L (the correct initial value). ✔

Check 2: Substitute $t \to \infty$ into the solution to obtain $C_A(\infty) = 7.50$ mol/L (the previously determined steady-state value). ✔

Check 3: Differentiate the equation to obtain an expression for dC_A/dt, and then substitute for both dC_A/dt and $C_A(t)$ in the original equation [$dC_A/dt = 1.50 - 0.200C_A$] to show that the solution satisfies the equation. ✔

Verify that the derived solution satisfies each of these conditions.

A plot of the solution matches the form of the plot previously sketched.



10.3 ENERGY BALANCES ON SINGLE-PHASE NONREACTIVE PROCESSES

The general energy balance has the form

$$\text{accumulation} = \text{input} - \text{output} \tag{10.3-1}$$

since energy can neither be generated nor consumed.

Suppose $E_{sys}(t)$ is the total energy (internal + kinetic + potential) of a system, and $\dot{m}_{in}$ and $\dot{m}_{out}$ are the mass flow rates of the system input and output streams. (If the system is closed, each flow rate equals zero.) Proceeding as in the development of the transient mass balance equation, we apply the general energy balance equation (10.3-1) to the system in a small time interval from t to $t + \Delta t$, during which time the properties of the input and output streams remain approximately constant. The terms of the equation are as follows (see Section 7.4):

$$\text{accumulation} = \Delta E_{sys} = \Delta U_{sys} + \Delta E_{k,sys} + \Delta E_{p,sys}$$

$$\text{input} = \dot{m}_{in}\left(\hat{H}_{in} + \frac{u_{in}^2}{2} + gz_{in}\right)\Delta t + \dot{Q}\Delta t + \dot{W}_s\Delta t$$

$$\text{output} = \dot{m}_{out}\left(\hat{H}_{out} + \frac{u_{out}^2}{2} + gz_{out}\right)\Delta t$$

where the quantities in parentheses are the specific enthalpies, kinetic energies, and potential energies of the input and output streams, and $\dot{Q}$ and $\dot{W}_s$ are the rates of transfer of heat and shaft work. (See Section 7.4c.) Any or all of the variables $\dot{m}$, $\hat{H}$, u, z, $\dot{Q}$, and $\dot{W}_s$ may vary with time.

If we now substitute the given expressions for accumulation, input, and output into Equation 10.3-1, divide by Δt, and let Δt approach zero, we obtain the general differential energy balance:

$$\frac{dU_{sys}}{dt} + \frac{dE_{k,sys}}{dt} + \frac{dE_{p,sys}}{dt} = \dot{m}_{in}\left(\hat{H}_{in} + \frac{u_{in}^2}{2} + gz_{in}\right) - \dot{m}_{out}\left(\hat{H}_{out} + \frac{u_{out}^2}{2} + gz_{out}\right) + \dot{Q} + \dot{W}_s \tag{10.3-2}$$

If there are several input and output streams, a term of the form

$$\dot{m}\left(\hat{H} + \frac{u^2}{2} + gz_{in}\right)$$

must be included in Equation 10.3-2 for each stream.

It is quite difficult to solve Equation 10.3-2 unless a number of simplifications are made. We will restrict our consideration to systems that satisfy the following conditions:

1. The system has at most a single input stream and a single output stream, each with the same mass flow rate.

$$\dot{m}_{in} = \dot{m}_{out} = \dot{m} \tag{10.3-3}$$

A consequence of this assumption is that the mass of the system contents does not change with time.

2. Kinetic and potential energy changes in the system and between the inlet and outlet streams are negligible.

$$\frac{dE_{k,sys}}{dt} \approx \frac{dE_{p,sys}}{dt} \approx 0 \tag{10.3-4}$$

$$\dot{m}\left(\frac{u_{in}^2}{2} - \frac{u_{out}^2}{2}\right) \approx 0 \tag{10.3-5}$$

$$\dot{m}(gz_{in} - gz_{out}) \approx 0 \tag{10.3-6}$$

Under these conditions, Equation 10.3-2 simplifies to

$$\frac{dU_{\text{sys}}}{dt} = \dot{m}(\hat{H}_{\text{in}} - \hat{H}_{\text{out}}) + \dot{Q} + \dot{W}_{\text{s}} \tag{10.3-7}$$

If the equation is applied to a closed system, $\dot{m} = 0$, and the rate of transfer of energy as shaft work, $\dot{W}_{\text{s}}$, must be replaced by the total rate of energy transfer as work, $\dot{W}$.

Equation 10.3-7 is simple in appearance, but its solution is still generally difficult to obtain. If, for example, the composition or temperature of the system contents varies with position in the system, it is difficult to express the total internal energy U_{sys} in terms of measurable quantities, and a similar problem occurs if phase changes or chemical reactions take place in the course of the process. To illustrate the solution of energy balance problems without becoming too involved in these thermodynamic complexities, we will impose the additional restrictions that follow.

3. The temperature and composition of the system contents do not vary with position within the system (i.e., the system is perfectly mixed). In consequence, the outlet stream and the system contents must be at the same temperature, or

$$T_{\text{out}} = T_{\text{sys}} = T \tag{10.3-8}$$

4. No phase changes or chemical reactions take place within the system; $\hat{U}$ and $\hat{H}$ are independent of pressure; and the mean heat capacities C_v and C_p of the system contents (and of the inlet and outlet streams) are independent of composition and temperature, and so do not change with time. Then, if T_{r} is a reference temperature at which $\hat{H}$ is defined to be zero and M is the mass (or number of moles) of the system contents,

$$U_{\text{sys}} = M\hat{U}_{\text{sys}} = M[\hat{U}(T_r) + C_v(T - T_{\text{r}})]$$

$$\Downarrow \; M, \hat{U}(T_{\text{r}}), \text{and } C_v \text{ are constant}$$

$$\frac{dU_{\text{sys}}}{dt} = MC_v\frac{dT}{dt} \tag{10.3-9}$$

$$\hat{H}_{\text{in}} = C_p(T_{\text{in}} - T_{\text{r}}) \tag{10.3-10}$$

$$\hat{H}_{\text{out}} = C_p(T_{\text{out}} - T_{\text{r}})$$

$$\Downarrow \text{ Equation 10.3-8}$$

$$\hat{H}_{\text{out}} = C_p(T - T_{\text{r}}) \tag{10.3-11}$$

Finally, we may substitute the expressions of Equations 10.3-3 through 10.3-11 into the general energy balance (Equation 10.3-2) to obtain for an open system

Open System:

$$\boxed{MC_v\frac{dT}{dt} = \dot{m}C_p(T_{\text{in}} - T) + \dot{Q} + \dot{W}_{\text{s}}} \tag{10.3-12}$$

(Verify this result for yourself.) For a closed system, the equation is

Closed System:

$$\boxed{MC_v\frac{dT}{dt} = \dot{Q} + \dot{W}} \tag{10.3-13}$$

To summarize, the conditions under which Equations 10.3-12 and 10.3-13 are valid are: (a) negligible kinetic and potential energy changes, (b) no accumulation of mass in the system,

(c) pressure independence of $\hat{U}$ and $\hat{H}$, (d) no phase changes or chemical reactions, and (e) a spatially uniform system temperature. Any or all of the variables T, T_{in}, $\dot{Q}$ and $\dot{W}_s$ (or $\dot{W}$) may vary with time, but the system mass, M, the mass throughput rate, $\dot{m}$, and the heat capacities, C_v and C_p, must be constants.

The following example illustrates the derivation and solution of an energy balance on a closed system that satisfies these conditions.

Example 10.3-1 Startup of a Batch Reactor

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A well-stirred batch reactor wrapped in an electrical heating mantle is charged with a liquid reaction mixture. The reactants must be heated from an initial temperature of 25°C to 250°C before the reaction can take place at a measurable rate. Use the data given below to determine the time required for this heating to take place.

Reactants:	Mass = 1.50 kg
	$C_v = 0.900\ \text{cal/(g·°C)}$
Reactor:	Mass = 3.00 kg
	$C_v = 0.120\ \text{cal/(g·°C)}$
Heating rate:	$\dot{Q} = 500.0\ \text{W}$

Negligible reaction and no phase changes during heating.
Negligible energy added to the system by the stirrer.

Solution We first note that the conditions of validity of the simplified closed system energy balance equation, Equation 10.3-13, are all satisfied (*verify*); moreover, since the system has constant volume and the energy input due to the stirrer is presumed negligible, $\dot{W} \approx 0$. The equation therefore becomes

$$MC_v \frac{dT}{dt} = \dot{Q}$$

$$t = 0, \quad T_{sys} = 25°\text{C}$$

The task is now to integrate this equation from the initial state of the system ($t = 0$, $T = 25°$C) to the final state ($t = t_f$, $T = 250°$C), and to solve the integrated equation for the heating time t_f. Rearranging the equation,

$$MC_v dT = \dot{Q} dt$$

$$\Downarrow \text{ Integrate}$$

$$\int_{25°\text{C}}^{250°\text{C}} MC_v dT = \int_0^{t_f} \dot{Q} dt$$

$$\Downarrow \dot{Q}, M, \text{ and } C_v \text{ are constant}$$

$$MC_v(250°\text{C} - 25°\text{C}) = \dot{Q} t_f$$

$$\Downarrow$$

$$t_f = \frac{225 MC_v}{\dot{Q}}$$

The heat capacity of the system is obtained from Equation 8.3-13 as

$$C_v = \frac{M_{\text{reactants}}}{M}(C_v)_{\text{reactants}} + \frac{M_{\text{reactor}}}{M}(C_v)_{\text{reactor}}$$

$$\Downarrow$$

$$MC_v = (1500\ \text{g})\left(0.900\ \frac{\text{cal}}{\text{g·°C}}\right) + (3000\ \text{g})\left(0.120\ \frac{\text{cal}}{\text{g·°C}}\right)$$

$$= (1710\ \text{cal/°C})(4.184\ \text{J/cal})$$

$$= 7150\ \text{J/°C}$$

The final result is

$$t_f = \frac{225 MC_v}{\dot{Q}}$$

$$\Big\Vert \quad MC_v = 7150\ \text{J/°C}$$

$$\Big\Downarrow \quad \dot{Q} = 500.0\ \text{W} = 500.0\ \text{J/s}$$

$$t_f = \frac{7150\ \text{J/°C}}{500.0\ \text{J/s}}(225\text{°C})$$

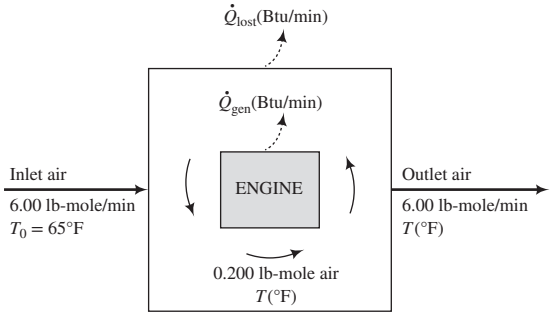
$$= 3220\ \text{s} \Longrightarrow \boxed{53.7\ \text{min}}$$

Question: Which restriction on the energy balance (Equation 10.3-13) would probably be violated if the reactants were not stirred?

The final example illustrates a transient energy balance on a continuous system.

Example 10.3-2 Transient Behavior of an Air-Cooling System

An air-cooled engine generates heat at a constant rate $\dot{Q}_{\text{gen}} = 8530$ Btu/min.



The air in the engine housing is circulated rapidly enough for its temperature to be considered uniform and equal to the temperature of the outlet air. Air passes through the engine housing at a rate of 6.00 lb-mole/min, entering at a temperature of 65°F, and an average of 0.200 lb-mole of air is contained within the engine housing. (We will neglect the variation of this quantity with the changing temperature of the gas.) Heat is lost from the housing to its surroundings at a rate

$$\dot{Q}_{\text{lost}}(\text{Btu/min}) = [33.0\ \text{Btu/(°F·min)}](T - 65\text{°F})$$

Suppose the engine is started with the inside air temperature equal to 65°F.

1. Calculate the steady-state air temperature if the engine runs continuously for a very long time, assuming

$$C_v = 5.00\ \text{Btu/(lb-mole·°F)}$$

2. Derive a differential equation for the variation of the outlet temperature with time from startup and solve it. Calculate how long it will take for the outlet temperature to reach one degree below its steady-state value.

Solution System = the air within the engine housing.

1. The steady-state energy balance equation may be obtained by setting dT/dt equal to zero in Equation 10.3-12.

$$0 = \dot{m}C_p(T_{\text{in}} - T) + \dot{Q} + \dot{W}_s$$

$$\Downarrow$$

$T_{\text{in}} = 65°\text{F}$ (given)
$T = T_s(°\text{F})$ (steady-state outlet temperature)
$\dot{W}_s = 0$ (no moving parts)
$\dot{Q} = \dot{Q}_{\text{gen}} - \dot{Q}_{\text{lost}}$

$$\dot{m}C_p(T_s - 65.0°\text{F}) = 8530\ \text{Btu/min} - 33.0(T_s - 65.0°\text{F})$$

Assuming ideal-gas behavior

$$C_p = C_v + R = (5.00 + 1.99)\ \text{Btu}/(\text{lb-mole}\cdot°\text{F}) \qquad \text{(Equation 8.3-12)}$$

$$\dot{m}C_p = \frac{6.00\ \text{lb-mole}}{\text{min}} \left| \frac{6.99\ \text{Btu}}{\text{lb-mole}\cdot°\text{F}} \right. = 41.9\ \frac{\text{Btu}}{\text{min}\cdot°\text{F}}$$

The energy balance then becomes

$$41.9(T_s - 65.0°\text{F}) = 8530\ \text{Btu/min} - 33.0(T_s - 65.0°\text{F})$$

$$\Downarrow$$

$$\boxed{T_s = 179°\text{F}}$$

2. The unsteady-state balance equation (10.3-12) is, for our system,

$$MC_v \frac{dT}{dt} = \dot{m}C_p(65°\text{F} - T) + \dot{Q}_{\text{gen}} - \dot{Q}_{\text{lost}}$$

$$\Downarrow$$

$M = 0.200$ lb-mole
$C_v = 5.00\ \text{Btu}/(\text{lb-mole}\cdot°\text{F})$
$\dot{m}C_p = 41.9\ \text{Btu}/(\text{min}\cdot°\text{F})$ [from Part 1]
$\dot{Q}_{\text{gen}} = 8530\ \text{Btu/min}$
$\dot{Q}_{\text{lost}} = 33.0(T - 65°\text{F})\text{Btu}/(\text{min}\cdot°\text{F})$

$$\boxed{\begin{gathered}\frac{dT}{dt} = -74.9T + 13{,}400°\text{F/min} \\ t = 0, \quad T = 65°\text{F}\end{gathered}}$$

You can check this result by setting $dT/dt = 0$ and solving the resulting equation for the steady-state value of T. The result is $(13{,}400/74.9)°\text{F} = 179°\text{F}$, in agreement with the result of Part 1.

The solution of the equation is obtained by separating variables and integrating:

$$\int_{65°\text{F}}^{T} \frac{dT}{(13{,}400 - 74.9T)} = \int_0^t dt$$

$$\Downarrow$$

$$-\frac{1}{74.9}\ln(13{,}400 - 74.9T)\Big]_{65°\text{F}}^{T} = t$$

$$\Downarrow$$

$$\ln\frac{(13{,}400 - 74.9T)}{[13{,}400 - (74.9)(65)]} = -74.9t$$

$$\Downarrow$$

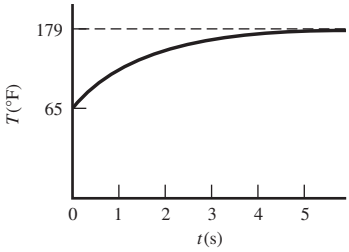
$$13{,}400 - 74.9T = 8530\exp(-74.9t)$$

$$\Downarrow$$

$$\boxed{T(°\text{F}) = 179 - 114\exp(-74.9t)}$$

A check on the solution may be obtained by substituting $t = 0$ and verifying that T equals the specified initial value, 65°F.

If you evaluate T from this equation for a number of values of $t(s)$, a plot appears as follows:



The plot starts from the initial condition of 65°F and asymptotically approaches the steady-state value of 179°F. It takes 3.8 seconds for the temperature to reach 178°F, one degree short of its final value.

Test Yourself

(Answers, p. 660)

1. Under what conditions is the simplified form of the energy balance (Equation 10.3-12) valid?
2. Suppose the heat capacity C_v is a function of T, which varies with time. Where would the derivation of Equation 10.3-12 break down?

10.4 SIMULTANEOUS TRANSIENT BALANCES

Throughout this book, we have seen that when more than one species is involved in a process or when energy balances are required, several balance equations must be derived and solved simultaneously. For steady-state systems the equations are algebraic, but when the systems are transient, simultaneous differential equations must be solved. For the simplest systems, analytical solutions may be obtained by hand, but more commonly numerical solutions are required. Software packages that solve general systems of ordinary differential equations—such as Mathematica®, Maple®, Matlab®, and Polymath®—are readily obtained for most computers.

Suppose $y_1(t), y_2(t), \ldots, y_n(t)$ are dependent variables in a process system (such as species flow rates, concentrations, mole fractions or temperature), and that at time $t = t_0$ (usually but not always 0) these variables have the values $y_{10}, y_{20}, \ldots, y_{n0}$. The goal is to derive a set of n differential equations that have the following form:

$$\frac{dy_1}{dt} = f_1(y_1, y_2, \ldots, y_n, t) \qquad y_1(t_0) = y_{10} \qquad \textbf{(10.4-1)}$$

$$\frac{dy_2}{dt} = f_2(y_1, y_2, \ldots, y_n, t) \qquad y_2(t_0) = y_{20} \qquad \textbf{(10.4-2)}$$

$$\vdots \qquad\qquad \vdots$$

$$\frac{dy_n}{dt} = f_n(y_1, y_2, \ldots, y_n, t) \qquad y_n(t_0) = y_{n0} \qquad \textbf{(10.4-n)}$$

The functions on the right-hand sides of these equations are derived from the input, output, generation, and consumption terms in the balance equations. The solutions of the equations may be expressed as a table of $y_1, y_2, \ldots, y_n$ for increasing values of t or as plots of y_1 versus t, y_2 versus t, . . . , y_n versus t. The next example provides an illustration.

Example 10.4-1 Transient Balances on a Semibatch Reactor

Equipment Encyclopedia
reactor: semi-batch

www.wiley.com/college/felder

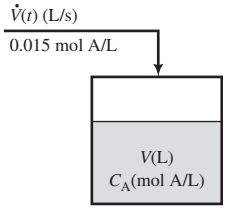
An aqueous solution containing 0.015 mol/L of species A is fed into a holding tank that initially contains 75 liters of pure water. The reactant decomposes at a rate

$$r[\text{mol A/(L·s)}] = 0.0375C_A$$

where C_A(mol A/L) is the concentration of A in the tank. The volumetric feed rate of the solution, $\dot{V}(t)$, increases linearly over a 10-second period from 0 to 25 L/s and stays constant at that rate thereafter until the tank is filled to the desired level. The density of the feed stream is constant.

1. Write transient balances for the total mass of the tank contents and the mass of A in the tank. Convert the equations to differential equations for $V(t)$ (the volume of the tank contents) and $C_A(t)$ (the concentration of A in the tank) that have the form of Equations 10.4-1 and 10.4-2, and provide initial conditions.
2. Sketch the shapes of the plots you would expect for the volume of the tank contents, V(L), and the concentration of A in the tank, C_A(mol/L), versus time.
3. Outline how the equations would be solved to derive an expression for $C_A(t)$ for the period from $t = 0$ to $t = 60$ s.

Solution A flowchart of the process is as follows:



The concentration of A in the tank changes with time because both the moles of A in the tank and the volume of the tank contents are changing.

1. ***Total mass balance:*** accumulation (kg/s) = input (kg/s). The total mass of the tank contents (kg) at any time is ρ(kg/L)V(L), and the mass flow rate of the feed stream (kg/s) is ρ(kg/L)$\dot{V}$(L/s). The mass balance thus becomes $d(\rho V)/dt = \rho\dot{V}$, or, bringing ρ (which we are told is constant) out of the derivative and canceling it,

$$\boxed{\begin{gathered}\frac{dV}{dt} = \dot{V} \\ V(0) = 75.0\,\text{L}\end{gathered}} \tag{1}$$

Balance on A: accumulation(mol A/s) = input − consumption. The number of moles of A in the tank at any time equals V(L)C_A(mol A/L). The balance equation therefore becomes

$$\frac{d}{dt}(VC_A) = \dot{V}\left(\frac{\text{L}}{\text{s}}\right) \times 0.015\ \frac{\text{mol A}}{\text{L}} - (0.0375C_A)\left(\frac{\text{mol A}}{\text{L·s}}\right)V(\text{L})$$

$$\Downarrow \text{product rule}$$

$$V\frac{dC_A}{dt} + C_A\frac{dV}{dt} = 0.015\dot{V} - 0.0375VC_A$$

$$\Downarrow \text{Substitute for } dV/dt \text{ from Equation 1, solve for } dC_A/dt$$

$$\boxed{\begin{gathered}\frac{dC_A}{dt} = \frac{\dot{V}}{V}(0.015\ \text{mol A/L} - C_A) - 0.0375C_A \\ C_A(0) = 0\ \text{mol A/L}\end{gathered}} \tag{2}$$

The initial condition in Equation 2 follows from the statement that the tank initially contains pure water. In Equations 1 and 2,

$$\dot{V}(t) = 2.5t \quad 0 \le t \le 10\ \text{s} \tag{3a}$$

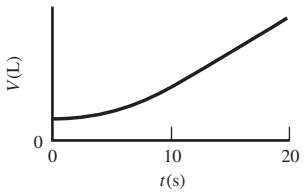
$$= 25\ \text{L/s} \quad t > 10\ \text{s} \tag{3b}$$

(Verify Equation 3a.)

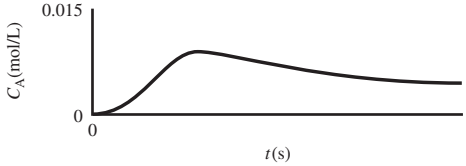
Equations 1 and 2 are two differential equations in two dependent variables that have the form of Equations 10.4-1 and 10.4-2, where V and C_A correspond to y_1 and y_2, respectively. The equations may therefore be solved with any of the computer programs mentioned at the beginning of this section.[3]

2. To predict the shape of the curve on a plot of V versus t, we need only remember that the slope of the curve is dV/dt, which in turn equals $\dot{V}(t)$ (from Equation 1). Try to follow this chain of reasoning:

- A point on the plot of V versus t is the initial condition ($t = 0$, $V = 75$ L).
- During the first 10 seconds, $dV/dt = 2.5t$ (from Equations 1 and 3a). The slope of the curve therefore equals zero at $t = 0$ (so that the curve is horizontal at the V axis) and increases over the first 10 seconds (so that the curve is concave up).
- At $t = 10$ seconds, dV/dt reaches a value of 25 L/s and thereafter remains constant at that value. A curve with a constant slope is a straight line. The plot of V versus t for $t \ge 10$ s must therefore be a straight line with a slope of 25 L/s.
- Putting the preceding observations together, we conclude that the plot of V versus t starts horizontally at ($t = 0$, $V = 75$ L), curves up for 10 seconds, and then becomes a straight line with a slope of 25 L/s. It should have the following appearance:



- The plot of C_A versus t must begin at ($t = 0$, $C_A = 0$), since the tank initially contains pure water.
- At $t = 0$, the expression of Equation 2 for dC_A/dt equals zero since both t and C_A are zero at this point. (*Verify.*) The plot of C_A versus t is therefore horizontal at the C_A axis. Since we are adding A to the tank, its concentration must increase, and so the curve must be concave up.
- As time proceeds, more and more of the tank volume is occupied by fluid in which the A has had a long time to react. We could anticipate that at a *very* long time, the tank would contain a huge volume with very little A in it, and the A being added would be diluted down to a concentration approaching zero. C_A should therefore increase near $t = 0$, rise to a maximum, start decreasing, and approach zero at long times.
- Furthermore, the concentration in the tank can never be greater than that in the feed stream (0.015 mol/L) and, in fact, must always be less than this amount since (a) the feed is diluted by the water initially in the tank and (b) some of the A in the feed reacts once it is in the tank. The maximum value of C_A must therefore be less than 0.015 mol A/L.
- All of these observations combine to predict a plot with the following shape:



[3] It would be easier in this particular problem to solve Equation 1 analytically and substitute for $V(t)$ in Equation 2. The methods we are illustrating now would work even if an analytical solution to Equation 1 could not be found.

3. The system of equations must be solved in two stages—the first from $t = 0$ to $t = 10$ s (when $\dot{V} = 2.5t$) and the second for $t > 10$ s, when $\dot{V} = 25$ L/s. The procedure is as follows:

- Substitute $2.5t$ for $\dot{V}(t)$ in Equations 1 and 2.

$$\frac{dV}{dt} = 2.5t \qquad V(0) = 75.0\ \text{L} \tag{1a}$$

$$\frac{dC_A}{dt} = \frac{2.5t}{V}(0.015 - C_A) - 0.0375C_A \qquad C_A(0) = 0 \tag{2a}$$

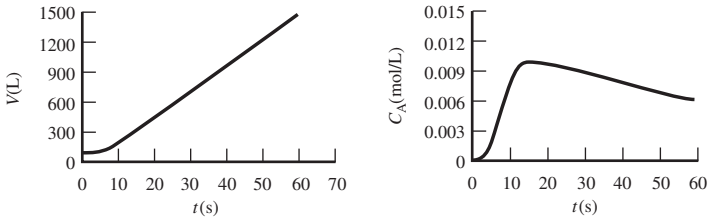
When this pair of equations is solved for $V(t)$ and $C_A(t)$ (we will omit details of the solution procedure), we determine that $V(10\ \text{s}) = 200$ L and $C_A(10\ \text{s}) = 0.00831$ mol A/L.

- Substitute $\dot{V}(t) = 25$ L/s in Equations 1 and 2 and substitute the dependent variable values at $t = 10$ s for the initial conditions:

$$\frac{dV}{dt} = 25\ \text{L/s} \qquad V(10) = 200\ \text{L} \tag{1b}$$

$$\frac{dC_A}{dt} = \frac{25}{V}(0.015 - C_A) - 0.0375C_A \qquad C_A(10) = 0.0831\ \text{mol A/L} \tag{2b}$$

These equations may be solved for $V(t)$ and $C_A(t)$ for $t > 10$ s. These solutions along with the previous solutions for $t \leq 10$ s are shown in the following plots:



10.5 SUMMARY

All batch and semibatch processes are transient, as are continuous processes being started up, shut down, or in transition from one operating state to another. The accumulation terms in balance equations for transient systems are not zero (as they are for steady-state systems) but rather are derivatives of system variables with respect to time, and balance equations are consequently differential rather than algebraic.

The procedure for writing and solving transient balances is as follows:

- Write an expression for the amount of the balanced quantity in the system (mass, moles of a particular species, energy) and set the accumulation term in the balance equation equal to the derivative of that amount with respect to time.
- Substitute for the input, output, generation, and consumption terms in the balance equation, and convert the resulting equation into one with the form

$$\frac{dy}{dt} = f(y, t) \qquad y(0) = y_0$$

where $y(t)$ is the dependent system variable to be determined (total mass or volume of the system contents, concentration or

mole fraction of a species, temperature) and y_0 is the specified initial value of y.

- Sketch the anticipated plot of y versus t, using the initial condition to locate the starting point and using what you know about the slope (which equals dy/dt) to predict the shape of the curve.
- If the balance equation can be solved analytically (e.g., by separation of variables and integration), do so; otherwise, solve it using differential equation-solving software.
- If the system involves more than one dependent variable (such as a semibatch unit in which both the volume and composition of the system contents vary or a reactor in which several reactions occur simultaneously), write balance equations for all the dependent variables and convert them to the form

$$\frac{dy_1}{dt} = f_1(y_1, y_2, \ldots, y_n, t)$$
$$y_1(t_0) = y_{10}$$
$$\vdots$$
$$\frac{dy_n}{dt} = f_n(y_1, y_2, \ldots, y_n, t)$$
$$y_n(t_0) = y_{n0}$$

Differential equation-solving software may then be used to generate tables and/or plots of the dependent variables versus time.

PROBLEMS

Most of the following problems ask you to write one or more transient balances, provide initial conditions for each derived equation, and integrate the equations. Whether or not such a problem explicitly requests it, you should always check your solution by verifying that (a) the initial condition is satisfied, (b) differentiating your solution yields the original balance equation, and (c) the previously determined steady-state solution (if one has been determined) is approached as $t \to \infty$ in the transient solution.

10.1. A solution containing hydrogen peroxide with a mass fraction x_{p0} (kg H_2O_2/kg solution) is added to a storage tank at a steady rate $\dot{m}_0$(kg/h). During this process, the liquid level reaches a corroded spot in the tank wall and a leak develops. As the filling continues, the leak rate $\dot{m}_1$(kg/h) becomes progressively worse. Moreover, once it is in the tank the peroxide begins to decompose at a rate

$$r_d(\text{kg/h}) = kM_p$$

where M_p(kg) is the mass of peroxide in the tank. The tank contents are well mixed, so that the peroxide concentration is the same at all positions. At a time $t = 0$ the liquid level reaches the corroded spot. Let M_0 and M_{p0} be the total liquid mass and mass of peroxide, respectively, in the tank at $t = 0$, and let $M(t)$ be the total mass of liquid in the tank at any time thereafter.

(a) Show that the leakage rate of hydrogen peroxide at any time is $\dot{m}_1 M_p/M$.

(b) Write differential balances on the total tank contents and on the peroxide in the tank, and provide initial conditions. Your solution should involve only the quantities $\dot{m}_0$, $\dot{m}_1$, x_{p0}, k, M, M_0, M_p, M_{p0}, and t.

10.2. One hundred fifty kmol of an aqueous phosphoric acid solution contains 5.00 mole% H_3PO_4. The solution is concentrated by adding pure phosphoric acid at a rate of 20.0 L/min.

(a) Write a differential mole balance on phosphoric acid and provide an initial condition. [Start by defining n_p(kmol) to be the total quantity of phosphoric acid in the tank at any time.] Without solving the equation, sketch a plot of n_p versus t and explain your reasoning.

(b) Solve the balance to obtain an expression for $n_p(t)$. Use the result to derive an expression for $x_p(t)$, the mole fraction of phosphoric acid in the solution. Without doing any numerical calculations, sketch a plot of x_p versus t from $t = 0$ to $t \to \infty$, labeling the initial and asymptotic values of x_p on the plot. Explain your reasoning.

(c) How long will it take to concentrate the solution to 15% H_3PO_4?

10.3. Methanol is added to a storage tank at a rate of 1200 kg/h and is simultaneously withdrawn at a rate $\dot{m}_w(t)$(kg/h) that increases linearly with time. At $t = 0$ the tank contains 750 kg of the liquid and $\dot{m}_w = 750$ kg/h. Five hours later $\dot{m}_w$ equals 1000 kg/h.

(a) Calculate an expression for $\dot{m}_w(t)$, letting $t = 0$ signify the time at which $\dot{m}_w = 750$ kg/h, and incorporate it into a differential methanol balance, letting M(kg) be the mass of methanol in the tank at any time.

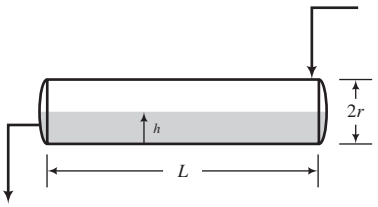
(b) Integrate the balance equation to obtain an expression for $M(t)$ and check the solution two ways. (See Example 10.2-1.) For now, assume that the tank has an infinite capacity.
(c) Calculate how long it will take for the mass of methanol in the tank to reach its maximum value, and calculate that value. Then calculate the time it will take to empty the tank.
(d) Now suppose the tank volume is 3.40 m^3. Draw a plot of M versus t, covering the period from $t = 0$ to an hour after the tank is empty. Write expressions for $M(t)$ in each time range when the function changes.

10.4. A 10.0-ft^3 compressed-air tank is being filled. Before the filling begins, the tank is open to the atmosphere. The reading on a Bourdon gauge mounted on the tank increases linearly from an initial value of 0.0 to 100 psi after 15 seconds. The temperature is constant at 72°F, and atmospheric pressure is 1 atm.
(a) Calculate the rate $\dot{n}$(lb-mole/s) at which air is being added to the tank, assuming ideal-gas behavior. (*Suggestion:* Start by calculating how much is in the tank at $t = 0$.)
(b) Let $N(t)$ equal the number of lb-moles of air in the tank at any time. Write a differential balance on the air in the tank in terms of N and provide an initial condition.
(c) Integrate the balance to obtain an expression for $N(t)$. Check your solution two ways.
(d) Estimate the lb-moles of *oxygen* in the tank after two minutes. List reasons your answer might be inaccurate, assuming there are no mistakes in your calculation.

SAFETY

**10.5.* A 7.35 million gallon tank used for storing liquefied natural gas (LNG, which may be taken to be pure methane) must be taken out of service and inspected. All the liquid that can be pumped from the tank is first removed, and the tank is allowed to warm from its service temperature of about −260°F to 80°F at 1 atm. The gas remaining in the tank is then purged in two steps: (1) Liquid nitrogen is sprayed gently onto the tank floor, where it vaporizes. As the cold nitrogen vapor is formed, it displaces the methane in a piston-like flow until the tank is completely filled with nitrogen. Once all the methane has been displaced, the nitrogen is allowed to warm to ambient temperature. (2) Air is blown into the tank where it rapidly and completely mixes with the nitrogen until the composition of the gas leaving the tank is very close to that of air.
(a) Use the ideal-gas equation of state to estimate the densities of methane at 80°F and 1 atm and of nitrogen at −260°F and 1 atm. How confident are you about the accuracy of each estimate? Explain.
(b) If the density of liquid nitrogen is 50 lb_m/ft^3, how many gallons will be required to displace all the methane from the tank?
(c) How many cubic feet of air will be required to increase the oxygen concentration to 20% by volume?
(d) Explain the logic behind vaporizing nitrogen in the manner described. Why purge with nitrogen first as opposed to purging with air?

10.6. The flow rate of a process stream has tended to fluctuate considerably, creating problems in the process unit to which the stream is flowing. A horizontal *surge drum* has been inserted in the line to maintain a constant downstream flow rate even when the upstream flow rate varies. A cross-section of the drum, which has length L and radius r, is shown below.



The level of liquid in the drum is h, and the expression for liquid volume in the drum is

$$V = L\left[r^2 \cos^{-1}\left(\frac{r-h}{r}\right) - (r-h)\sqrt{r^2-(r-h)^2}\right]$$

* Adapted from "Safety, Health, and Loss Prevention in Chemical Processes: Problems for Undergraduate Engineering Curricula," The Center for Chemical Process Safety of the American Institute of Chemical Engineers, AIChE (1990), Volume 1, p. 13.

Here is how the drum works. The rate of drainage of a liquid from a container varies with the height of the liquid in the container: the greater the height, the faster the drainage rate. The drum is initially charged with enough liquid so that when the input rate has its desired value, the liquid level is such that the drainage rate from the drum has the same value. A sensor in the drum sends a signal proportional to the liquid level to a control valve in the downstream line. If the input flow rate increases, the liquid level starts to rise; the control valve detects the rise from the transmitted signal and opens to increase the drainage rate, stopping when the level comes back down to its set-point value. Similarly, if the input flow rate drops, the control valve closes enough to bring the level back up to its set point.

(a) The drum is to be charged initially with benzene (density = 0.879 g/cm^3) at a constant rate $\dot{m}$(kg/min) until the tank is half full. If $L = 5$ m, $r = 1$ m, and $\dot{m} = 10$ kg/min, how long should it take to reach that point?

(b) Now suppose the flow rate into the tank is unknown. A sight gauge on the tank allows determination of the liquid level, and instructions are to stop the flow when the tank contains 3000 kg. At what value of h should this be done?

(c) After the tank has been charged, the flow rate into the drum, $\dot{m}_1$, varies with upstream operations, and the flow rate out is 10 kg/min. Write a mass balance around the drum so that you obtain a relationship between $\dot{m}_1$ and the rate of change in the height of liquid in the tank (dh/dt) as a function of h. Estimate the flow rate into the tank when h has an approximate value of 50 cm, and $dh/dt = 1$ cm/min. (*Hint:* Although an analytical solution is feasible, you may find it easier to create plots of V and dV/dh at 0.1 m increments in h, which can be used in obtaining an approximate solution to the problem.)

(d) Speculate on why the drum would provide better performance than feeding a signal proportional to the flow rate directly to the control valve that would cause the valve to close if the flow rate drops below the set point and to open if the flow rate rises above that point.

10.7. A gas storage tank with a floating roof receives a steady input of 540 m^3/h of a natural gas. The rate of withdrawal of gas from the tank, $\dot{V}_w$, varies more or less randomly during the day and is recorded at 10-min intervals. At 8:00 a.m. one morning the volume of stored gas is 3.00×10^3 m^3. The withdrawal rate data for the next 4 hours are as follows:

Hour Beginning at	$\dot{V}_w$(m^3/min)
8:00	11.4, 11.9, 12.1, 11.8, 11.5, 11.3
9:00	11.4, 11.1, 10.6, 10.8, 10.4, 10.2
10:00	10.2, 9.8, 9.4, 9.5, 9.3, 9.4
11:00	9.5, 9.3, 9.6, 9.6, 9.4, 9.9
12:00	9.8

The temperature and pressure of the inlet, stored, and outlet gases are equal and nearly constant throughout the given time period.

(a) Write a differential balance on the moles of gas in the tank, and prove that when integrated it yields the following equation for the gas volume:

$$V(t) = 3.00 \times 10^3 \text{ m}^3 + \left(9.00 \frac{\text{m}^3}{\text{min}}\right) t - \int_0^t \dot{V}_w dt$$

where t(min) is the time elapsed since 8:00 a.m.

(b) Calculate the stored gas volume at noon, using Simpson's rule (Appendix A.3) to evaluate the integral.

(c) Although a running estimate of the tank volume is important to have, in practice it would probably not be obtained in the manner indicated. Speculate on how it would more likely be obtained. What might you infer if the value estimated in Part (b) is greater than that obtained by the more accurate method?

10.8. Water is added at varying rates to a 300-liter holding tank. When a valve in a discharge line is opened, water flows out at a rate proportional to the height and hence to the volume V of water in the tank. The flow of water into the tank is slowly increased and the level rises in consequence, until at a steady

input rate of 60.0 L/min the level just reaches the top but does not spill over. The input rate is then abruptly decreased to 40.0 L/min.

(a) Write the equation that relates the discharge rate, $\dot{V}_{out}$(L/min), to the volume of water in the tank, V(L), and use it to calculate the steady-state volume when the input rate is 40 L/min.

(b) Write a differential balance on the water in the tank for the period from the moment the input rate is decreased ($t = 0$) to the attainment of steady state ($t \to \infty$), expressing it in the form $dV/dt = \cdots$. Provide an initial condition.

(c) Without integrating the equation, use it to confirm the steady-state value of V calculated in Part (a) and then to predict the shape you would anticipate for a plot of V versus t. Explain your reasoning.

(d) Separate variables and integrate the balance equation to derive an expression for $V(t)$. Calculate the time in minutes required for the volume to decrease to within 1% of its steady-state value.

10.9. The production supervisor of a small pharmaceutical firm has observed a decreasing demand for potassium regurgitol (PRG) over a two-month period, and since the plant manager has been throwing up the low sales of this product at the weekly staff meetings, the supervisor decides to discontinue its production immediately. On the day of this decision, the inventory of PRG is 28,000 kg. Based on the orders on hand, the manager projects the following weekly demand for the next six weeks:

Week	1	2	3	4	5	6
Demand $\dot{D}$(kg/wk)	2385	1890	1506	1196	950	755

(a) Use a semilog plot of the projected demand figures to derive an equation for $\dot{D}$ as a function of t (weeks) from the present time.

(b) Write a differential balance on the inventory I(kg) of PRG, and integrate it to determine I as a function of t.

(c) If the demand continues to follow the projected trend of the next six weeks, how much PRG will eventually have to be discarded?

SAFETY

10.10. A ventilation system has been designed for a large laboratory with a volume of 1100 m^3. The volumetric flow rate of ventilation air is 700 m^3/min at 22°C and 1 atm. (The latter two values may also be taken as the temperature and pressure of the room air.) A reactor in the laboratory is capable of emitting as much as 1.50 mol of sulfur dioxide into the room if a seal ruptures. An SO_2 mole fraction in the room air greater than 1.0×10^{-6}(1 ppm) constitutes a health hazard.

(a) Suppose the reactor seal ruptures at a time $t = 0$, and the maximum amount of SO_2 is emitted and spreads uniformly throughout the room almost instantaneously. Assuming that the air flow is sufficient to make the room air composition spatially uniform, write a differential SO_2 balance, letting N be the total moles of gas in the room (assume constant) and $x(t)$ the mole fraction of SO_2 in the laboratory air. Convert the balance into an equation for dx/dt and provide an initial condition. (Assume that all of the SO_2 emitted is in the room at $t = 0$.)

(b) Predict the shape of a plot of x versus t. Explain your reasoning, using the equation of Part (a) in your explanation.

(c) Separate variables and integrate the balance to obtain an expression for $x(t)$. Check your solution.

(d) Convert the expression for $x(t)$ into an expression for the concentration of SO_2 in the room, C_{SO_2} (mol SO_2/L). Calculate (i) the concentration of SO_2 in the room two minutes after the rupture occurs, and (ii) the time required for the SO_2 concentration to reach the "safe" level.

(e) Why would it probably not yet be safe to enter the room after the time calculated in Part (d)? (*Hint*: One of the assumptions made in the problem is probably not a good one.)

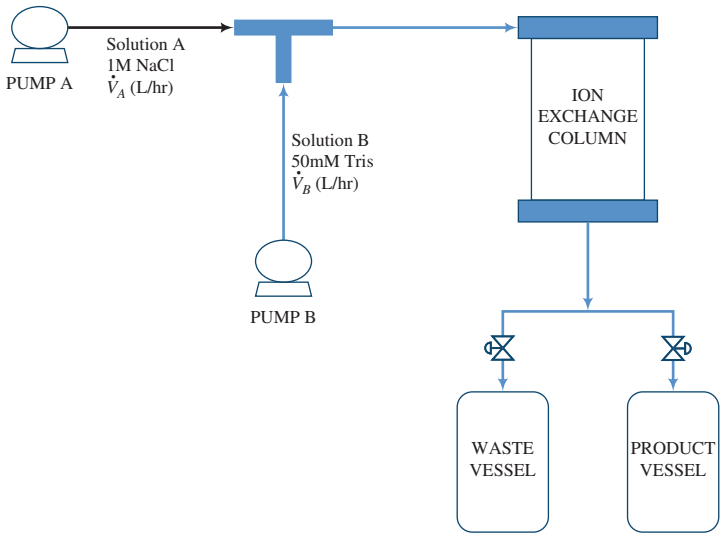
BIOENGINEERING

*__10.11.__ Purification of proteins for use as biopharmaceuticals is often accomplished by *ion exchange chromatography*, in which a process fluid passes through a column packed with small resin beads whose ionic surface charge causes them to adsorb some stream components more strongly than others. An ion-exchange run takes place in two steps: (1) the load step, in which the process stream flows through the column and the target protein (the product) and some undesired impurities are adsorbed onto the resin; and (2) the elution step, during which another fluid passes through the column and

* Adapted from a problem contributed by Gary Gilleskie of North Carolina State University.

desorbs the impurities and the protein from the resin. The elution fluid consists of an aqueous solution of a solute known as Tris diluted with an NaCl solution, with the NaCl-to-Tris ratio starting at 0 and steadily increasing with time. The impurities desorb into the fluid when the NaCl concentration is low, and the effluent is collected in a waste vessel. As the NaCl concentration increases, the target protein desorbs. When analysis of the effluent reveals the presence of the target protein, the flow is switched to the product collection vessel, and the effluent is collected until no more product is detected in the effluent. The collected product is then subjected to additional process steps to further isolate the protein, and the column is cleaned for reuse.

Consider an elution step in which solutions of 1 M NaCl (solution A) and 50 mM Tris (solution B) are mixed and fed to a loaded ion-exchange column. The system is programmed to keep the total volumetric flow rate ($\dot{V}_A + \dot{V}_B$) into the column constant at 120 L/h while linearly increasing the volume fraction of solution A in the feed from 0% to 20% over a period of 33.6 minutes, at which point the elution is declared to be complete. The flowchart is shown below:



(a) Calculate V_t(L), the total amount of solution fed to the column.

(b) Derive an equation for the volumetric flow rate of solution A, $\dot{V}_A(t)$, assuming that the densities of both fluids are the same. Use the calculated value to determine calculate V_A(L), the total volume of that solution fed to the column, and m_A(g NaCl), the total mass of NaCl fed. Then determine $\dot{V}_B(t)$, and V_B(L) and n_B(mol Tris), the total volume of solution B and total moles of Tris fed, respectively. (*Hint:* Once you've done the calculations for solution A, those for B should be trivial.)

(c) Suppose in one run product is detected in the effluent at the same time impurities are detected—that is, product protein starts desorbing earlier than in previous runs. List up to five possible causes of the problem.

SAFETY

10.12. A gas leak has led to the presence of 1.00 mole% carbon monoxide in a 350-m^3 laboratory.[4] The leak was discovered and sealed, and the laboratory is to be purged with clean air to a point at which the air contains less than the OSHA (Occupational Safety and Health Administration) specified Permissible Exposure Level (PEL) of 35 ppm (molar basis). Assume that the clean air and the air in the laboratory are at the same temperature and pressure and that the laboratory air is perfectly mixed throughout the purging process.

(a) Let t_r(h) be the time required for the specified reduction in the carbon monoxide concentration. Write a differential CO mole balance, letting N equal the total moles of gas in the room (assume constant), the mole fraction of CO in the room air, and $\dot{V}_p$(m^3/h) the flow rate of purge air entering the room (and also the flow rate of laboratory air leaving the room). Convert the balance into an equation for dx/dt and provide an initial condition. Sketch a plot of x versus t, labeling the value of x at $t = 0$ and the asymptotic value at $t \to \infty$.

[4] D. A. Crowl, D. W. Hubbard, and R. M. Felder, *Problem Set: Stoichiometry*, AIChE/CCPS, New York, 1993.

(b) Integrate the balance to derive an equation for t_r in terms of $\dot{V}_p$.

(c) If the volumetric flow rate is 700 m^3/h (representing a turnover of two room volumes per hour), how long will the purge take? What would the volumetric flow rate have to be to cut the purge time in half?

(d) Give several reasons why it might not be safe to resume work in the laboratory after the calculated purge time has elapsed. What precautionary steps would you advise taking at this point?

ALTERNATIVE ENERGY
BIOENGINEERING
ENVIRONMENTAL

*__10.13.__ Methane is generated via the *anaerobic decomposition* (biological degradation in the absence of oxygen) of solid waste in landfills. Collecting the methane for use as a fuel rather than allowing it to disperse into the atmosphere provides a useful supplement to natural gas as an energy source.

If a batch of waste with mass M (tonnes) is deposited in a landfill at $t = 0$, the rate of methane generation at time t is given by

$$\dot{V}_{CH_4}(t) = kL_0M_{waste}e^{-kt} \quad \textbf{(1)}$$

where $\dot{V}_{CH_4}$ is the rate at which methane is generated in standard cubic meters per year, k is a rate constant, L_0 is the total potential yield of landfill gas in standard cubic meters per tonne of waste, and M_{waste} is the tonnes of waste in the landfill at $t = 0$.

(a) Starting with Equation 1, derive an expression for the mass generation rate of methane, $\dot{M}_{CH_4}(t)$. Without doing any calculations, sketch the shape of a plot of $\dot{M}_{CH_4}$ versus t from $t = 0$ to $t = 3$ y, and graphically show on the plot the total masses of methane generated in Years 1, 2, and 3. Then derive an expression for $M_{CH_4}(t)$, the total mass of methane (tonnes) generated from $t = 0$ to a time t.

(b) A new landfill has a yield potential $L_0 = 100$ SCM CH_4/tonne waste and a rate constant $k = 0.04\ y^{-1}$. At the beginning of the first year, 48,000 tonnes of waste are deposited in the landfill. Calculate the tonnes of methane generated from this deposit over a three-year period.

(c) A colleague solving the problem of Part (b) calculates the methane produced in three years from the 4.8×10^4 tonnes of waste as

$$M_{CH_4}(t = 3) = \dot{M}_{CH_4}(t = 0) \times 1\ y + \dot{M}_{CH_4}(t = 1) \times 1\ y + \dot{M}_{CH_4}(t = 2) \times 1\ y$$

where $\dot{M}_{CH_4}$ is the first expression derived in Part (a). Briefly state what has been assumed about the rate of methane generation. Calculate the value determined with this method and the percentage error in the calculation. Show graphically what the calculated value corresponds to on another sketch of $\dot{M}_{CH_4}$ versus t.

(d) The following amounts of waste are deposited in the landfill on January 1 in each of three consecutive years.

	Waste (tonnes)
Year 1	48,000
Year 2	45,000
Year 3	54,000

Calculate the metric tons of CH_4 generated through the end of the third year.

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(e) Explain in your own words the benefits of reducing the release of methane from landfills and of using the methane as a fuel instead of natural gas.

(f) One way to avoid the environmental hazard of methane generation is to incinerate the waste before it has a chance to decompose. What problems might this alternative process introduce?

10.14. Ninety kilograms of sodium nitrate is dissolved in 110 kg of water. When the dissolution is complete (at time $t = 0$), pure water is fed to the tank at a constant rate $\dot{m}$(kg/min), and solution is withdrawn from the tank at the same rate. The tank may be considered perfectly mixed.

(a) Write a total mass balance on the tank and use it to prove that the total mass of liquid in the tank remains constant at its initial value.

* Adapted from a problem contributed by Joseph F. DeCarolis of North Carolina State University.

(b) Write a balance on sodium nitrate, letting $x(t, \dot{m})$ equal the mass fraction of $NaNO_3$ in the tank and outlet stream. Convert the balance into an equation for dx/dt and provide an initial condition.

(c) On a single graph of x versus t, sketch the shapes of the plots you would expect to obtain for $\dot{m} = 50$ kg/min, 100 kg/min, and 200 kg/min. (Don't do any calculations.) Explain your reasoning, using the equation of Part (b) in your explanation.

(d) Separate variables and integrate the balance to obtain an expression for $x(t, \dot{m})$. Check your solution. Then generate the plots of x versus t for $\dot{m} = 50$ kg/min, 100 kg/min, and 200 kg/min and show them on a single graph. (A spreadsheet is a convenient tool for carrying out this step.)

(e) If $\dot{m} = 100$ kg/min, how long will it take to flush out 90% of the sodium nitrate originally in the tank? How long to flush out 99%? 99.9%?

(f) The stream of water enters the tank at a point near the top, and the exit pipe from the tank is located on the opposite side toward the bottom. One day the plant technician forgot to turn on the mixing impeller in the tank. On the same chart, sketch the shapes of the plots of x versus t you would expect to see with the impeller on and off, clearly showing the differences between the two curves at small values and large values of t. Explain your reasoning.

10.15. A stirred tank contains 1500 lb_m of pure water at 70°F. At time $t = 0$, two streams begin to flow into the tank and one is withdrawn. One input stream is a 20.0 wt% aqueous solution of NaCl at 85°F flowing at a rate of 15 lb_m/min, and the other is pure water at 70°F flowing at 10 lb_m/min. The mass of liquid in the tank is held constant at 1500 lb_m. Perfect mixing in the tank may be assumed, so that the outlet stream has the same NaCl mass fraction (x) and temperature (T) as the tank contents. Also assume that the heat of mixing is zero and the heat capacity of all fluids is $C_p = 1$ Btu/($lb_m \cdot$°F).

(a) Write differential material and energy balances and use them to derive expressions for dx/dt and dT/dt.

(b) Without solving the equations derived in Part (a), sketch plots of T and x as a function of time (t). Clearly identify values at time zero and as $t \to \infty$.

10.16. A radioactive isotope decays at a rate proportional to its concentration. If the concentration of an isotope is C(mg/L), then its rate of decay may be expressed as

$$r_d[\text{mg}/(\text{L}\cdot\text{s})] = kC$$

where k is a constant.

(a) A volume V(L) of a solution of a radioisotope whose concentration is C_0(mg/L) is placed in a closed vessel. Write a balance on the isotope in the vessel and integrate it to prove that the **half-life** $t_{1/2}$ of the isotope—by definition, the time required for the isotope concentration to decrease to half of its initial value—equals $(\ln 2)/k$.

SAFETY

(b) The half-life of ^{56}Mn is 2.6 h. A batch of this isotope that was used in a radiotracing experiment has been collected in a holding tank. The radiation safety officer declares that the activity (which is proportional to the isotope concentration) must decay to 1% of its present value before the solution can be discarded. How long will this take?

10.17. A *tracer* is used to characterize the degree of mixing in a continuous stirred tank. Water enters and leaves the mixer at a rate of $\dot{V}(m^3/\text{min})$. Scale has built up on the inside walls of the tank, so that the effective volume $V(m^3)$ of the tank is unknown. At time $t = 0$, a mass m_0(kg) of the tracer is injected into the tank and the tracer concentration in the outlet stream, $C(\text{kg}/m^3)$, is monitored.

(a) Write a differential balance on the tracer in the tank in terms of V, C, and $\dot{V}$, assuming that the tank contents are perfectly mixed, and convert the balance into an equation for dC/dt. Provide an initial condition, assuming that the injection is rapid enough so that all of the tracer may be considered to be in the tank at $t = 0$. Without doing any calculations, sketch a plot of C versus t, labeling the value of C at $t = 0$ and the asymptotic value at $t \to \infty$.

(b) Integrate the balance to prove that

$$C(t) = (m_0/V)\exp(-\dot{V}t/V)$$

(c) Suppose the flow rate through the mixer is $\dot{V} = 30.0\ m^3/\text{min}$ and that the following data are taken:

Time from injection, t(min)	1	2	3	4
$C \times 10^3(\text{kg}/m^3)$	0.223	0.050	0.011	0.0025

(For example, at $t = 1$ min, $C = 0.223 \times 10^{-3}$ kg/m^3.) Verify graphically that the tank is functioning as a perfect mixer—that is, that the expression of Part (b) fits the data—and determine the effective volume V(m^3) from the slope of your plot.

(d) A solution of a radioactive element with a fairly short half-life (see Problem 10.16) is often used as a tracer for applications like the one in this problem. The advantage of doing so is that the concentration of the tracer at the outlet can be measured with a sensitive radiation detector mounted outside the exit pipe rather than having to draw fluid samples from the pipe and analyze them. What is a potential drawback of radiotracers? Why is it important that the half-life of the tracer be neither too short nor too long?

10.18. A 40.0-ft^3 oxygen tent initially contains air at 68°F and 14.7 psia. At a time $t = 0$ an enriched air mixture containing 35.0% v/v O_2 and the balance N_2 is fed to the tent at 68°F and 1.3 psig at a rate of 60.0 ft^3/min, and gas is withdrawn from the tent at 68°F and 14.7 psia at a molar flow rate equal to that of the feed gas.

(a) Calculate the total lb-moles of gas ($O_2 + N_2$) in the tent at any time.

(b) Let $x(t)$ equal the mole fraction of oxygen in the outlet stream. Write a differential mole balance on oxygen, assuming that the tent contents are perfectly mixed (so that the temperature, pressure, and composition of the contents are the same as those properties of the exit stream). Convert the balance into an equation for dx/dt and provide an initial condition.

(c) Integrate the equation to obtain an expression for $x(t)$. How long will it take for the mole fraction of oxygen in the tent to reach 0.33? Sketch a plot of x versus t, labeling the value of x at $t = 0$ and the asymptotic value at $t \to \infty$.

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10.19. A chemical reaction with stoichiometry A → products is said to follow an *n^{th}-order rate law* if A is consumed at a rate proportional to the nth power of its concentration in the reaction mixture. If r_A is the rate of consumption of A per unit reactor volume, then

$$r_A[\text{mol}/(\text{L}\cdot\text{s})] = kC_A^n$$

where C_A(mol/L) is the reactant concentration, and the constant of proportionality k is the reaction *rate constant*. A reaction that follows this law is referred to as an *n^{th} order reaction*. The rate constant is a strong function of temperature but is independent of the reactant concentration.

(a) Suppose a first-order reaction ($n = 1$) is carried out in an isothermal batch reactor of constant volume V. Write a material balance on A and integrate it to derive the expression

$$C_A = C_{A0}\exp(-kt)$$

where C_{A0} is the concentration of A in the reactor at $t = 0$.

(b) The gas-phase decomposition of sulfuryl chloride

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

is thought to follow a first-order rate law. The reaction is carried out in a constant-volume isothermal batch reactor and the concentration of SO_2Cl_2 is measured at several reaction times, with the following results:

t(min)	4.0	21.3	39.5	63.4	120.0	175.6
C_A(mol/L)	0.0279	0.0262	0.0246	0.0226	0.0185	0.0152

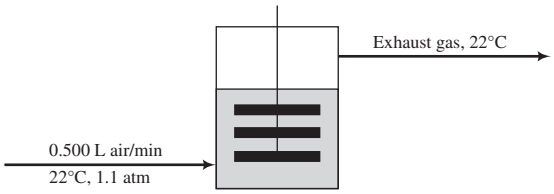
Verify the proposed rate law graphically [i.e., demonstrate that the expression given in Part (a) fits the data for $C_A(t)$] and determine the rate constant k, giving both its value and its units.

BIOENGINEERING

*10.20. The demand for biopharmaceutical products in the form of complex proteins is growing. These proteins are most often produced by cells genetically engineered to produce the protein of interest, known as a **recombinant protein**. The cells are grown in a liquid culture, and the protein is harvested and purified to generate the final product.

* Adapted from a problem contributed by John Falconer and Garret Nicodemus of the University of Colorado at Boulder.

Sf9 cells obtained from the fall armyworm can be used to produce protein therapeutics. Consider the growth of Sf9 cells in a bench-top bioreactor operating at 22°C, with a liquid volume of 4.0 liters that may be assumed constant.



Oxygen required for cell growth and protein production is supplied in air fed at 22°C and 1.1 atm. During the process, the gas leaving the bioreactor at 22°C and 1 atm is analyzed continuously. The data can be used to calculate the rate at which oxygen is taken up in the culture, which in turn can be used to determine the Sf9 cell growth rate (a quantity difficult to measure directly) and consistency of the operation from batch to batch.

(a) Analysis of the exhaust gas at a time 25 hours after the process is started shows a composition of 15.5 mol% O_2, 78.7% N_2, and the balance CO_2 and small amounts of other gases. Determine the value of the oxygen use rate (OUR) in mmol O_2 consumed/(L·h) at that point in time. Assume that nitrogen is not absorbed by the culture.

(b) OUR is related to cell concentration, X(g cells/L), by OUR $= q_{O_2}X$, where q_{O_2} is the *specific rate of oxygen consumption*. Analysis of a sample of the culture taken at $t = 25$ h finds that the concentration of cells is 5.0 g cells/L. What is the value of q_{O_2}? (Do not forget to include its units.)

(c) Six hours after this measurement, the exhaust gas contains 14.5 mol% O_2 and the percentage of N_2 is unchanged. What is the concentration of cells, X, at that point? Assume that the specific rate of oxygen consumption does not change as long as the process temperature is constant.

(d) The growth rate of cells can be expressed as:

$$\frac{dX}{dt} = \mu_g X$$

where μ_g is the specific growth rate, with units of h^{-1}. Beginning with this equation and treating μ_g as a constant, derive an expression for $t(X)$. Use the data from the previous parts of the problem to determine μ_g (include units). Then calculate the *cell-doubling time* (t_d), defined as the time for the cell concentration to double.

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10.21. A gas-phase decomposition reaction with stoichiometry $2A \rightarrow 2B + C$ follows a second-order rate law (see Problem 10.19):

$$r_d[\text{mol}/(\text{m}^3\cdot\text{s})] = kC_A^2$$

where C_A is the reactant concentration in mol/m^3. The rate constant k varies with the reaction temperature according to the **Arrhenius law**

$$k[\text{m}^3/(\text{mol}\cdot\text{s})] = k_0 \exp(-E/RT)$$

where

$k_0[\text{m}^3/(\text{mol}\cdot\text{s})]$ = the *preexponential factor*
E(J/mol) = the reaction *activation energy*
R = the gas constant
T(K) = the reaction temperature

(a) Suppose the reaction is carried out in a batch reactor of constant volume $V(\text{m}^3)$ at a constant temperature T(K), beginning with pure A at a concentration C_{A0}. Write a differential balance on A and integrate it to obtain an expression for $C_A(t)$ in terms of C_{A0} and k.

(b) Let P_0(atm) be the initial reactor pressure. Prove that $t_{1/2}$, the time required to achieve a 50% conversion of A in the reactor, equals RT/kP_0, and derive an expression for $P_{1/2}$, the reactor pressure at this point, in terms of P_0. Assume ideal-gas behavior.

(c) The decomposition of nitrous oxide (N_2O) to nitrogen and oxygen is carried out in a 5.00-liter batch reactor at a constant temperature of 1015 K, beginning with pure N_2O at several initial pressures. The reactor pressure $P(t)$ is monitored, and the times ($t_{1/2}$) required to achieve 50% conversion of N_2O are noted.

P_0(atm)	0.135	0.286	0.416	0.683
$t_{1/2}$(s)	1060	500	344	209

Use these results to verify that the N_2O decomposition reaction is second-order and determine the value of k at $T = 1015$ K.

(d) The same experiment is performed at several other temperatures at a single initial pressure of 1.00 atm, with the following results:

T(K)	900	950	1000	1050
$t_{1/2}$(s)	5464	1004	219	55

Use a graphical method to determine the Arrhenius law parameters (k_0 and E) for the reaction.

(e) Suppose the reaction is carried out in a batch reactor at $T = 980$ K, beginning with a mixture at 1.20 atm containing 70 mole% N_2O and the balance a chemically inert gas. How long (minutes) will it take to achieve a 90% conversion of N_2O?

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10.22. In an enzyme-catalyzed reaction with stoichiometry A → B, A is consumed at a rate given by an expression of the **Michaelis–Menten** form:

$$r_A[\text{mol/(L}\cdot\text{s)}] = \frac{k_1 C_A}{1 + k_2 C_A}$$

where C_A(mol/L) is the reactant concentration, and k_1 and k_2 depend only on temperature.

(a) The reaction is carried out in an isothermal batch reactor with constant reaction mixture volume V (liters), beginning with pure A at a concentration C_{A0}. Derive an expression for dC_A/dt, and provide an initial condition. Sketch a plot of C_A versus t, labeling the value of C_A at $t = 0$ and the asymptotic value as $t \to \infty$.

(b) Solve the differential equation of Part (a) to obtain an expression for the time required to achieve a specified concentration C_A.

(c) Use the expression of Part (b) to devise a graphical method of determining k_1 and k_2 from data for C_A versus t. Your plot should involve fitting a straight line and determining the two parameters from the slope and intercept of the line. (There are several possible solutions.) Then apply your method to determine k_1 and k_2 for the following data taken in a 2.00-liter reactor, beginning with A at a concentration $C_{A0} = 5.00$ mol/L.

t(s)	60.0	120.0	180.0	240.0	480.0
C_A(mol/L)	4.484	4.005	3.561	3.154	1.866

10.23. Phosgene ($COCl_2$) is formed by CO and Cl_2 reacting in the presence of activated charcoal:

$$CO + Cl_2 \rightarrow COCl_2$$

At $T = 303.8$ K the rate of formation of phosgene in the presence of 1 gram of charcoal is

$$R_f(\text{mol/min}) = \frac{8.75 C_{CO} C_{Cl_2}}{(1 + 58.6 C_{Cl_2} + 34.3 C_{COCl_2})^2}$$

where C denotes concentration in mol/L.

(a) Suppose the charge to a 3.00-liter batch reactor is 1.00 g of charcoal and a gas initially containing 60.0 mole% CO and the balance Cl_2 at 303.8 K and 1 atm. Calculate the initial concentrations (mol/L) of both reactants, neglecting the volume occupied by the charcoal. Then, letting $C_P(t)$ be the concentration of phosgene at an arbitrary time t, derive relations for C_{CO} and C_{Cl_2} in terms of C_P.

(b) Write a differential balance on phosgene and show that it simplifies to

$$\frac{dC_P}{dt} = \frac{2.92(0.02407 - C_P)(0.01605 - C_P)}{(1.941 - 24.3C_P)^2}$$

Provide an initial condition for this equation.

(c) A plot of C_P versus t starts at $C_P = 0$ and asymptotically approaches a maximum value. Explain how you could predict that behavior from the form of the equation of Part (b). Without attempting to solve the differential equation, determine the maximum value of C_P.

(d) Starting with the equation of Part (b), derive an expression for the time required to achieve a 75% conversion of the limiting reactant. *Your solution should have the form t = a definite integral.*

(e) The integral you derived in Part (d) can be evaluated analytically; however, more complex rate laws than the one given for the phosgene formation reaction would yield an integral that must be evaluated numerically. One procedure is to evaluate the integrand at a number of points between the limits of integration and to use a quadrature formula such as the trapezoidal rule or Simpson's rule (Appendix A.3) to estimate the value of the integral.

Use a spreadsheet to evaluate the integrand of the integral of Part (c) at n_p equally spaced points between and including the limits of integration, where n_p is an odd number, and then to evaluate the integral using Simpson's rule. Perform the calculation for $n_p = 5, 21,$ and 51. What can you conclude about the number of points needed to obtain a result accurate to three significant figures?

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10.24. A gas that contains CO_2 is contacted with liquid water in an agitated batch absorber. The equilibrium solubility of CO_2 in water is given by Henry's law (Section 6.4b)

$$C_A = p_A/H_A$$

where C_A(mol/cm^3) = concentration of CO_2 in solution, p_A(atm) = partial pressure of CO_2 in the gas phase, and H_A[atm/(mol/cm^3)] = Henry's law constant. The rate of absorption of CO_2 (i.e., the rate of transfer of CO_2 from the gas to the liquid per unit area of gas–liquid interface) is given by the expression

$$r_A\left[\text{mol}/(\text{cm}^2\cdot\text{s})\right] = k\left(C_A^* - C_A\right)$$

where C_A = actual concentration of CO_2 in the liquid, C_A^* = concentration of CO_2 in the liquid that would be in equilibrium with the CO_2 in the gas phase, and k(cm/s) = a *mass transfer coefficient*.

The gas phase is at a total pressure P(atm) and contains y_A(mol CO_2/mol gas), and the liquid phase initially consists of V(cm^3) of pure water. The agitation of the liquid phase is sufficient for the composition to be considered spatially uniform, and the amount of CO_2 absorbed is low enough for P, V, and y_A to be considered constant throughout the process.

(a) Derive an expression for dC_A/dt and provide an initial condition. Without doing any calculations, sketch a plot of C_A versus t, labeling the value of C_A at $t = 0$ and the asymptotic value at t $\to \infty$. Give a physical explanation for the asymptotic value of the concentration.

(b) Prove that

$$C_A(t) = \frac{p_A}{H_A}[1 - \exp(-kSt/V)]$$

where S(cm^2) is the effective contact area between the gas and liquid phases.

(c) Suppose the system pressure is 20.0 atm, the liquid volume is 5.00 liters, the tank diameter is 10.0 cm, the gas contains 30.0 mole% CO_2, the Henry's law constant is 9230 atm/(mole/cm^3), and the mass transfer coefficient is 0.020 cm/s. Calculate the time required for C_A to reach 0.620 mol/L if the gas-phase properties remain essentially constant.

(d) If A were not CO_2 but instead a gas with a moderately high solubility in water, the expression for C_A given in Part (b) would be incorrect. Explain where the derivation that led to it would break down.

10.25. A liquid-phase chemical reaction with stoichiometry A $\to$ B takes place in a semibatch reactor. The rate of consumption of A per unit volume of the reactor contents is given by the first-order rate expression (see Problem 10.19)

$$r_A[\text{mol}/(\text{L}\cdot\text{s})] = kC_A$$

where C_A(mol A/L) is the reactant concentration. The tank is initially empty. Beginning at a time $t = 0$, a solution containing A at a concentration C_{A0}(mol A/L) is fed to the tank at a constant rate $\dot{V}$(L/s).

(a) Write a differential balance on the total mass of the reactor contents. Assuming that the density of the contents always equals that of the feed stream, convert the balance into an equation for dV/dt, where V is the total volume of the contents, and provide an initial condition. Then write a differential mole balance on the reactant, A, letting $N_A(t)$ equal the total moles of A in the vessel, and provide an initial condition. Your equations should contain only the variables N_A, V, and t and the constants $\dot{V}$ and C_{A0}. (You should be able to eliminate C_A as a variable.)

(b) Without attempting to integrate the equations, derive a formula for the steady-state value of N_A.

(c) Integrate the two equations to derive expressions for $V(t)$ and $N_A(t)$, and then derive an expression for $C_A(t)$. Determine the asymptotic value of N_A as $t \to \infty$ and verify that the steady-state value obtained in Part (b) is correct. Briefly explain how it is possible for N_A to reach a steady value when you keep adding A to the reactor and then give two reasons why this value would never be reached in a real reactor.

(d) Determine the limiting value of C_A as $t \to \infty$ from your expressions for $N_A(t)$ and $V(t)$. Then explain why your result makes sense in light of the results of Part (c).

10.26. A kettle containing 3.00 liters of water at a temperature of 18°C is placed on an electric stove and begins to boil in three minutes.

(a) Write an energy balance on the water and determine an expression for dT/dt, neglecting evaporation of water before the boiling point is reached, and provide an initial condition. Sketch a plot of T versus t from $t = 0$ to $t = 4$ minutes.

(b) Calculate the average rate (W) at which heat is being added to the water. Then calculate the rate (g/s) at which water vaporizes once boiling begins.

(c) The rate of heat output from the stove element differs significantly from the heating rate calculated in Part (b). In which direction, and why?

10.27. An electrical coil is used to heat 20.0 kg of water in a closed well-insulated vessel. The water is initially at 25°C and 1 atm. The coil delivers a steady 3.50 kW of power to the vessel and its contents.

(a) Write a differential energy balance on the water, assuming that 97% of the energy delivered by the coil goes into heating the water. What happens to the other 3%?

(b) Integrate the equation of Part (a) to derive an expression for the water temperature as a function of time.

(c) How long will it take for the water to reach the normal boiling point? Will it boil at this temperature? Explain your answer.

10.28. An iron bar 2.00 cm × 3.00 cm × 10.0 cm at a temperature of 95°C is dropped into a barrel of water at 25°C. The barrel is large enough so that the water temperature rises negligibly as the bar cools. The rate at which heat is transferred from the bar to the water is given by the expression

$$\dot{Q}(\text{J/min}) = UA(T_b - T_w)$$

where U[= 0.050 J/(min·cm^2·°C)] is a *heat transfer coefficient*, A(cm^2) is the exposed surface area of the bar, and T_b(°C) and T_w(°C) are the surface temperature of the bar and the water temperature, respectively. The heat capacity of the bar is 0.460 J/(g·°C). Heat conduction in iron is rapid enough for the temperature $T_b(t)$ to be considered uniform throughout the bar.

(a) Write an energy balance on the bar, assuming that all six sides are exposed. Your result should be an expression for dT_b/dt and an initial condition.

(b) Without integrating the equation, sketch the expected plot of T_b versus t, labeling the values of T_b at $t = 0$ and $t \to \infty$.

(c) Derive an expression for $T_b(t)$ and check it three ways. How long will it take for the bar to cool to 30°C?

10.29. A steam coil is immersed in a stirred tank. Saturated steam at 7.50 bar condenses within the coil, and the condensate emerges at its saturation temperature. A solvent with a heat capacity of 2.30 kJ/(kg·°C) is fed to the tank at a steady rate of 12.0 kg/min and a temperature of 25°C, and the heated solvent is discharged at the same flow rate. The tank is initially filled with 760 kg of solvent at 25°C, at which point the flows of both steam and solvent are commenced. The rate at which heat is transferred from

the steam coil to the solvent is given by the expression

$$\dot{Q} = UA(T_{\text{steam}} - T)$$

where UA (the product of a heat transfer coefficient and the coil surface area through which the heat is transferred) equals 11.5 kJ/(min·°C). The tank is well stirred, so that the temperature of the contents is spatially uniform and equals the outlet temperature.

(a) Prove that an energy balance on the tank contents reduces to the equation given below and supply an initial condition.

$$\frac{dT}{dt} = 1.50°\text{C/min} - 0.0224T$$

(b) Without integrating the equation, calculate the steady-state value of T and sketch the expected plot of T versus t, labeling the values of T_b at $t = 0$ and $t \to \infty$.

(c) Integrate the balance equation to obtain an expression for $T(t)$ and calculate the solvent temperature after 40 minutes.

(d) The tank is shut down for routine maintenance, and a technician notices that a thin mineral scale has formed on the outside of the steam coil. The coil is treated with a mild acid that removes the scale and reinstalled in the tank. The process described above is run again with the same steam conditions, solvent flow rate, and mass of solvent charged to the tank, and the temperature after 40 minutes is 55°C instead of the value calculated in Part (c). One of the system variables listed in the problem statement must have changed as a result of the change in the stirrer. Which variable would you guess it to be, and by what percentage of its initial value did it change?

SAFETY

10.30. At 9:30 one morning, a graduate student measures 350 grams of liquid benzene at 20°C into a glass flask dirty enough that its contents cannot be seen, puts the open flask on a bunsen burner, turns the burner on, and goes for a coffee break. The conversation at the break is lively, and he doesn't get back until 10:10 a.m. He looks down into the flask, sees the liquid is boiling, turns the burner off, feels a little irritation in his eye and rubs the eye with his hand, picks up the flask, says "Ouch" (or something roughly equivalent), puts the flask down on his laboratory partner's thermodynamics homework, and starts to prepare the next step of the experiment.

(a) Suppose the heat input rate to the flask contents is 40.2 W. Calculate the time at which the benzene temperature reaches 40°C. Neglect evaporation of benzene during the heating and take the heat capacity of liquid benzene to be constant at 1.77 J/(g·°C).

(b) Calculate the quantity of benzene left in the flask at 10:10 a.m., assuming that once the benzene starts boiling, the rate of heat input to the flask (40.2 W) equals the rate of vaporization (g/s) times the heat of vaporization (J/g).

(c) The graduate student was lucky. First, neither his faculty advisor nor the departmental safety officer came into the laboratory during this episode. More importantly, he was still alive and well at the end of the day. Identify as many of his safety violations as you can, explaining the danger and suggesting for each violation what he should have done instead.

10.31. A steam radiator is used to heat a 60-m^3 room. Saturated steam at 3.0 bar condenses in the radiator and emerges as a liquid at the saturation temperature. Heat is lost from the room to the outside at a rate

$$\dot{Q}(\text{kJ/h}) = 30.0(T - T_0)$$

where T(°C) is the room temperature and $T_0 = 0$°C is the outside temperature. At the moment the radiator is turned on, the temperature in the room is 10°C.

(a) Let $\dot{m}_s$(kg/h) denote the rate at which steam condenses in the radiator and n(kmol) the quantity of air in the room. Write a differential energy balance on the room air, assuming that n remains constant at its initial value, and evaluate all numerical coefficients. Take the heat capacity of air (C_v) to be constant at 20.8 J/(mol·°C).

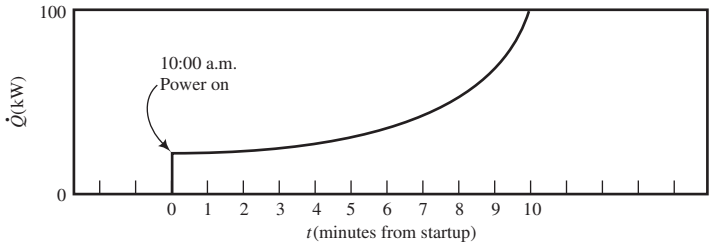
(b) Write the steady-state energy balance on the room air and use it to calculate the steam condensation rate required to maintain a constant room temperature of 24°C. Without integrating the transient balance, sketch a plot of T versus t, labeling both the initial and maximum values of T.

(c) Integrate the transient balance to calculate the time required for the room temperature to rise by 99% of the interval from its initial value to its steady-state value, assuming that the steam condensation rate is that calculated in Part (b).

SAFETY

10.32. An immersed electrical heater is used to raise the temperature of a liquid from 20°C to 60°C in 20.0 min. The combined mass of the liquid and the container is 250 kg, and the mean heat capacity of the system is 4.00 kJ/(kg·°C). The liquid decomposes explosively at 85°C.

At 10:00 a.m. a batch of liquid is poured into the vessel, and the operator turns on the heater and answers a call on his cell phone. Ten minutes later, his supervisor walks by and looks at the computer display of the power input. This what she sees.



The supervisor immediately shuts off the heater and charges off to pass on to the operator several brief observations that come to her mind.

(a) Calculate the required constant power input $\dot{Q}$(kW), neglecting energy losses from the container.

(b) Write and integrate using Simpson's rule (Appendix A.3) an energy balance on the system to estimate the system temperature at the moment the heater is shut off. Use the following data from the recorder chart:

t(s)	0	30	60	90	120	150	180	210	240	270	300
$\dot{Q}$(kW)	33	33	34	35	37	39	41	44	47	50	54

t(s)	330	360	390	420	450	480	510	540	570	600
$\dot{Q}$(kW)	58	62	66	70	75	80	85	90	95	100

(c) Suppose that if the heat had not been shut off, $\dot{Q}$ would have continued to increase linearly at a rate of 10 kW/min. At what time would everyone in the plant realize that something was wrong?

10.33. A 2000-liter tank initially contains 400 liters of pure water. Beginning at $t = 0$, an aqueous solution containing 1.00 g/L of potassium chloride flows into the tank at a rate of 8.00 L/s and an outlet stream simultaneously starts flowing at a rate of 4.00 L/s. The contents of the tank are perfectly mixed, and the densities of the feed stream and of the tank solution, ρ(g/L), may be considered equal and constant. Let $V(t)$(L) denote the volume of the tank contents and $C(t)$(g/L) the concentration of potassium chloride in the tank contents and outlet stream.

(a) Write a balance on total mass of the tank contents, convert it to an equation for dV/dt, and provide an initial condition. Then write a potassium chloride balance, show that it reduces to

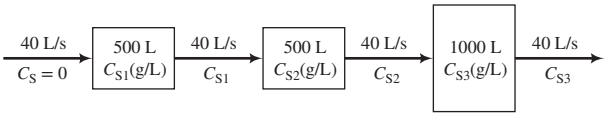
$$\frac{dC}{dt} = \frac{8 - 8C}{V}$$

and provide an initial condition. (*Hint:* You will need to use the mass balance expression in your derivation.)

(b) Without solving either equation, sketch the plots you expect to obtain for V versus t and C versus t. If the plot of C versus t has an asymptotic limit as $t \to \infty$, determine what it is and explain why it makes sense.

(c) Solve the mass balance to obtain an expression for $V(t)$. Then substitute for V in the potassium chloride balance and solve for $C(t)$ up to the point when the tank overflows. Calculate the KCl concentration in the tank at that point.

10.34. The diagram below shows three continuous stirred tanks connected in series and initially filled with water.



The flow and mixing patterns in this system are studied by dissolving 1500 g of a salt (S) in the first tank, and then starting the 40 L/s flow through the system. Each tank outlet stream is monitored with an on-line thermal conductivity detector calibrated to provide instantaneous readings of salt concentration. The data are plotted versus time, and the results are compared with the plots that would be expected if the tanks are all perfectly mixed. Your job is to generate the latter plots.

(a) Assuming that pure water is fed to the first tank and that each tank is perfectly mixed (so that the salt concentration in a tank is uniform and equal to the concentration in the outlet stream from that tank), write salt balances on each of the three tanks, convert them to expressions for dC_{S1}/dt, dC_{S2}/dt, and dC_{S3}/dt, and provide appropriate initial conditions.

(b) Without doing any calculations, on a single graph sketch the forms of the plots of C_{S1} versus t, C_{S2} versus t, and C_{S3} versus t you would expect to obtain. Briefly explain your reasoning.

(c) Use a differential equation-solving program to solve the three equations, proceeding to a time at which C_{S3} has fallen below 0.01 g/L, and plot the results.

10.35. The following chemical reactions take place in a liquid-phase batch reactor of constant volume V.

$$\text{A} \rightarrow 2\text{B} \quad r_1[\text{mol A consumed/(L}\cdot\text{s)}] = 0.100C_A$$
$$\text{B} \rightarrow \text{C} \quad r_2[\text{mol C generated/(L}\cdot\text{s)}] = 0.200C_B^2$$

where the concentrations C_A and C_B are in mol/L. The reactor is initially charged with pure A at a concentration of 1.00 mol/L.

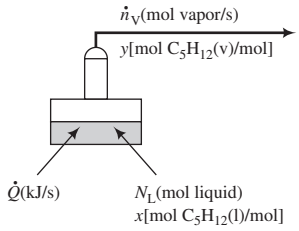
(a) Write expressions for (*i*) the rate of generation of B in the first reaction and (*ii*) the rate of consumption of B in the second reaction. (If this takes you more than about 10 seconds, you're missing the point.)

(b) Write mole balances on A, B, and C, convert them into expressions for dC_A/dt, dC_B/dt, and dC_C/dt, and provide boundary conditions.

(c) Without doing any calculations, sketch on a single graph the plots you would expect to obtain of C_A versus t, C_B versus t, and C_C versus t. Clearly show the function values at $t = 0$ and $t \rightarrow \infty$ and the curvature (concave up, concave down, or linear) in the vicinity of $t = 0$. Briefly explain your reasoning.

(d) Solve the equations derived in Part (b) using a differential equation-solving program. On a single graph, show plots of C_A versus t, C_B versus t, and C_C versus t from $t = 0$ to $t = 50$ s. Verify that your predictions in Part (c) were correct. If they were not, change them and revise your explanation.

10.36. A liquid mixture containing 70.0 mol of *n*-pentane and 30.0 mol of *n*-hexane initially at 46°C is partially vaporized at $P = 1$ atm in a single-stage distillation apparatus (**Rayleigh still**).



The heat added to the system, $\dot{Q}$, vaporizes liquid at the rate $\dot{n}_V$(mol/s). The vapor product and remaining liquid at a given moment are always in equilibrium with each other. The relationship between the mole fraction of pentane in the liquid (x) and that in the vapor (y) is of the form

$$y = \frac{ax}{x + b}$$

so that the system involves four time-dependent variables—N_L, $\dot{n}_V$, x, and y, where N_L is the total moles of liquid in the still at any time. (We will suppose that the rate of heat transfer to the evaporator, $\dot{Q}$, is constant and known.) Four equations relating the unknowns will be required to determine these variables. The equations are two material balances, an energy balance, and the vapor–liquid equilibrium relationship just given.

(a) When $x = 1$, what must y equal? (Think of the definitions of these quantities.) Use your answer and the vapor–liquid equilibrium expression to derive an equation relating the parameters a and b.

(b) Use Raoult's law (Equation 6.4-1) and the Antoine equation to calculate the mole fraction of pentane in the vapor phase in equilibrium with the 70% pentane–30% hexane feed mixture at the initial system temperature of 46°C and a pressure of 1 atm. Then use this result and that of Part (a) to estimate a and b. (Assume that these values remain the same over the range of compositions and temperatures to be undergone by the system.)

(c) Taking the residual liquid in the still as your system, write a differential balance on total moles to obtain an expression for dN_L/dt. Then write a balance on pentane, recognizing that both N_L and x are functions of time. (*Hint*: Remember the product rule for differentiation.) Prove that the pentane balance can be converted into the following equation:

$$\frac{dx}{dt} = \frac{\dot{n}_V}{N_L}\left(\frac{ax}{x+b} - x\right)$$

Supply initial conditions for your two differential equations.

(d) In Part (c), you derived two equations in three unknown dependent variables—$\dot{n}_V(t)$, $N_L(t)$, and $x(t)$. To determine these variables, we need a third relationship. An energy balance provides it.

A rigorous energy balance would take into account the changing composition of the liquid, the slightly different heats of vaporization of pentane and hexane, and the enthalpy changes associated with temperature changes, and would make the problem relatively hard to solve. A reasonable approximation is to assume that (i) the liquid has a constant heat of vaporization of 27.0 kJ/mol, independent of composition and temperature; and (ii) all heat supplied to the still [$\dot{Q}$(kJ/s)] goes to vaporize liquid (i.e., we neglect energy that goes into raising the temperature of the liquid or the vapor). Make these assumptions, consider $\dot{Q}$ to be constant and known, and derive a simple expression for $\dot{n}_V$ that can be used to eliminate this variable in the differential equations of Part (c). From there, derive the following expression:

$$\frac{dx}{dt} = -\frac{\dot{Q}/27.0}{100.0\ \text{mol} - \dot{Q}t/27.0}\left(\frac{ax}{x+b} - x\right)$$

(e) Use a differential equation-solving program to calculate x, y, N_L, and $\dot{n}_V$ from $t = 0$ until the time at which the liquid completely evaporates. Do the calculation for (i) $\dot{Q} = 1.5$ kJ/s and (ii) $\dot{Q} = 3.0$ kJ/s. On a single graph, plot x and y versus t, showing curves for both values of $\dot{Q}$.

(f) In a short paragraph, describe what happens to the compositions of the vapor product and residual liquid over the course of a run. Include a statement of what the initial and final vapor compositions are and how the heating rate affects the system behavior.

APPENDIX
A

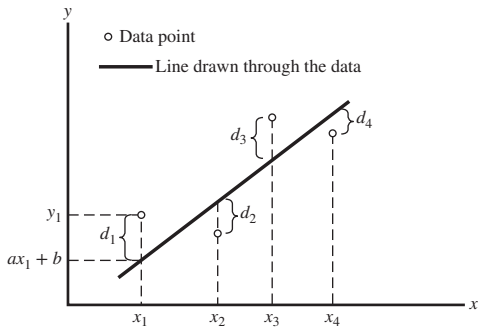
Computational Techniques

This appendix introduces several mathematical concepts and methods that have widespread applicability in the analysis of chemical processes. The presentation presumes a knowledge of elementary calculus, but not of linear algebra or numerical analysis. The student who wishes a broader or deeper treatment of the subjects discussed is advised to refer to a numerical analysis reference.

Appendix A.1 THE METHOD OF LEAST SQUARES

In this section we outline a statistical technique for fitting a straight line to y versus x data. You should be aware, however, that in doing so we are barely scratching the surface of the field of statistical analysis; we will not discuss techniques for fitting functions of several variables, for determining quantitatively the uncertainties associated with a fit, or for comparing alternative functions used to fit a given data set.

Suppose you measure y at four values of x, plot the data on a graph of y versus x, and draw a line through the data points.



If the line you draw is $y = ax + b$, then at an abscissa point x_i ($i = 1, 2, 3,$ or 4) the measured value of y is y_i, and the corresponding value of y on the line is $ax_i + b$. The vertical distance d_i from the ith data point to the line (called the ith **residual**) is therefore

$$d_i = y_i - (ax_i + b), \quad i = 1, 2, 3, 4 \qquad \textbf{(A.1-1)}$$

If d_i is positive then the ith data point must be above the line (why?), if d_i is negative the point is below the line, and if d_i equals zero the line passes through the point. A line is said to fit the data well if the values of most of the residuals are close to zero.

There are several ways to determine the line that best fits a set of data, which differ primarily in their definitions of "best." The most common method is the **method of least squares**.

Suppose there are n plotted points $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$, so that a line $y = ax + b$ drawn through the points yields a set of n residuals $d_1, d_2, \ldots, d_n$. According to the method of least squares, *the best line through the data is the one that minimizes the sum of the squares of the residuals.*[1]

[1] We could also choose the best line as the one that minimizes the sum of the absolute values of the residuals, or the sum of the fourth powers of the residuals. Using the squares simply provides computational convenience.

The task is therefore to find the values of a and b that minimize

$$\phi(a,b) = \sum_{i=1}^{n} d_i^2 = \sum_{i=1}^{n} (y_i - ax_i - b)^2 \tag{A.1-2}$$

You can obtain expressions for the best values of a and b in terms of known quantities by differentiating the equation for ϕ (Equation A.1-2) with respect to both a and b, setting the derivatives equal to zero, and solving the resulting algebraic equations for a and b. The results of these calculations are as follows. If we define

$$\begin{aligned} s_x &= \frac{1}{n}\sum_{i=1}^{n} x_i \qquad s_{xx} = \frac{1}{n}\sum_{i=1}^{n} x_i^2 \\ s_y &= \frac{1}{n}\sum_{i=1}^{n} y_i \qquad s_{xy} = \frac{1}{n}\sum_{i=1}^{n} x_i y_i \end{aligned} \tag{A.1-3}$$

then

1. Best line: $y = ax + b$

Slope: $$a = \frac{s_{xy} - s_x s_y}{s_{xx} - (s_x)^2} \tag{A.1-4}$$

Intercept: $$b = \frac{s_{xx} s_y - s_{xy} s_x}{s_{xx} - (s_x)^2} \tag{A.1-5}$$

2. Best line through the origin: $y = ax$

Slope: $$a = \frac{s_{xy}}{s_{xx}} = \frac{\sum x_i y_i}{\sum x_i^2} \quad \text{(The intercept equals 0.0.)} \tag{A.1-6}$$

Once you determine a and b, you should plot the line $y = ax + b$ on the same graph as the data to get an idea of how good the fit is.

Example A.1-1 The Method of Least Squares

Two variables, P and t, are related by the equation

$$P = \frac{1}{mt^{1/2} + r}$$

The following data are taken:

P	0.279	0.194	0.168	0.120	0.083
t	1.0	2.0	3.0	5.0	10.0

Calculate m and r using the method of least squares.

Solution The equation may be rewritten in the form

$$\frac{1}{P} = mt^{1/2} + r$$

so that a plot of $1/P$ versus $t^{1/2}$ should be a line with slope m and intercept r. From the tabulated data,

$y = 1/P$	3.584	5.155	5.952	8.333	12.048
$x = t^{1/2}$	1.00	1.414	1.732	2.236	3.162

$$\frac{1}{P} = mt^{1/2} + r$$

$$\Downarrow\ y = 1/P,\ x = t^{1/2}$$

$$y = mx + r$$

Evaluate the quantities of Equation A.1-3:

$$s_x = \tfrac{1}{5}(1.000 + 1.414 + 1.732 + 2.236 + 3.162) = 1.909$$

$$s_y = 7.014$$

$$s_{xx} = 4.200$$

$$s_{xy} = 15.582$$

Hence, from Equation A.1-4,

Slope: $$m = \frac{s_{xy} - s_x s_y}{s_{xx} - (s_x)^2} = 3.94$$

and from Equation A.1-5,

Intercept: $$r = \frac{s_{xx}s_y - s_{xy}s_x}{s_{xx} - (s_x)^2} = -0.517$$

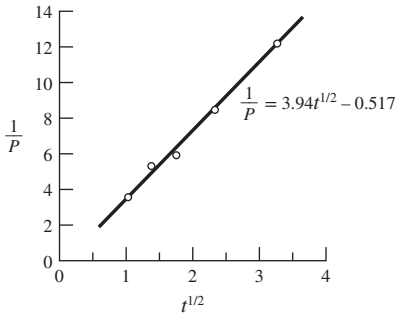
so that the final result is

$$\boxed{P = \frac{1}{3.94t^{1/2} - 0.517}}$$

A check on the results is to plot $1/P$ versus $t^{1/2}$, showing both the data points and the line

$$\frac{1}{P} = 3.94t^{1/2} - 0.517$$

If the choice of this function to fit the given data was reasonable and if no mistakes were made in the calculations, the data points should be scattered about the line. This is in fact the case, as shown in the following diagram.



Test Yourself

(Answers, p. 660)

1. A line $y = 3x + 2$ has been fit to a set of data including the points $(x = 1, y = 4)$ and $(x = 3, y = 13)$. What are the residuals at these two points?
2. What is the definition of the best line through a set of data points that forms the basis of the method of least squares?
3. Could the method of least squares be used to fit a straight line to data points that fall on a distinct curve? (*Corollary:* Does the line that "best" fits the data necessarily fit the data well?)
4. An alternative to the method of least squares might be to minimize the sum of the residuals rather than the sum of squares of the residuals. What would be wrong with this method?

Appendix A.2 ITERATIVE SOLUTION OF NONLINEAR ALGEBRAIC EQUATIONS

A.2a Linear and Nonlinear Equations

Given below is the van der Waal's equation of state:

$$(P + a/\hat{V})(\hat{V} - b) = RT$$

Solving this equation to calculate P for a given $\hat{V}$ and T is easy, while solving for $\hat{V}$ for specified values of P and T is relatively difficult.

What makes an equation easy or difficult to solve is its **linearity** or **nonlinearity** in the unknown variable. Equations that contain unknown variables raised to the first power only (x, but not x^2 or $x^{1/2}$), and that do not contain products (xy) or transcendental functions ($\sin x$, e^x) of unknown variables, are called **linear equations**. Equations that do not satisfy these conditions are called **nonlinear equations**.

For example, if a, b, and c are constants, and x, y, and z *are* variables,

$$\begin{aligned} ax + by &= c && \text{is linear} \\ ax^2 &= by + c && \text{is nonlinear (contains } x^2\text{)} \\ x - \ln x + b &= 0 && \text{is nonlinear (contains } \ln x\text{)} \\ ax + by &= cx && \text{is linear} \end{aligned}$$

Linear equations that contain a single unknown variable have one and only one solution (one **root**).

$$7x - 3 = 2x + 4 \Longrightarrow x = 1.2$$

$$\left.\begin{array}{l} P\hat{V} = RT \\ P = 3, R = 2, T = 300 \end{array}\right\} \Longrightarrow \hat{V} = RT/P = (2)(300)/(3) = 200$$

In contrast, nonlinear equations that contain a single unknown variable may have any number of real roots (as well as imaginary and complex roots). For example,

$$\begin{aligned} x^2 + 1 = 0 &\quad \text{has no real roots} \\ x^2 - 1 = 0 &\quad \text{has two real roots } (x = +1 \text{ and } x = -1) \\ x - e^{-x} = 0 &\quad \text{has one real root } (x = 0.56714\ldots) \\ \sin x = 0 &\quad \text{has an infinite number of real roots } (x = 0, \pi, 2\pi, \ldots) \end{aligned}$$

The roots of some nonlinear equations, such as the second of the equations given above, can be obtained directly using simple algebra, but most nonlinear equations must be solved using an iterative or trial-and-error technique.

A single equation containing several variables may be linear with respect to some variables and nonlinear with respect to others. For example,

$$xy - e^{-x} = 3$$

is linear in y and nonlinear in x. If x is known, the equation may easily be solved for y, while the solution for x from a known variable of y is much harder to obtain. Another example is the three-term virial equation of state:

$$P\hat{V} = RT\left(1 + \frac{B(T)}{\hat{V}} + \frac{C(T)}{\hat{V}^2}\right)$$

where B and C are known functions of temperature. This equation is linear in P and nonlinear in $\hat{V}$ and T. It is consequently easy to solve for P from given values of T and $\hat{V}$ and difficult to solve for either $\hat{V}$ or T from given values of the other two variables.

Most of the problems you are called on to solve in this text reduce to one or two linear equations in as many unknowns. The hard part of the problems, if there is a hard part, is deriving the equations; solving them is a matter of simple algebra. However, many process problems involve nonlinear equations. Techniques for solving such problems are the subject of this section.

Test Yourself

(Answers, p. 660)

Classify the following single-variable equations as linear or nonlinear, considering a, b, and c as constants.

1. $3x + 17 = 23x - 12$

2. $3x = a(\ln x) + b$

3. $x \exp(x) = 14$

4. $axy - b^2 = cy/x$

(a) x is known

(b) y is known

5. $14x \cos(y) - 8/z = 23$

(a) x and y are known

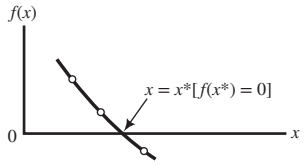
(b) x and z are known

(c) y and z are known

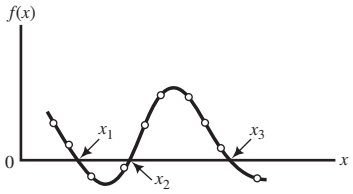
A.2b Graphical Solution

In this and the next several sections, we will discuss methods for solving one nonlinear equation in one unknown. Extensions to multivariable problems will be presented in Section A.2i.

Suppose you have to solve an equation of the form $f(x) = 0$ — that is, find the root or roots of the function $f(x)$. [Any equation can be written in this form by bringing every term to the left side. For example, $x = e^{-x}$ becomes $f(x) = x - e^{-x} = 0$.] An obvious solution technique is to plot $f(x)$ versus x and to locate by graphical interpolation the point at which the curve crosses the axis.



There are several problems with this technique. It is a manual method; it is relatively slow; and it is not very precise. Its principal advantage is that it enables you to see how f varies with x, which is particularly useful when you are dealing with functions that have several roots.



The points x_1, x_2, and x_3 are all *roots* (solutions) of the equation $f(x) = 0$. The computational techniques we will describe shortly would locate one or another of these roots, depending on the initial guess; however, for all but simple polynomial functions a plot is the only convenient method to detect the existence and approximate location of multiple roots. Therefore, unless you know that only one root exists, or you know the approximate location of each root you need to

determine, a good procedure is to plot f versus x and use the plot to determine initial estimates for more precise root-finding methods.

Test Yourself

(Answers, p. 660)

1. Use a graphical argument to justify the statement that a linear function has only one root.
2. How many roots does the function $f(x) = x - \exp(-x)$ have? [*Suggestion:* Sketch plots of $f_1(x) = x$ and $f_2(x) = \exp(-x)$ versus x, and use these plots to obtain your answer.]

A.2c Spreadsheet Solution

If you have access to a spreadsheet program, finding solutions of nonlinear single-variable equations is relatively easy. If the equation has the form $f(x) = 0$, you need only enter a guessed value of x in one cell of the spreadsheet, insert the formula for $f(x)$ in an adjacent cell, and then vary the value in the first cell until the value in the second cell is close enough to zero to meet a specified convergence criterion. The next example illustrates this approach.

Example A.2-1 Spreadsheet Solution of a Nonlinear Equation

Estimate the solution of the equation $x = e^{-x}$ using a spreadsheet.

Solution The first step is to express the equation in a form $f(x) = 0$ by bringing all terms to one side of the equation. The result is

$$f(x) = x - e^{-x} = 0$$

We might set up the spreadsheet as follows, taking an initial guess of 1.0 for the solution of the equation.

	A	B
1	x	$f(x)$
2	1	0.632121

The formula entered in Cell B2 would be = A2 – exp (−A2). As the value of x in Cell A2 is changed, the value of $f(x)$ in Cell B2 changes accordingly. The strategy is to find the value in Cell A2 that drives the value in Cell B2 satisfactorily close to zero. If this is done, the following result is obtained:

	A	B
1	x	$f(x)$
2	0.56714	-5.2E-06

The desired solution is $\boxed{x = 0.56714}$, for which $f(x) = -0.0000052$. If we wanted a more precise solution we could add a sixth significant figure to the given value of x, but it is rare to need even five significant figures.

The solution is even easier to obtain if the spreadsheet program is equipped with a *goalseek* tool. Once the first of the spreadsheets shown above has been constructed, select *Goal Seek* (it can normally be found under the pull-down "Tools" menu), and enter **B2** as the target cell, 0.0 as the target, and **A2** as the variable cell. The spreadsheet will then search for and (usually) converge on the solution within a fraction of a second.

One limitation to this method (and to all other numerical methods for solving nonlinear equations) is that once you have found one solution, you cannot be sure that there are no additional solutions. The way to determine the existence of multiple roots is to evaluate $f(x)$ over a wide range of x values and find the intervals in which $f(x)$ changes sign (see the second figure in

the previous section). Initial guesses can then be made within each of these intervals and the spreadsheet used to determine the roots precisely.

A.2d *Regula-falsi* Method

In this and the next subsection, we outline algorithms for finding roots of single-variable equations of the form $f(x) = 0$. The first procedure, termed the **regula-falsi method**, is appropriately used when an analytical expression for the derivative of f with respect to x is not available—as, for example, when $f(x)$ is obtained as the output of a computer program for an input value of x. The algorithm is as follows:

1. Find a pair of values of x (use x_n and x_p) such that $f_n = f[x_n] < 0$ and $f_p = f[x_p] > 0$.

2. Estimate the value of the root of $f(x)$ from the following formula:

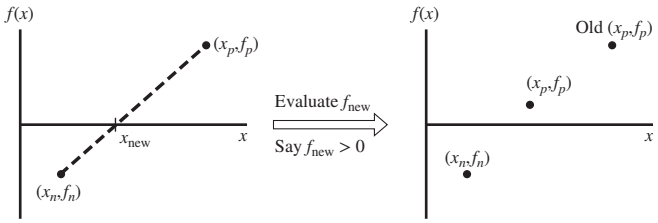
$$x_{\text{new}} = \frac{x_n f_p - x_p f_n}{f_p - f_n} \qquad \textbf{(A.2-1)}$$

and evaluate $f_{\text{new}} = f[x_{\text{new}}]$.

3. Use the new point to replace one of the original points, keeping the two points on opposite sides of the x axis. If $f_{\text{new}} < 0$, replace the old x_n and f_n with x_{new} and f_{new}. If $f_{\text{new}} > 0$, replace x_p and f_p with x_{new} and f_{new}. (If $f_{\text{new}} = 0$, you have found the root and need go no further.)

4. See if the new x_n and x_p are close enough for convergence to be declared (see Section A.2h). If they are not, go back to step 2.

What you are doing with this procedure is the algebraic equivalent of drawing a straight line between the two points $[x_n, f_n]$ and $[x_p, f_p]$ on a plot of f versus x and using the intersection of this line with the x axis as the next estimate of the root.



Successive points determined in this manner clearly approach the x axis (where $f = 0$). The procedure terminates when f_{new} is close enough to zero to satisfy a specified convergence criterion.

The *regula-falsi* method is the procedure used by many spreadsheet programs in their goalseek algorithms.

Test Yourself

(Answers, p. 661)

1. Suppose a "black box" computer program gives values of a function $f(x)$ for specified values of x. Unknown to the programmer, the function is

$$f = 4 - (x - 2)^2$$

(a) What are the roots of this function? (You should be able to do it by inspection.)

(b) Suppose the programmer tries values $x_p = 3$ and $x_n = 5$. If she uses the regula-falsi method, what will the next pair be? To which root will the method ultimately converge?

2. Derive Equation A.2-1.

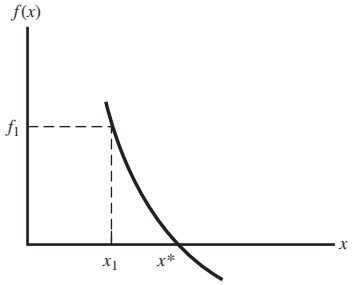
A.2e Newton's Rule

The next algorithm for finding the root of a function $f(x)$ is **Newton's rule**. It is considerably more efficient than *regula-falsi*, but only for functions for which the derivative $f'(x) = df/dx$ can be evaluated analytically. The formula for proceeding from one estimate of the root to the next is

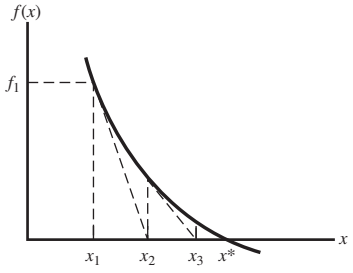
$$x_{k+1} = x_k - \frac{f_k}{f'_k} \tag{A.2-2}$$

where x_k is the k th estimate of the root, $f_k = f(x_k)$, and $f'_k = df/dx$ evaluated at $x = x_k$. As always, you begin by estimating a value of the root, x_1. Successive estimates are then generated from Equation A.2-2, with a test for convergence (Section A.2h) being applied after each estimate is obtained.

The easiest way to understand how Newton's rule works is graphically. Suppose the plot of f versus x appears as follows:

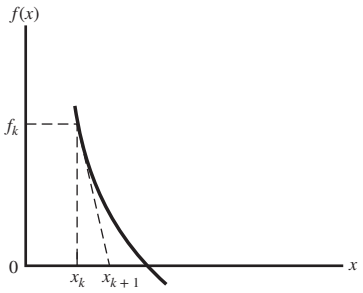


Although it may not be obvious at first glance, Newton's rule is equivalent to choosing a value of x_1 and calculating $f_1 = f(x_1)$, drawing a line tangent to the curve at (x_1, f_1) and using the intersection of this line with the x axis as the next estimate (x_2). As the following diagram shows, the successive values of x generated in this manner $(x_2, x_3, x_4, \ldots)$ may converge on the root x^*, although convergence is not guaranteed.



The formula for each estimate (x_{k+1}) in terms of the previous estimate (x_k) may easily be derived. The graphical representation of one step of the procedure is shown on the next page. The slope of the tangent line is $(df/dx)_{x_k} = f'_k$; however, two known points on this line are $(x_{k+1}, 0)$ and (x_k, f_k) so that the slope is also equal to $(0 - f_k)/(x_{k+1} - x_k)$. Equating these two expressions for the slope yields

$$f'_k = \frac{-f_k}{x_{k+1} - x_k}$$



The solution of this equation for x_{k+1} is Newton's rule, Equation A.2-2:

$$x_{k+1} = x_k - \frac{f_k}{f'_k}$$

Example A.2-2 Newton's Rule

Determine the root of the equation $x = e^{-x}$ using Newton's rule.

Solution

$$f(x) = x - e^{-x}$$
$$f'(x) = df/dx = 1 + e^{-x}$$

When $x = 0$, $f(x)$ is negative, while when $x = 1$, $f(x)$ is positive (*verify*). The root x^* must therefore be between 0 and 1. Try $x_1 = 0.2$ as a first guess.

First Iteration: $x_1 = 0.2$

$$\Downarrow$$

$$f(x_1) = 0.2 - e^{-0.2} = -0.6187$$

$$\Downarrow$$

$$f'(x_1) = 1 + e^{-0.2} = 1.8187$$

$$\Downarrow$$

$$x_2 = x_1 - f(x_1)/f'(x_1) = 0.5402$$

Second Iteration: $x_2 = 0.5402$

$$\Downarrow$$

$$f(x_2) = 0.5402 - e^{-0.5402} = -0.0424$$

$$\Downarrow$$

$$f'(x_2) = 1 + e^{-0.5402} = 1.5826$$

$$\Downarrow$$

$$x_3 = x_2 - f(x_2)/f'(x_2) = 0.5670$$

Third Iteration: $x_3 = 0.5670$

$$\Downarrow$$

$$f(x_3) = 0.5670 - e^{-0.5670} = 2.246 \times 10^{-4}$$

$$\Downarrow$$

$$f'(x_3) = 1 + e^{-0.5670} = 1.5672$$

$$\Downarrow$$

$$x_4 = x_3 - f(x_3)/f'(x_3) = 0.56714$$

The successive estimates of x^* are therefore

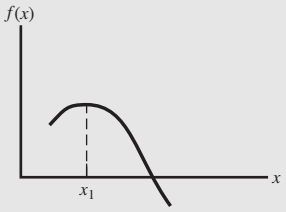
$$0.2 \Longrightarrow 0.5402 \Longrightarrow 0.5670 \Longrightarrow 0.56714$$

This is clearly a converging sequence. Depending on how much precision you require, you might stop here or carry out one or two additional iterations. Let us stop here, and say that $x^* \approx 0.56714$.

Test Yourself

(Answers, p. 661)

1. Could you use Newton's rule to find a root of the equation $x^2 - 3x - 3 = 0$? Would you use it? Why not?
2. Suppose you wish to find a root of $f(x) = 0$, where $f(x)$ versus x appears as shown here.



What would happen if you took as a first guess the value of x_1 shown? (What would happen shows that Newton's rule does not necessarily work if a poor choice of x_1 is made.)

A.2f Successive Substitution and Modified Successive Substitution

Problems involving the solution of nonlinear equations can often be expressed in the form

$$x = f(x)$$

where $f(x)$ is a nonlinear function. (*Example:* $x = e^{-x}$.) As shown in Chapter 10, balance equations for multiple unit processes with recycle often fall into this category: x would be the assumed value of a tear stream variable, and $f(x)$ would be the value generated by calculating around the cycle.

The simplest solution method is **successive substitution**. An initial estimate, $x^{(1)}$, is selected; $f(x^{(1)})$ is calculated; and the calculated value is used as the next estimate of the root. The formula is

$$x^{(i+1)} = f(x^{(i)}) \qquad \textbf{(A.2-3)}$$

The procedure is repeated until the specified convergence criterion is satisfied.

Sometimes successive substitution works very well, converging in a few steps. Three unsatisfactory convergence patterns are also observed from time to time, however. In the first, the successive estimates oscillate about a central value:

$$37.6, 2.3, 36.8, 2.6, 34.4, 2.9, \ldots$$

The root lies somewhere between 3 and 30, but the procedure will clearly take a large number of iterations to get there.

The problem here is that successive substitution generates overly large steps. Instead of jumping all the way from 37.6 to 2.3, as successive substitution dictates, we should only go part of the way from the first to the second value to obtain our estimate of $x^{(2)}$. To do this, we may use **modified successive substitution** (also called damped successive substitution). The formula is

$$x^{(i+1)} = x^{(i)} + p[f(x^{(i)}) - x^{(i)}] \qquad \textbf{(A.2-4)}$$

where p, the **damping parameter**, is a number between 0 and 1. If $p = 1$, the procedure reduces to pure successive substitution, and as p approaches zero, the size of the step becomes smaller and smaller. A few trial-and-error iterations should yield a good value of p for a specific problem.

The second case of slow convergence in successive substitution involves a creeping progression, such as

$$151.7, 149.5, 147.4, 145.6, 143.8, \ldots$$

Again, it appears that the procedure could be converging to a solution, but it is equally clear that it is in no hurry to get there.

The remedy for this problem is to **accelerate** the convergence procedure—to jump over many of the intermediate solutions to which continued successive substitution would lead. The next section outlines Wegstein's method, one of the most commonly used acceleration algorithms.

The third unsatisfactory convergence pattern is instability. For example, if successive substitution yields a sequence like

$$1.0, 2.5, -6.8, 23.5, 97.0, \ldots$$

then successive substitution will clearly not work, no matter how many iterations are attempted. A better first estimate might yield a convergent sequence, or the problem might be intrinsically unstable and must be restructured or solved by a different technique. Texts on numerical analysis outline stability conditions for nonlinear equation solution algorithms; their consideration is beyond the scope of this appendix.

Test Yourself

(Answers, p. 661)

1. For each of the following sequences of successive estimates of a root, indicate whether successive substitution seems to be adequate or whether you would resort to modified successive substitution or an acceleration method (state which).
   (a) $165, 132, 163, 133, 162, 133, \ldots$
   (b) $43, 28, 26, 26.7, 26.71, \ldots$
   (c) $21.0, 21.2, 21.4, 21.59, 21.79, \ldots$
2. Suppose $x^{(i)} = 14.0, f(x^{(i)}) = 13.0$, and you are using modified successive substitution with $p = 0.4$. What is your next estimate of the root?

A.2g Wegstein Algorithm

The procedure outlined in this section encompasses successive substitution and modified successive substitution as special cases, and in addition provides acceleration capability.

1. Begin by choosing $x^{(1)}$. Calculate $f(x^{(1)})$, and let $x^{(2)} = f(x^{(1)})$. (That is, carry out a successive substitution step.) Let $k = 2$.
2. Calculate $f(x^{(k)})$.
3. Check for convergence. If $x^{(k)}$ and $f(x^{(k)})$ are close enough together to meet the convergence criterion, terminate the procedure. If convergence is not achieved, calculate

$$w = \frac{f(x^{(k)}) - f(x^{(k-1)})}{x^{(k)} - x^{(k-1)}} \qquad \textbf{(A.2-5a)}$$

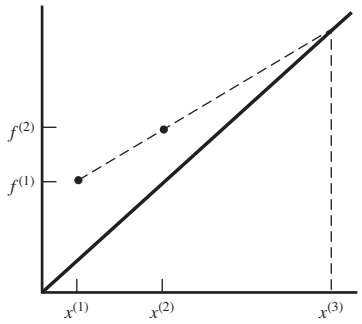
$$q = w/(w - 1) \qquad \textbf{(A.2-5b)}$$

4. Calculate

$$x^{(k+1)} = qx^{(k)} + (1 - q)f(x^{(k)}) \qquad \textbf{(A.2-6)}$$

5. Increase k by 1 and go back to step 2.

It is not difficult to show that Wegstein's method is tantamount to generating two points on the curve of $f(x)$ versus x and determining as the next estimate the intersection of the line between these two points and the 45° line [at which $x = f(x)$].



If you examine Equation A.2-6, you will see that if the parameter q equals zero, the procedure reduces to successive substitution; if q is between zero and 1 the procedure is modified successive substitution; and if q is negative the procedure involves acceleration.

Test Yourself

(Answers, p. 661)

An effort to solve the equation $x = f(x)$ begins with two successive substitution steps:

$$x = 2.00 \rightarrow f(x) = 2.30$$
$$x = 2.30 \rightarrow f(x) = 2.45$$

1. Calculate the next value of x using the Wegstein algorithm.
2. Sketch a plot of $f(x)$ versus x, showing the two given points, and show graphically that the value of x you calculated is correct.

A.2h Convergence Criteria

A problem common to all iterative computational methods is knowing when to quit. An iterative method rarely yields a precise root, but rather gives successive approximations that (if the method converges) approach the root more and more closely. Whether you are doing the calculation by hand or writing a program to do it, you must specify how close is close enough.

Suppose we wish to find a solution of the equation $f(x) = 0$ using a method that gives successive estimates $x^{(1)}$, $x^{(2)}$, and so on. Several different criteria may be used to determine when to terminate the procedure. The most straightforward one calls for termination when the absolute value of $f(x^{(i)})$ falls within a specified interval about $f = 0$:

$$|f(x^{(i)})| < \varepsilon \qquad \textbf{(A.2-7)}$$

where ε, the *convergence tolerance*, is chosen to be several orders of magnitude smaller than typical values of $f(x)$ in the range being searched. Decreasing the value of ε leads to a more accurate estimate of the solution but increases the number of steps (and hence computation time) required to get there. There are formal ways to choose the value of ε, but it can be just as easy to choose a value (e.g., 0.0001 times the value of f at the first guessed value of x), find the root, then decrease the value of ε by a factor of 10, search again starting with the previous converged value, and see if the solution changes enough to care about.

The convergence criterion (A.2-7) may yield a false solution if the function $f(x)$ is almost horizontal over a wide range around the root, so that $|f(x^{(i)})|$ may be less than ε (meeting the convergence criterion) when $x^{(i)}$ is still a long way from the root. In this case, one of the following

convergence criteria might be more appropriate to use:

$$|x^{(i)} - x^{(i-1)}| < \varepsilon \tag{A.2-8}$$

$$\frac{|x^{(i)} - x^{(i-1)}|}{x^{(i)}} < \varepsilon \tag{A.2-9}$$

Equation A.2-8 is an *absolute convergence criterion.* If the value of x changes by less than ε from one iteration to the next, the procedure is terminated and the last value of x is taken to be the desired root. The strictness of this criterion for a given ε depends on the magnitude of the estimated values. If $\varepsilon = 0.01$, for example, and successive estimates of x are 358,234.5 and 358,234.6, the procedure would not be terminated, even though the estimates are undoubtedly close enough for any realistic purpose. On the other hand, successive estimates of 0.0003 and 0.0006 would lead to termination for the same value of ε, despite the fact that the two estimates differ by a factor of two.

Equation A.2-9, a *relative convergence criterion*, avoids this difficulty. If this criterion is used, a value of $\varepsilon = 0.01$ specifies that the procedure will be terminated when the value of x changes from one iteration to the next by less than 1%, regardless of the magnitude of that value. This criterion does not work if successive estimates of x converge to a value of zero.

A.2i Multivariable Root-Finding Algorithms

Solving n nonlinear equations in n unknowns is usually a difficult problem, and a general treatment is well beyond the scope of this text. In this section we present several approaches without proof or much explanation. For additional details, standard texts on numerical analysis should be consulted.

Three methods that can be used to find the values of $x_1, \ldots, x_n$ that satisfy n simultaneous equations are extensions of methods given previously for single-variable problems. They are (a) successive substitution, (b) the Wegstein algorithm, and (c) the Newton–Raphson method (a multivariable extension of Newton's rule). The example that concludes this section illustrates all three algorithms.

Successive Substitution. Suppose the equations can be cast in the form

$$\begin{aligned} x_1 &= f_1(x_1, x_2, \ldots, x_n) \\ x_2 &= f_2(x_1, x_2, \ldots, x_n) \\ &\vdots \\ x_n &= f_n(x_1, x_2, \ldots, x_n) \end{aligned} \tag{A.2-10}$$

(A cycle with n tear stream variables falls into this category.) The successive substitution method consists of assuming values for each of the n unknown variables, evaluating the functions $f_1, \ldots, f_n$, and using the calculated values as the next estimates of the variables. The procedure is terminated when all variable values meet a specified convergence criterion. For example, if $x_i^{(k)}$ is the value of the ith variable at the kth iteration, the procedure might be terminated when

$$\frac{|x_i^{(k)} - x_i^{(k-i)}|}{x_i^{(k)}} < \varepsilon, \quad i = 1, 2, \ldots, n \tag{A.2-11}$$

This approach is simple but generally inefficient. The greater the number of variables, the longer it takes for the procedure to converge, if it converges at all. It is generally preferable to use Wegstein's method or the Newton–Raphson method, depending on whether or not the partial derivatives of the functions $f_1, \ldots, f_n$ can be evaluated analytically. (Use Newton–Raphson if they can be, otherwise try Wegstein, but don't be too surprised if it doesn't converge.)

Wegstein Algorithm. If the equations to be solved have the form of Equation A.2-10 [i.e., $x_i = f_i(x_1, x_2, \ldots, x_n)$], guess values for all n variables and apply the procedure of Section A.2g separately to each variable. Terminate when the convergence criteria are satisfied for all variables.

This procedure will work reasonably well if the generating function f_1 depends almost entirely on x_1, f_2 depends only on x_2, and so on (i.e., if there is little interaction among the variables). If this is not the case, convergence will generally be very difficult to achieve.

Newton–Raphson Method. Suppose now that the equations to be solved take the form

$$\begin{aligned} g_1(x_1, x_2, \ldots, x_n) &= 0 \\ g_2(x_1, x_2, \ldots, x_n) &= 0 \\ &\vdots \\ g_n(x_1, x_2, \ldots, x_n) &= 0 \end{aligned} \tag{A.2-12}$$

The Newton–Raphson method is as follows:

1. Estimate (or just guess) values of the n variables $(x_1, x_2, \ldots, x_n)$, calling the estimates, $x_1^{(1)}, x_2^{(1)}, \ldots, x_n^{(1)}$. Let $k = 1$ (the number of the iteration).

2. Evaluate the function values $(g_1, \ldots, g_n)$ corresponding to the most recent estimate of the x_i values:

$$g_i^{(k)} = g_i[x_1^{(k)}, \ldots, x_n^{(k)}], \quad i = 1, 2, \ldots, n \tag{A.2-13}$$

3. If the g_i values are to be used as the basis of a convergence test, declare the procedure to have converged if

$$|g_i^{(k)}| < \varepsilon_i, \quad i = 1, 2, \ldots, n$$

The convergence tolerance for the ith equation, ε_i, should be a very small fraction of typical values of g_i (e.g., $0.0001 g_i^{(1)}$). If the procedure has not converged, go on to step 4.

4. Evaluate the partial derivatives with respect to each variable

$$a_{ij} = \left(\frac{\partial g_i}{\partial x_j}\right) \quad \text{at} \quad \left[x_1^{(k)}, x_2^{(k)}, \ldots, x_n^{(k)}\right] \tag{A.2-14}$$

5. Solve the following set of linear equations for the variables $d_1, d_2, \ldots, d_n$.

$$\begin{aligned} a_{11}d_1 + a_{12}d_2 + \cdots + a_{1n}d_n &= -g_1^{(k)} \\ a_{21}d_1 + a_{22}d_2 + \cdots + a_{2n}d_n &= -g_2^{(k)} \\ &\vdots \\ a_{n1}d_1 + a_{n2}d_2 + \cdots + a_{nn}d_n &= -g_n^{(k)} \end{aligned} \tag{A.2-15}$$

If there are only two or three equations, you can solve them by simple algebraic techniques. For larger systems of equations, an equation-solving computer program should be used.

6. Calculate the next set of x_i values as

$$x_i^{(k+1)} = x_i^{(k)} + d_i \tag{A.2-16}$$

7. If the changes in the x values are to be used as the basis of a convergence test, declare the procedure to have converged to $[x_1^{(k+1)}, x_2^{(k+1)}, \ldots, x_n^{(k+1)}]$ if either an absolute or relative convergence criterion is satisfied,

$$|d_i| < \varepsilon_i, \quad i = 1, 2, \ldots, n \quad \text{or} \quad |d_i / x_i^{(k)}| < \varepsilon_i, \quad i = 1, 2, \ldots, n$$

Otherwise, increase the value of k by 1 (so that what was calculated in step 6 as $x_i^{(k+1)}$ is now $x_i^{(k)}$) and return to step 2.

The Newton–Raphson method is based on a linearization of the functions $g_1, \ldots, g_n$ about each estimated set of roots and a solution of the resulting linear equations to get the next estimate. (If you have no idea what all that means, don't worry about it.) It is an efficient procedure to use when analytical partial derivatives of the functions $g_1, \ldots, g_n$ are convenient to evaluate. When there is only one equation ($n = 1$), the algorithm reduces to Newton's rule (Section A.2e).

The next example illustrates the three multivariable nonlinear equation-solving methods described in this section.

Example A.2-3 Solving Multivariable Nonlinear Equations

Find the solutions of the following simultaneous equations:

$$g_1(x, y) = 2x + y - (x + y)^{1/2} - 3 = 0$$
$$g_2(x, y) = 4 - y - 5/(x + y) = 0$$

1. By successive substitution.
2. Using the Wegstein algorithm.
3. Using the Newton–Raphson method.

In each case, use a starting value ($x = 2, y = 2$) and stop when the relative changes in x and y from one iteration to the next are each less than 0.001. (See Equation A.2-11.)

Solution

1. ***Successive substitution.*** The equations $g_1 = 0$ and $g_2 = 0$ must be rewritten to provide explicit expressions for x and y. One way of doing this is the following:

$$x_c = 0.5[3 - y_a + (x_a + y_a)^{1/2}]$$
$$y_c = 4 - 5/(x_a + y_a)$$

where the subscript "a" stands for assumed and "c" stands for calculated. We assume values of x and y, recalculate x and y using these expressions, and iterate until convergence is achieved. The calculation proceeds as follows:

	Assumed		Calculated	
Iteration	x	y	x	y
1	2.000	2.000	1.500	2.750
2	1.500	2.750	1.156	2.824
3	1.156	2.824	1.086	2.744
4	1.086	2.744	1.107	2.694
5	1.107	2.694	1.128	2.684
6	1.128	2.684	1.134	2.688
7	1.134	2.688	1.133	2.692
8	1.133	2.692	1.132	2.693
9	1.1320	2.6929	1.1314	2.6928

Since the relative changes in x and y in the last iteration are each less than 0.001, the calculation is terminated at this point, and the final values are accepted as the roots of the two given equations.

2. ***Wegstein algorithm.*** The same functions are used to generate calculated values of x and y from assumed values, only now the equations of Section A.2g are used to generate new assumed values after the first iteration. The results are as follows. (Check the first series of numbers with a hand calculator to make sure you know how to apply the formulas.)

	Assumed		Calculated	
Iteration	x	y	x	y
1	2.000	2.000	1.500	2.750
2	1.500	2.750	1.156	2.824
3	0.395	2.832	0.982	2.450
4	1.092	2.641	1.146	2.660
5	1.162	2.651	1.151	2.689
6	1.150	2.670	1.142	2.691
7	1.123	2.694	1.130	2.690
8	1.136	2.690	1.133	2.693
9	1.1320	2.6919	1.1318	2.6924

In this case, Wegstein's method did not accelerate the convergence. In fact, the large jump in the value of x in iteration 3 (when the Wegstein procedure was first used) could have been the first symptom of an instability, but the algorithm recovered well.

3. ***Newton–Raphson method.*** The necessary formulas are as follows:

$$
\begin{aligned}
g_1(x,y) &= 2x + y - (x+y)^{1/2} - 3 \\
g_2(x,y) &= 4 - y - 5/(x+y) \\
a_{11}(x,y) &= \partial g_1/\partial x = 2 - 0.5(x+y)^{-1/2} \\
a_{12}(x,y) &= \partial g_1/\partial y = 1 - 0.5(x+y)^{-1/2} \\
a_{21}(x,y) &= \partial g_2/\partial x = 5/(x+y)^2 \\
a_{22}(x,y) &= \partial g_2/\partial y = -1 + 5/(x+y)^2
\end{aligned}
$$

Equations A.2-15 reduce for this two-dimensional problem to

$$
\begin{aligned}
a_{11}d_1 + a_{12}d_2 &= -g_1 \\
a_{21}d_1 + a_{22}d_2 &= -g_2
\end{aligned}
$$

The procedure is to assume values of x and y; calculate $g_1, g_2, a_{11}, a_{12}, a_{21}$, and a_{22} from the given formulas; solve the two preceding equations for d_1 and d_2; and calculate the new estimates of the roots as

$$
\begin{aligned}
x_c &= x_a + d_1 \\
y_c &= y_a + d_2
\end{aligned}
$$

The convergence test is then applied, and if the assumed and calculated values are not close enough together, the latter values are used to replace the former ones and the calculation is repeated. The results are shown here.

	Assumed		Calculated	
Iteration	x	y	x	y
1	2.000	2.000	1.130	2.696 (verify!)
2	1.130	2.696	1.1315	2.6925
3	1.1315	2.6925	1.1315	2.6925

The superiority of the Newton–Raphson method to others tested is clear in this example and is even more dramatic when more than two equations are to be solved simultaneously. Generally, when analytical derivatives are available, the Newton–Raphson method should be used for solving multiple nonlinear algebraic equations.

Appendix A.3 NUMERICAL INTEGRATION

In Chapter 8, we showed that the enthalpy change associated with the heating or cooling of a substance is evaluated by integrating the substance heat capacity $C_p(T)$ from the initial temperature to the final temperature. This is one of many instances you will encounter in process analysis where an integration is required as part of a problem solution.

It often happens that required values of definite integrals cannot be obtained using the methods of elementary calculus. If, for example, you are called on to evaluate something like

$$\int_0^{10} e^{-x^3} dx$$

you will not find help in a calculus book or a table of integrals—an analytical expression for the integral of exp $(-x^3)$ simply does not exist.

It is possible, however, to substitute for any mathematical operation such as differentiation or integration a series of arithmetic operations that yield approximately the same result. The arithmetic operations are usually simple but numerous and repetitious and so are ideally suited to computers.

A.3a Quadrature

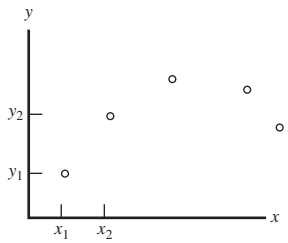
The general problem we will discuss is the evaluation of a definite integral:

$$I = \int_a^b y(x)dx \qquad \textbf{(A.3-1)}$$

There are several possible reasons why you might not be able to evaluate I analytically: $y(x)$ may be a nonintegrable analytical function, such as exp $(-x^3)$, or it may be a series of tabulated (x, y) data points or a plot of y versus x.

A method of **numerical integration** (or **quadrature**, as it is also called) is required to evaluate I in any of these cases. The specific techniques we will present are algebraic, but the general approach to the problem is best visualized graphically. For the moment, we will suppose that all we have relating x and y is a table of data points, which we may graph on a plot of y versus x.

x	$x_1(=a)$	x_2		x_{n-1}	$x_n(=b)$
y	y_1	y_2		y_{n-1}	y_n

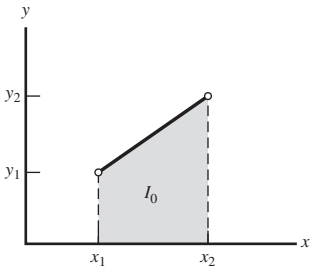


The integral we are trying to evaluate (I of Equation A.3-1) equals the area under the continuous curve of y versus x, but this curve is not available—we only know the function values at the discrete data points. The procedure generally followed is to fit approximating functions to the data points, and then to integrate these function analytically.

The many existing quadrature formulas differ only in the choice of functions to fit to the data points. Two of the simplest approximations are to fit straight lines between successive points and sum the area under the lines, and to fit parabolas to successive triplets of points and sum the areas under the parabolas. These approximations lead to the quadrature formulas known respectively as the **trapezoidal rule** and **Simpson's rule**. We will discuss each in turn.

A.3b The Trapezoidal Rule

The area under a line through (x_1, y_1) and (x_2, y_2) on a plot of y versus x is easily calculated.



$$\Longrightarrow I_0 = \int_{x_1}^{x_2} y\,dx = (x_2 - x_1)\left(\frac{y_1 + y_2}{2}\right)$$

The area under a series of points from x_1 to x_n is obtained by a summation of such terms:

$$I = \tfrac{1}{2}[(x_2 - x_1)(y_1 + y_2) + (x_3 - x_2)(y_2 + y_3) + \cdots + (x_n - x_{n-1})(y_{n-1} + y_n)]$$

$$\Downarrow$$

Trapezoidal Rule:

$$\boxed{\int_{x_1}^{x_n} y(x)dx \approx \frac{1}{2}\sum_{j=1}^{n-1}(x_{j+1} - x_j)(y_j + y_{j+1})} \qquad \textbf{(A.3-2)}$$

If the abscissa values of the data points are spaced at equal intervals, then the trapezoidal rule simplifies to

$$I = \frac{h}{2}[(y_1 + y_2) + (y_2 + y_3) + \cdots + (y_{n-1} + y_n)]$$

$$\Downarrow$$

Trapezoidal Rule—Equal Intervals:

$$\boxed{\int_{x_1}^{x_n} y(x)\,dx \approx \frac{h}{2}\left(y_1 + y_n + 2\sum_{j=2}^{n-1} y_j\right)} \qquad \textbf{(A.3-3)}$$

where h is the distance between the x values of adjacent data points. Observe that to use the trapezoidal rule, you need not plot anything—simply substitute the tabulated data into Equation A.3-2 or (for equal spacing) Equation A.3-3.

The trapezoidal rule is an approximation, as are all quadrature formulas. Figure A.3-1 illustrates the nature of the error introduced by its use. The integral to be evaluated

$$I = \int_a^b y(x)dx$$

is the area under the dashed curve of Figure A.3-1, while the trapezoidal rule, Equation A.3-2, would yield the area under the straight-line segments, which could differ significantly from the correct value of I. Note also, however, that if there were many more data points in the interval between a and b, the approximating series of lines would follow the dashed curve much more closely, and the estimate of the integral would accordingly be more accurate.

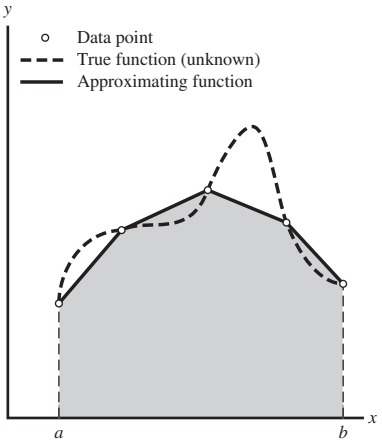
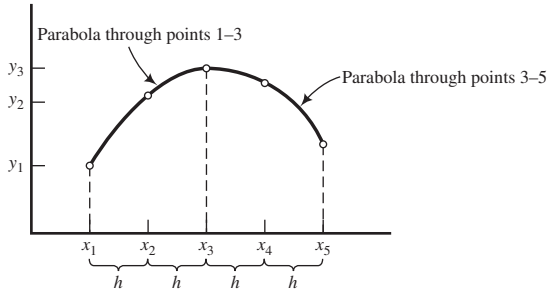


FIGURE A.3-1 Graphical illustration of the trapezoidal rule.

A.3c Simpson's Rule

A second and more accurate quadrature formula is the one most often used. It is applicable only to an odd number of equally spaced data points and is based on fitting parabolic functions to successive groups of three points.



It can be shown after a fair amount of algebra that the area under a parabola through equally spaced points $(x_1, y_1), (x_2, y_2)$, and (x_3, y_3) is

$$I_0 = \frac{h}{3}(y_1 + 4y_2 + y_3)$$

where h is the interval between successive x values. Consequently, the area under a series of such parabolas fitted to n equally spaced points is

$$I = \frac{h}{3}[(y_1 + 4y_2 + y_3) + (y_3 + 4y_4 + y_5) + \cdots + (y_{n-2} + 4y_{n-1} + y_n)]$$

$$\Downarrow$$

Simpson's Rule:

$$\int_{x_1}^{x_n} y(x)dx \approx \frac{h}{3}\left(y_1 + y_n + 4\sum_{\substack{j=2,\\4,\ldots,\\n-1}} y_j + 2\sum_{\substack{j=3\\5,\ldots,\\n-2}} y_j \right) \qquad \textbf{(A.3-4)}$$

If you happen to have an even number of data points, you may integrate over all but the first or last subinterval (omit whichever subinterval contributes least to the integral) using Simpson's rule, and over the remaining subinterval using the trapezoidal rule.

Example A.3-1 Simpson's Rule

The heat capacity of a gas is tabulated at a series of temperatures:

T(°C)	20	50	80	110	140	170	200	230
C_p[J/(mol·°C)]	28.95	29.13	29.30	29.48	29.65	29.82	29.99	30.16

Calculate the change in enthalpy for 3.00 g-moles of this gas going from 20°C to 230°C.

Solution

$$\Delta H(J) = n \int_{20°C}^{230°C} C_p \, dT$$

The data points are evenly spaced in the independent variable (T), so that Simpson's rule can be applied to the integration, but since there are an even number of points the trapezoidal rule must be applied over the first or last temperature interval. Since C_p increases with temperature, we will apply the less accurate trapezoidal rule to the interval from 20°C to 50°C and use Simpson's rule between 50°C and 230°C. If $\Delta T(= 30°C)$ is the temperature interval between data points, Equations A.3-3 and A.3-4 yield

$$\int_{T_1}^{T_a} C_p \, dT \approx \frac{\Delta T}{2}(C_{p1} + C_{p2}) + \frac{\Delta T}{3}\left[C_{p2} + C_{p8} + 4(C_{p3} + C_{p5} + C_{p7}) + 2(C_{p4} + C_{p6})\right]$$

$$= 6208 \text{ J/mol}$$

$$\Downarrow$$

$$\Delta H = (3.00 \text{ mol})(6208 \text{ J/mol}) = \boxed{1.86 \times 10^4 \text{ J}}$$

The trapezoidal rule is exact if the function to be integrated is in fact linear in each interval between data points, while Simpson's rule is exact if the real function is parabolic *or cubic* in each interval. (The latter point is far from obvious; for proof, see any reference on numerical analysis.)

A.3d Numerical Integration of Analytical Functions

When you have an analytical expression for an integrand $y(x)$ but you cannot perform the integration from $x = a$ to $x = b$ analytically, the procedure is to evaluate y at a series of values of x from a to b—that is, to generate a data table—and then to use a quadrature formula such as Simpson's rule to estimate the integral. Now, however, you have the choice of the number of evaluations of $y(x)$ to make.

As a rule, the accuracy of a quadrature formula increases with the number of points in the interval of integration, but so does the required computation time. Choosing the number of points to provide a suitable combination of accuracy and low computation time can be done using sophisticated numerical analysis techniques, but simple trial and error often suffices very well. A common procedure is to evaluate the integral using (say) 9 points, then 17, then 33, and so on ($n_{\text{new}} = 2n_{\text{old}} - 1$), until successively calculated values agree within a specified tolerance. The last value should be a good approximation to the exact value of the integral.

Test Yourself

Suppose $f(x) = x^3 + 4$. Evaluate $\int_0^4 f(x)\,dx$:

(Answers, p. 661)

1. Analytically.
2. Using the trapezoidal rule, with points at $x = 0, 1, 2, 3, 4$.
3. Using Simpson's rule, with points at $x = 0, 1, 2, 3, 4$. Explain the relationship between the answers to 1 and 3.

APPENDIX
B

Physical Property Tables

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TABLE B.1 Selected Physical Property Data

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[a]	$\Delta\hat{H}_m(T_m)$[b,i] kJ/mol	T_b(°C)[c]	$\Delta\hat{H}_v(T_b)$[d,i] kJ/mol	T_c(K)[e]	P_c(atm)[f]	$(\Delta\hat{H}_f°)$[g,i] kJ/mol	$(\Delta\hat{H}_c°)$[h,i] kJ/mol
Acetaldehyde	CH_3CHO	44.05	$0.783^{18°}$	−123.7	—	20.2	25.1	461.0	—	−166.2(g)	−1192.4(g)
Acetic acid	CH_3COOH	60.05	1.049	16.6	12.09	118.2	24.39	594.8	57.1	−486.18(l)	−871.69(l)
										−438.15(g)	−919.73(g)
Acetone	C_3H_6O	58.08	0.791	−95.0	5.69	56.0	30.2	508.0	47.0	−248.2(l)	−1785.7(l)
										−216.7(g)	−1821.4(g)
Acetylene	C_2H_2	26.04	—	—	—	−81.5	17.6	309.5	61.6	+226.75(g)	−1299.6(g)
Ammonia	NH_3	17.03	—	−77.8	5.653	−33.43	23.351	405.5	111.3	−67.20(l)	
										−46.19(g)	−382.58(g)
Ammonium hydroxide	NH_4OH	35.03	—	—	—	—	—	—	—	−366.48(aq)	—
Ammonium nitrate	NH_4NO_3	80.05	$1.725^{25°}$	169.6	5.4		Decomposes at 210°C			365.14(c)	—
										−399.36(aq)	
Ammonium sulfate	$(NH_4)_2SO_4$	132.14	1.769	513	—		Decomposes at 513°C after melting			−1179.3(c)	
										−1173.1(aq)	
Aniline	C_6H_7N	93.12	1.022	−6.3	—	184.2	—	699	52.4	—	—
Benzaldehyde	C_6H_5CHO	106.12	1.046	−26.0	—	179.0	38.40	—	—	−88.83(l)	−3520.0(l)
										−40.04(g)	—
Benzene	C_6H_6	78.11	0.879	5.53	9.837	80.10	30.765	562.6	48.6	+48.66(l)	−3267.6(l)
										+82.93(g)	3301.5(g)
Benzoic acid	$C_7H_6O_2$	122.12	$1.266^{15°}$	122.2	—	249.8	—	—	—	—	−3226.7(g)
Benzyl alcohol	C_7H_8O	108.13	1.045	−15.4	—	205.2	—	—	—	—	−3741.8(l)
Bromine	Br_2	159.83	3.119	−7.4	10.8	58.6	31.0	584	102	0(l)	—
1,2-Butadiene	C_4H_6	54.09	—	−136.5	—	10.1	—	446	—	—	—
1,3-Butadiene	C_4H_6	54.09	—	−109.1	—	−4.6	—	425	42.7	—	—
n-Butane	C_4H_{10}	58.12	—	−138.3	4.661	−0.6	22.305	425.17	37.47	−147.0(l)	−2855.6(l)
										−124.7(g)	−2878.5(g)
Isobutane	C_4H_{10}	58.12	—	−159.6	4.540	−11.73	21.292	408.1	36.0	−158.4(l)	−2849.0(l)
										−134.5(g)	−2868.8(g)
1-Butene	C_4H_8	56.10	—	−185.3	3.8480	−6.25	21.916	419.6	39.7	+1.17(g)	−2718.6(g)
Calcium carbide	CaC_2	64.10	$2.22^{18°}$	2300	—	—	—	—	—	−62.76(c)	—
Calcium carbonate	$CaCO_3$	100.09	2.93			Decomposes at 825°C				−1206.9(c)	—
Calcium chloride	$CaCl_2$	110.99	$2.152^{15°}$	782	28.37	>1600	—	—	—	−794.96(c)	—

Calcium hydroxide	$Ca(OH)_2$	74.10	2.24			($-H_2O$ at 580°C)				−986.59(c)	—
Calcium oxide	CaO	56.08	3.32	2570	50	2850	—	—	—	−635.6(c)	—
Calcium phosphate	$Ca_3(PO_4)_2$	310.19	3.14	1670	—	—	—	—	—	−4138(c)	—
Calcium silicate	$CaSiO_3$	116.17	2.915	1530	48.62	—	—	—	—	−1584(c)	—
Calcium sulfate	$CaSO_4$	136.15	2.96	—	—	—	—	—	—	−1432.7(c) −1450.4(aq)	—
Calcium sulfate (gypsum)	$CaSO_4{\cdot}2H_2O$	172.18	2.32		($-1.5\ H_2O$ at 128°C)		—	—	—	−2021(c)	—
Carbon (graphite)	C	12.010	2.26	3600	46.0	4200	—	—	—	0(c)	−393.51(c)
Carbon dioxide	CO_2	44.01	—	−56.6 at 5.2 atm	8.33	(Sublimes at −78°C)		304.2	72.9	−412.9(l) −393.5(g)	— —
Carbon disulfide	CS_2	76.14	$1.261^{22°/20°}$	−112.1	4.39	46.25	26.8	552.0	78.0	+87.9(l) +115.3(g)	−1075.2(l) 1102.6(g)
Carbon monoxide	CO	28.01	—	−205.1	0.837	−191.5	6.042	133.0	34.5	−110.52(g)	−282.99(g)
Carbon tetrachloride	CCl_4	153.84	1.595	22.9	2.51	76.7	30.0	556.4	45.0	139.5(l) −106.7(g)	352.2(l) −385.0(g)
Chlorine	Cl_2	70.91	—	−101.00	6.406	−34.06	20.4	417.0	76.1	0(g)	—
Chlorobenzene	C_6H_5Cl	112.56	1.107	−45	—	132.10	36.5	632.4	44.6	—	—
Chloroethane	C_2H_5Cl	See ethyl chloride									

[a] Melting point at 1 atm.

[b] Heat of fusion at T_m and 1 atm.

[c] Boiling point at 1 atm.

[d] Heat of vaporization at T_b and 1 atm.

[e] Critical temperature.

[f] Critical pressure.

[g] Heat of formation at 25°C and 1 atm.

[h] Heat of combustion at 25°C and 1 atm. Standard states of products are $CO_2(g)$, $H_2O(l)$, $SO_2(g)$, HCl(aq), and $N_2(g)$. To calculate $\Delta\hat{H}_c^\circ$ with $H_2O(g)$ as a product, add $44.01n_w$ to the tabulated value, where n_w = moles H_2O formed/mole fuel burned.

[i] To convert $\Delta\hat{H}$ to kcal/mol, divide given value by 4.184; to convert to Btu/lb-mole, multiply by 430.28.

(*continued*)

TABLE B.1 (*Continued*)

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[a]	$\Delta\hat{H}_m(T_m)^{b,i}$ kJ/mol	T_b(°C)[c]	$\Delta\hat{H}_v(T_b)^{d,i}$ kJ/mol	T_c(K)[e]	P_c(atm)[f]	$(\Delta\hat{H}_f°)^{g,i}$ kJ/mol	$(\Delta\hat{H}_c°)^{h,i}$ kJ/mol
Chloroform	$CHCl_3$	119.39	1.489	−63.7	—	61.0		536.0	54.0	−131.8(l)	−373(l)
Copper	Cu	63.54	8.92	1083	13.01	2595	304.6	—		0(c)	—
Cupric sulfate	$CuSO_4$	159.61	$3.606^{15°}$			Decomposes > 600°C				−769.9(c) −843.1(aq)	—
Cyclohexane	C_6H_{12}	84.16	0.779	6.7	2.677	80.7	30.1	553.7	40.4	−156.2(l) −123.1(g)	−3919.9(l) −3953.0(g)
Cyclopentane	C_5H_{10}	70.13	0.745	−93.4	0.609	49.3	27.30	511.8	44.55	−105.9(l) −77.2(g)	−3290.9(l) −3319.5(g)
n-Decane	$C_{10}H_{22}$	142.28	0.730	−29.9	—	173.8	—	619.0	20.8	−249.7(l) —	−6778.3(l) −6829.7(g)
Diethyl ether	$(C_2H_5)_2O$	74.12	$0.708^{25°}$	−116.3	7.30	34.6	26.05	467	35.6	−272.8(l)	−2726.7(l)
Ethane	C_2H_6	30.07	—	−183.3	2.859	−88.6	14.72	305.4	48.2	−84.67(g)	−1559.9(g)
Ethyl acetate	$C_4H_8O_2$	88.10	0.901	−83.8	—	77.0	—	523.1	37.8	−463.2(l) −426.8(g)	−2246.4(l) —
Ethyl alcohol (Ethanol)	C_2H_5OH	46.07	0.789	−114.6	5.021	78.5	38.58	516.3	63.0	−277.63(l) −235.31(g)	−1366.91(l) −1409.25(g)
Ethyl benzene	C_8H_{10}	106.16	0.867	−94.67	9.163	136.2	35.98	619.7	37.0	−12.46(l) +29.79(g)	−4564.9(l) −4607.1(g)
Ethyl bromide	C_2H_5Br	108.98	1.460	−119.1	—	38.2	—	504	61.5	−54.4(g)	—
Ethyl chloride	C_2H_5Cl	64.52	$0.903^{15°}$	−138.3	4.452	13.1	24.7	460.4	52.0	−105.0(g)	—
3-Ethyl hexane	C_8H_{18}	114.22	0.717	—	—	118.5	34.27	567.0	26.4	−250.5(l) −210.9(g)	−5407.1(l) −5509.8(g)
Ethylene	C_2H_4	28.05	—	−169.2	3.350	−103.7	13.54	283.1	50.5	+52.28(g)	−1410.99(g)
Ethylene glycol	$C_2H_6O_2$	62.07	$1.113^{19°}$	−13	11.23	197.2	56.9	—	—	−451.5(l) −387.1(g)	−1179.5(l) —
Ferric oxide	Fe_2O_3	159.70	5.12			Decomposes at 1560°C				−822.2(c)	
Ferrous oxide	FeO	71.85	5.7	—	—	—	—	—	—	−266.5(c)	—
Ferrous sulfide	FeS	87.92	4.84	1193	—	—	—	—	—	−95.1(c)	—
Formaldehyde	H_2CO	30.03	$0.815^{-20°}$	−92	—	−19.3	24.48	—	—	−115.90(g)	−563.46(g)
Formic acid	CH_2O_2	46.03	1.220	8.30	12.68	100.5	46.3	—	—	−425.5(l) 379.2(g)	−253.8(l) —
Glycerol	$C_3H_8O_3$	92.09	$1.260^{50°}$	18.20	18.30	290.0	—	—	—	−665.9(l)	−1661.1(l)
Helium	He	4.00	—	−269.7	0.02	−268.9	0.084	5.26	2.26	0(g)	—

n-Heptane	C_7H_{16}	100.20	0.684	−90.59	14.03	98.43	31.69	540.2	27.0	−224.4(l) −187.8(g)	−4816.9(l) −4853.5(g)
n-Hexane	C_6H_{14}	86.17	0.659	−95.32	13.03	68.74	28.85	507.9	29.9	−198.8(l) −167.2(g)	−4163.1(l) −4194.8(g)
Hydrogen	H_2	2.016	—	−259.19	0.12	−252.76	0.904	33.3	12.8	0(g)	−285.84(g)
Hydrogen bromide	HBr	80.92	—	−86	—	−67	—	—	—	−36.23(g)	—
Hydrogen chloride	HCl	36.47	—	−114.2	1.99	−85.0	16.1	324.6	81.5	−92.31(g)	—
Hydrogen cyanide	HCN	27.03	—	−14	—	26	—	—	—	+130.54(g)	—
Hydrogen fluoride	HF	20.0	—	−83	—	20	—	503.2	—	−268.6(g) −316.9(aq, 200)	— —
Hydrogen sulfide	H_2S	34.08	—	−85.5	2.38	−60.3	18.67	373.6	88.9	−19.96(g)	−562.59(g)
Iodine	I_2	253.8	4.93	113.3	—	184.2	—	826.0	—	0(c)	—
Iron	Fe	55.85	7.7	1535	15.1	2800	354.0	—	—	0(c)	—
Lead	Pb	207.21	$11.337^{20°/20°}$	327.4	5.10	1750	179.9	—		0(c)	—
Lead oxide	PbO	223.21	9.5	886	11.7	1472	213	—	—	−219.2(c)	—
Magnesium	Mg	24.32	1.74	650	9.2	1120	131.8	—	—	0(c)	—
Magnesium chloride	$MgCl_2$	95.23	$2.325^{25°}$	714	43.1	1418	136.8	—	—	−641.8(c)	—
Magnesium hydroxide	$Mg(OH)_2$	58.34	2.4		Decomposes at 350°C			—			—
Magnesium oxide	MgO	40.32	3.65	2900	77.4	3600	—	—	—	−601.8(c)	—
Mercury	Hg	200.61	13.546	−38.87	—	−356.9	—	—	—	0(c)	—
Methane	CH_4	16.04	—	−182.5	0.94	−161.5	8.179	190.70	45.8	−74.85(g)	−890.36(g)
Methyl acetate	$C_3H_6O_2$	74.08	0.933	−98.9	—	57.1	—	506.7	46.30	−409.4(l)	−1595(l)
Methyl alcohol (Methanol)	CH_3OH	32.04	0.792	−97.9	3.167	64.7	35.27	513.20	78.50	−238.6(l) −201.2(g)	−726.6(l) −764.0(g)
Methyl amine	CH_5N	31.06	$0.699^{-11°}$	−92.7	—	−6.9	—	429.9	73.60	−28.0(g)	−1071.5(l)
Methyl chloride	CH_3Cl	50.49	—	−97.9	—	−24	—	416.1	65.80	−81.92(g)	—

(*continued*)

TABLE B.1 (*Continued*)

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[a]	$\Delta\hat{H}_m(T_m)$[b,i] kJ/mol	T_b(°C)[c]	$\Delta\hat{H}_v(T_b)$[d,i] kJ/mol	T_c(K)[e]	P_c(atm)[f]	$(\Delta\hat{H}_f°)$[g,i] kJ/mol	$(\Delta\hat{H}_c°)$[h,i] kJ/mol
Methyl ethyl ketone	C_4H_8O	72.10	0.805	−87.1	—	78.2	32.0	—	—	—	−2436(l)
Naphthalene	$C_{10}H_8$	128.16	1.145	80.0	—	217.8	—	—	—	—	−5157(g)
Nickel	Ni	58.69	8.90	1452	—	2900	—	—	—	0(c)	—
Nitric acid	HNO_3	63.02	1.502	−41.6	10.47	86	30.30	—	—	−173.23(l) −206.57(aq)	—
Nitrobenzene	$C_6H_5O_2N$	123.11	1.203	5.5	—	210.7	—	—	—	—	−3092.8(l)
Nitrogen	N_2	28.02	—	−210.0	0.720	−195.8	5.577	126.20	33.5	0(g)	—
Nitrogen dioxide	NO_2	46.01	—	−9.3	7.335	21.3	14.73	431.0	100.0	+33.8(g)	—
Nitric oxide	NO	30.01	—	−163.6	2.301	−151.8	13.78	179.20	65.0	+90.37(g)	—
Nitrogen pentoxide	N_2O_5	108.02	$1.63^{18°}$	30	—	47	—	—	—	—	—
Nitrogen tetraoxide	N_2O_4	92.0	1.448	−9.5	—	21.1	—	431.0	99.0	+9.3(g)	—
Nitrous oxide	N_2O	44.02	$1.226^{-89°}$	−91.1	—	−88.8	—	309.5	71.70	+81.5(g)	—
n-Nonane	C_9H_{20}	128.25	0.718	53.8	—	150.6	—	595	23.0	229.0(l) —	6124.5(l) −6171.0(g)
n-Octane	C_8H_{18}	114.22	0.703	−57.0	—	125.5	—	568.8	24.5	−249.9(l) −208.4(g)	−5470.7(l) −5512.2(g)
Oxalic acid	$C_2H_2O_4$	90.04	1.90	Decomposes at 186°C				—	—	−826.8(c)	−251.9(s)
Oxygen	O_2	32.00	—	−218.75	0.444	−182.97	6.82	154.4	49.7	0(g)	—
n-Pentane	C_5H_{12}	72.15	$0.63^{18°}$	−129.6	8.393	36.07	25.77	469.80	33.3	−173.0(l) −146.4(g)	−3509.5(l) −3536.1(g)
Isopentane	C_5H_{12}	72.15	$0.62^{19°}$	−160.1	—	27.7	— —	461.00	32.9	−179.3(l) −152.0(g)	−3507.5(l) −3529.2(g)
1-Pentene	C_5H_{10}	70.13	0.641	−165.2	4.94	29.97		474	39.9	−20.9(g)	−3375.8(g)
Phenol	C_6H_5OH	94.11	$1.071^{25°}$	42.5	11.43	181.4	—	692.1	60.5	−158.1(l) −90.8(g)	−3063.5(s) —
Phosphoric acid	H_3PO_4	98.00	$1.834^{18°}$	42.3	10.54	$(-\frac{1}{2}H_2O$ at 213°C)		—	—	−1281.1(c) −1278.6(aq, $1H_2O$)	— —
Phosphorus (red)	P_4	123.90	2.20	$590^{43\ atm}$	81.17	Ignites in air, 725°C		—	—	−17.6(c) 0(c)	—

Phosphorus (white)	P_4	123.90	1.82	44.2	2.51	280	49.71	—	—		—
Phosphorus pentoxide	P_2O_5	141.95	2.387	Sublimes at 250°C				—	—	−1506.2(c)	—
Propane	C_3H_8	44.09	—	−187.69	3.52	−42.07	18.77	369.9	42.0	−119.8(l) −103.8(g)	−2204.0(l) −2220.0(g)
Propylene	C_3H_6	42.08	—	−185.2	3.00	−47.70	18.42	365.1	45.4	+20.41(g)	−2058.4(g)
n-Propyl alcohol	C_3H_7OH	60.09	0.804	−127	—	97.04	—	536.7	49.95	−300.70(l) −255.2(g)	−2010.4(l) −2068.6(g)
Isopropyl alcohol	C_3H_7OH	60.09	0.785	−89.7	—	82.24	—	508.8	53.0	−310.9(l)	−1986.6(l)
n-Propyl benzene	C_9H_{12}	120.19	0.862	99.50	8.54	159.2	38.24	638.7	31.3	38.40(l) +7.82(g)	5218.2(l) −5264.48(g)
Silicon dioxide	SiO_2	60.09	2.25	1710	14.2	2230	—	—	—	−851.0(c)	—
Sodium bicarbonate	$NaHCO_3$	84.01	2.20	Decomposes at 270°C				—	—	−945.6(c)	—
Sodium bisulfate	$NaHSO_4$	120.07	2.742	—	—	—	—	—	—	−1126.3(c)	—
Sodium carbonate	Na_2CO_3	105.99	2.533	Decomposes at 854°C				—	—	−1130.9(c)	—
Sodium chloride	NaCl	58.45	2.163	808	28.5	1465	170.7	—	—	−411.0(c)	—
Sodium cyanide	NaCN	49.01	—	562	16.7	1497	155	—	—	−89.79(c)	—
Sodium hydroxide	NaOH	40.00	2.130	319	8.34	1390	—	—	—	−426.6(c) −469.4(aq)	— —
Sodium nitrate	$NaNO_3$	85.00	2.257	310	15.9	Decomposes at 380°C			—	−466.7(c)	—
Sodium nitrite	$NaNO_2$	69.00	$2.168^{0°}$	271	—	Decomposes at 320°C			—	−359.4(c)	—
Sodium sulfate	Na_2SO_4	142.05	2.698	890	24.3	—	—	—	—	−1384.5(c)	—
Sodium sulfide	Na_2S	78.05	1.856	950	6.7	—	—	—	—	−373.2(c)	—
Sodium sulfite	Na_2SO_3	126.05	$2.633^{15°}$	Decomposes				—	—	−1090.3(c)	—

(*continued*)

TABLE B.1 (*Continued*)

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[a]	$\Delta\hat{H}_m(T_m)$[b,i] kJ/mol	T_b(°C)[c]	$\Delta\hat{H}_v(T_b)$[d,i] kJ/mol	T_c(K)[e]	P_c(atm)[f]	$(\Delta\hat{H}_f°)$[g,i] kJ/mol	$(\Delta\hat{H}_c°)$[h,i] kJ/mol
Sodium thiosulfate	$Na_2S_2O_3$	158.11	1.667	—	—	—	—	—	—	−1117.1(c)	—
Sulfur (rhombic)	S_8	256.53	2.07	113	10.04	444.6	83.7	—	—	0(c)	—
Sulfur (monoclinic)	S_8	256.53	1.96	119	14.17	444.6	83.7	—	—	+0.30(c)	—
Sulfur dioxide	SO_2	64.07	—	−75.48	7.402	−10.02	24.91	430.7	77.8	−296.90(g)	—
Sulfur trioxide	SO_3	80.07	—	16.84	25.48	43.3	41.80	491.4	83.8	−395.18(g)	—
Sulfuric acid	H_2SO_4	98.08	$1.834^{18°}$	10.35	9.87	Decomposes at 340°C		—	—	−811.32(l)	—
										−907.51(aq)	—
Toluene	C_7H_8	92.13	0.866	−94.99	6.619	110.62	33.47	593.9	40.3	+12.00(l)	−3909.9(l)
										+50.00(g)	−3947.9(g)
Water	H_2O	18.016	$1.00^{4°}$	0.00	6.0095	100.00	40.656	647.4	218.3	−285.84(l)	—
										−241.83(g)	—
m-Xylene	C_8H_{10}	106.16	0.864	−47.87	11.569	139.10	36.40	619	34.6	−25.42(l)	−4551.9(l)
										+17.24(g)	−4594.5(g)
o-Xylene	C_8H_{10}	106.16	0.880	−25.18	13.598	144.42	36.82	631.5	35.7	−24.44(l)	−4552.9(l)
										+18.99(g)	−4596.3(g)
p-Xylene	C_8H_{10}	106.16	0.861	13.26	17.11	138.35	36.07	618	33.9	−24.43(l)	−4552.91(l)
										17.95(g)	−4595.2(g)
Zinc	Zn	65.38	7.140	419.5	6.674	907	114.77	—	—	0(c)	—

TABLE B.2 Heat Capacities

Form 1: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^2 + dT^3$
Form 2: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] $= a + bT + cT^{-2}$

Example: $(C_p)_{\text{acetone(g)}} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$, where T is in °C.

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal-gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Acetone	CH_3COCH_3	58.08	l	1	°C	123.0	18.6			−30–60
			g	1	°C	71.96	20.10	−12.78	34.76	0–1200
Acetylene	C_2H_2	26.04	g	1	°C	42.43	6.053	−5.033	18.20	0–1200
Air		29.0	g	1	°C	28.94	0.4147	0.3191	−1.965	0–1500
			g	1	K	28.09	0.1965	0.4799	1.965	273–1800
Ammonia	NH_3	17.03	g	1	°C	35.15	2.954	0.4421	−6.686	0–1200
Ammonium sulfate	$(NH_4)_2SO_4$	132.15	c	1	K	215.9				275–328
Benzene	C_6H_6	78.11	l	1	°C	126.5	23.4			6–67
			g	1	°C	74.06	32.95	−25.20	77.57	0–1200
Isobutane	C_4H_{10}	58.12	g	1	°C	89.46	30.13	−18.91	49.87	0–1200
n-Butane	C_4H_{10}	58.12	g	1	°C	92.30	27.88	−15.47	34.98	0–1200
Isobutene	C_4H_8	56.10	g	1	°C	82.88	25.64	−17.27	50.50	0–1200
Calcium carbide	CaC_2	64.10	c	2	K	68.62	1.19	-8.66×10^{10}	—	298–720
Calcium carbonate	$CaCO_3$	100.09	c	2	K	82.34	4.975	-12.87×10^{10}	—	273–1033
Calcium hydroxide	$Ca(OH)_2$	74.10	c	1	K	89.5				276–373
Calcium oxide	CaO	56.08	c	2	K	41.84	2.03	-4.52×10^{10}		273–1173
Carbon	C	12.01	c	2	K	11.18	1.095	-4.891×10^{10}		273–1373
Carbon dioxide	CO_2	44.01	g	1	°C	36.11	4.233	−2.887	7.464	0–1500
Carbon monoxide	CO	28.01	g	1	°C	28.95	0.4110	0.3548	−2.220	0–1500
Carbon tetrachloride	CCl_4	153.84	l	1	K	93.39	12.98			273–343
Chlorine	Cl_2	70.91	g	1	°C	33.60	1.367	−1.607	6.473	0–1200
Copper	Cu	63.54	c	1	K	22.76	0.6117			273–1357

(*continued*)

TABLE B.2 (*Continued*)

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Cumene (Isopropyl benzene)	C_9H_{12}	120.19	g	1	°C	139.2	53.76	−39.79	120.5	0–1200
Cyclohexane	C_6H_{12}	84.16	g	1	°C	94.140	49.62	−31.90	80.63	0–1200
Cyclopentane	C_5H_{10}	70.13	g	1	°C	73.39	39.28	−25.54	68.66	0–1200
Ethane	C_2H_6	30.07	g	1	°C	49.37	13.92	−5.816	7.280	0–1200
Ethyl alcohol (Ethanol)	C_2H_5OH	46.07	l	1	°C	103.1				0
			l	1	°C	158.8				100
			g	1	°C	61.34	15.72	−8.749	19.83	0–1200
Ethylene	C_2H_4	28.05	g	1	°C	40.75	11.47	−6.891	17.66	0–1200
Ferric oxide	Fe_2O_3	159.70	c	2	K	103.4	6.711	-17.72×10^{10}	—	273–1097
Formaldehyde	CH_2O	30.03	g	1	°C	34.28	4.268	0.0000	−8.694	0–1200
Helium	He	4.00	g	1	°C	20.8				0–1200
n-Hexane	C_6H_{14}	86.17	l	1	°C	216.3				20–100
			g	1	°C	137.44	40.85	−23.92	57.66	0–1200
Hydrogen	H_2	2.016	g	1	°C	28.84	0.00765	0.3288	−0.8698	0–1500
Hydrogen bromide	HBr	80.92	g	1	°C	29.10	−0.0227	0.9887	−4.858	0–1200
Hydrogen chloride	HCl	36.47	g	1	°C	29.13	−0.1341	0.9715	−4.335	0–1200
Hydrogen cyanide	HCN	27.03	g	1	°C	35.3	2.908	1.092		0–1200
Hydrogen sulfide	H_2S	34.08	g	1	°C	33.51	1.547	0.3012	−3.292	0–1500
Magnesium chloride	$MgCl_2$	95.23	c	1	K	72.4	1.58			273–991
Magnesium oxide	MgO	40.32	c	2	K	45.44	0.5008	-8.732×10^{10}		273–2073
Methane	CH_4	16.04	g	1	°C	34.31	5.469	0.3661	−11.00	0–1200
			g	1	K	19.87	5.021	1.268	−11.00	273–1500
Methyl alcohol (Methanol)	CH_3OH	32.04	l	1	°C	75.86	16.83			0–65
			g	1	°C	42.93	8.301	−1.87	−8.03	0–700
Methyl cyclohexane	C_7H_{14}	98.18	g	1	°C	121.3	56.53	37.72	100.8	0–1200
Methyl cyclopentane	C_6H_{12}	84.16	g	1	°C	98.83	45.857	−30.44	83.81	0–1200
Nitric acid	NHO_3	63.02	l	1	°C	110.0				25
Nitric oxide	NO	30.01	g	1	°C	29.50	0.8188	−0.2925	0.3652	0–3500

Nitrogen	N_2	28.02	g	1	°C	29.00	0.2199	0.5723	−2.871	0–1500
Nitrogen dioxide	NO_2	46.01	g	1	°C	36.07	3.97	−2.88	7.87	0–1200
Nitrogen tetraoxide	N_2O_4	92.02	g	1	°C	75.7	12.5	−11.3		0–300
Nitrous oxide	N_2O	44.02	g	1	°C	37.66	4.151	−2.694	10.57	0–1200
Oxygen	O_2	32.00	g	1	°C	29.10	1.158	−0.6076	1.311	0–1500
n-Pentane	C_5H_{12}	72.15	l	1	°C	155.4	43.68			0–36
			g	1	°C	114.8	34.09	−18.99	42.26	0–1200
Propane	C_3H_8	44.09	g	1	°C	68.032	22.59	−13.11	31.71	0–1200
Propylene	C_3H_6	42.08	g	1	°C	59.580	17.71	−10.17	24.60	0–1200
Sodium carbonate	Na_2CO_3	105.99	c	1	K	121				288–371
Sodium carbonate decahydrate	$Na_2CO_3 \cdot 10H_2O$	286.15	c	1	K	535.6				298
Sulfur	S	32.07	c (Rhombic)	1	K	15.2	2.68			273–368
			c (Monoclinic)	1	K	18.3	1.84			368–392
Sulfuric acid	H_2SO_4	98.08	l	1	°C	139.1	15.59			10–45
Sulfur dioxide	SO_2	64.07	g	1	°C	38.91	3.904	−3.104	8.606	0–1500
Sulfur trioxide	SO_3	80.07	g	1	°C	48.50	9.188	−8.540	32.40	0–1000
Toluene	C_7H_8	92.13	l	1	°C	148.8	32.4			0–110
			g	1	°C	94.18	38.00	−27.86	80.33	0–1200
Water	H_2O	18.016	l	1	°C	75.4				0–100
			g	1	°C	33.46	0.6880	0.7604	−3.593	0–1500

TABLE B.3 Vapor Pressure of Water[a]

p_v(mm Hg) versus T (°C)

Example: The vapor pressure of liquid water at 4.3°C is 6.230 mm Hg

	T(°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
↓	−14	1.361	1.348	1.336	1.324	1.312	1.300	1.288	1.276	1.264	1.253
↓	−13	1.490	1.477	1.464	1.450	1.437	1.424	1.411	1.399	1.386	1.373
Ice	−12	1.632	1.617	1.602	1.588	1.574	1.559	1.546	1.532	1.518	1.504
	−11	1.785	1.769	1.753	1.737	1.722	1.707	1.691	1.676	1.661	1.646
	−10	1.950	1.934	1.916	1.899	1.883	1.866	1.849	1.833	1.817	1.800
	−9	2.131	2.122	2.093	2.075	2.057	2.039	2.021	2.003	1.985	1.968
	−8	2.326	2.306	2.285	2.266	2.246	2.226	2.207	2.187	2.168	2.149
	−7	2.537	2.515	2.493	2.472	2.450	2.429	2.408	2.387	2.367	2.346
	−6	2.765	2.742	2.718	2.695	2.672	2.649	2.626	2.603	2.581	2.559
	−5	3.013	2.987	2.962	2.937	2.912	2.887	2.862	2.838	2.813	2.790
	−4	3.280	3.252	3.225	3.198	3.171	3.144	3.117	3.091	3.065	3.039
	−3	3.568	3.539	3.509	3.480	3.451	3.422	3.393	3.364	3.336	3.308
	−2	3.880	3.848	3.816	3.785	3.753	3.722	3.691	3.660	3.630	3.599
	−1	4.217	4.182	4.147	4.113	4.079	4.045	4.012	3.979	3.946	3.913
	−0	4.579	4.542	4.504	4.467	4.431	4.395	4.359	4.323	4.287	4.252
↓	0	4.579	4.613	4.647	4.681	4.715	4.750	4.785	4.820	4.855	4.890
↓	1	4.926	4.962	4.998	5.034	5.070	5.107	5.144	5.181	5.219	5.256
Liquid	2	5.294	5.332	5.370	5.408	5.447	5.486	5.525	5.565	5.605	5.645
water	3	5.685	5.725	5.766	5.807	5.848	5.889	5.931	5.973	6.015	6.058
	4	6.101	6.144	6.187	6.230	6.274	6.318	6.363	6.408	6.453	6.498
	5	6.543	6.589	6.635	6.681	6.728	6.775	6.822	6.869	6.917	6.965
	6	7.013	7.062	7.111	7.160	7.209	7.259	7.309	7.360	7.411	7.462
	7	7.513	7.565	7.617	7.669	7.722	7.775	7.828	7.882	7.936	7.990
	8	8.045	8.100	8.155	8.211	8.267	8.323	8.380	8.437	8.494	8.551
	9	8.609	8.668	8.727	8.786	8.845	8.905	8.965	9.025	9.086	9.147
	10	9.209	9.271	9.333	9.395	9.458	9.521	9.585	9.649	9.714	9.779
	11	9.844	9.910	9.976	10.042	10.109	10.176	10.244	10.312	10.380	10.449
	12	10.518	10.588	10.658	10.728	10.799	10.870	10.941	11.013	11.085	11.158
	13	11.231	11.305	11.379	11.453	11.528	11.604	11.680	11.756	11.833	11.910
	14	11.987	12.065	12.144	12.223	12.302	12.382	12.462	12.543	12.624	12.706
	15	12.788	12.870	12.953	13.037	13.121	13.205	13.290	13.375	13.461	13.547
	16	13.634	13.721	13.809	13.898	13.987	14.076	14.166	14.256	14.347	14.438
	17	14.530	14.622	14.715	14.809	14.903	14.997	15.092	15.188	15.284	15.380
	18	15.477	15.575	15.673	15.772	15.871	15.971	16.771	16.171	16.272	16.374
	19	16.477	16.581	16.685	16.789	16.894	16.999	17.105	17.212	17.319	17.427
	20	17.535	17.644	17.753	17.863	17.974	18.085	18.197	18.309	18.422	18.536
	21	18.650	18.765	18.880	18.996	19.113	19.231	19.349	19.468	19.587	19.707
	22	19.827	19.948	20.070	20.193	20.316	20.440	20.565	20.690	20.815	20.941
	23	21.068	21.196	21.324	21.453	21.583	21.714	21.845	21.977	22.110	22.243
	24	22.377	22.512	22.648	22.785	22.922	23.060	23.198	23.337	23.476	23.616

[a]From R. H. Perry and C. H. Chilton, Eds., *Chemical Engineers' Handbook,* 5th Edition, McGraw-Hill, New York, 1973, Tables 3-3 and 3-5. Reprinted by permission of McGraw-Hill Book Co.

(*continued*)

TABLE B.3 (*Continued*)

T(°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
25	23.756	23.897	24.039	24.182	24.326	24.471	24.617	24.764	24.912	25.060
26	25.209	25.359	25.509	25.660	25.812	25.964	26.117	26.271	26.426	26.582
27	26.739	26.897	27.055	27.214	27.374	27.535	27.696	27.858	28.021	28.185
28	28.349	28.514	28.680	28.847	29.015	29.184	29.354	29.525	29.697	29.870
29	30.043	30.217	30.392	30.568	30.745	30.923	31.102	31.281	31.461	31.642
30	31.824	32.007	32.191	32.376	32.561	32.747	32.934	33.122	33.312	33.503
31	33.695	33.888	34.082	34.276	34.471	34.667	34.864	35.062	35.261	35.462
32	35.663	35.865	36.068	36.272	36.477	36.683	36.891	37.099	37.308	37.518
33	37.729	37.942	38.155	38.369	33.584	38.801	38.018	39.237	39.457	39.677
34	39.898	40.121	40.344	40.569	40.796	41.023	41.251	41.480	41.710	41.942
35	42.175	42.409	42.644	42.880	43.117	43.355	43.595	43.836	44.078	44.320
36	44.563	44.808	45.054	45.301	45.549	45.799	46.050	46.302	46.556	46.811
37	47.067	47.324	47.582	47.841	48.102	48.364	48.627	48.891	49.157	49.424
38	49.692	49.961	50.231	50.502	50.774	51.048	51.323	51.600	51.879	52.160
39	52.442	52.725	53.009	53.294	53.580	53.867	54.156	54.446	54.737	55.030
40	55.324	55.61	55.91	56.21	56.51	56.81	57.11	57.41	57.72	58.03
41	58.34	58.65	58.96	59.27	59.58	59.90	60.22	60.54	60.86	61.18
42	61.50	61.82	62.14	62.47	62.80	63.13	63.46	63.79	64.12	64.46
43	64.80	65.14	65.48	65.82	66.16	66.51	66.86	67.21	67.56	67.91
44	68.26	68.61	68.97	69.33	69.69	70.05	70.41	70.77	71.14	71.51
45	71.88	72.25	72.62	72.99	73.36	73.74	74.12	74.50	74.88	75.26
46	75.65	76.04	76.43	76.82	77.21	77.60	78.00	78.40	78.80	79.20
47	79.60	80.00	80.41	80.82	81.23	81.64	82.05	82.46	82.87	83.29
48	83.71	84.13	84.56	84.99	85.42	85.85	86.28	86.71	87.14	87.58
49	88.02	88.46	88.90	89.34	89.79	90.24	90.69	91.14	91.59	92.05

T(°C)	0	1	2	3	4	5	6	7	8	9
50	92.51	97.20	102.09	107.20	112.51	118.04	123.80	129.82	136.08	142.60
60	149.38	156.43	163.77	171.38	179.31	187.54	196.09	204.96	214.17	223.73
70	233.7	243.9	254.6	265.7	277.2	289.1	301.4	314.1	327.3	341.0
80	355.1	369.7	384.9	400.6	416.8	433.6	450.9	468.7	487.1	506.1

T(°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
90	525.76	527.76	529.77	531.78	533.80	535.82	537.86	539.90	541.95	544.00
91	546.05	548.11	550.18	552.26	554.35	556.44	558.53	560.64	562.75	564.87
92	566.99	569.12	571.26	573.40	575.55	577.71	579.87	582.04	584.22	586.41
93	588.60	590.80	593.00	595.21	597.43	599.66	601.89	604.13	606.38	608.64
94	610.90	613.17	615.44	617.72	620.01	622.31	624.61	626.92	629.24	631.57
95	633.90	636.24	938.59	640.94	643.30	645.67	648.05	650.43	652.82	655.22
96	657.62	660.03	662.45	664.88	667.31	669.75	672.20	674.66	677.12	679.69
97	682.07	684.55	687.04	689.54	692.05	694.57	697.10	699.63	702.17	704.71
98	707.27	709.83	712.40	714.98	717.56	720.15	722.75	725.36	727.98	730.61
99	733.24	735.88	738.53	741.18	743.85	746.52	749.20	751.89	754.58	757.29
100	760.00	762.72	765.45	768.19	770.93	773.68	776.44	779.22	782.00	784.78
101	787.57	790.37	793.18	796.00	798.82	801.66	804.50	807.35	810.21	813.08

TABLE B.4 Antoine Equation Constants[a]

$$\log_{10} p^* = A - \frac{B}{T + C} \qquad p^* \text{ in mm Hg}, \quad T \text{ in °C}$$

Example: The vapor pressure of acetaldehyde at 25°C is determined as follows:

$$\log_{10} p^*_{C_2H_4O}(25°C) = 8.00552 - \frac{1600.017}{25 + 291.809} = 2.9551$$

$$\Longrightarrow p^*_{C_2H_4O}(25°C) = 10^{2.9551} = 902 \text{ mm Hg}$$

Compound	Formula	Range (°C)	*A*	*B*	*C*
Acetaldehyde	C_2H_4O	−0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	$C_2H_4O_2$	29.8 to 126.5	7.38782	1533.313	222.309
Acetic acid*	$C_2H_4O_2$	0 to 36	7.18807	1416.7	225
Acetic anhydride	$C_4H_6O_3$	62.8 to 139.4	7.14948	1444.718	199.817
Acetone	C_3H_6O	−12.9 to 55.3	7.11714	1210.595	229.664
Acrylic acid	$C_3H_4O_2$	20.0 to 70.0	5.65204	648.629	154.683
Ammonia*	NH_3	−83 to 60	7.55466	1002.711	247.885
Aniline	C_6H_7N	102.6 to 185.2	7.32010	1731.515	206.049
Benzene	C_6H_6	14.5 to 80.9	6.89272	1203.531	219.888
n-Butane	n-C_4H_{10}	−78.0 to −0.3	6.82485	943.453	239.711
i-Butane	i-C_4H_{10}	−85.1 to −11.6	6.78866	899.617	241.942
1-Butanol	$C_4H_{10}O$	89.2 to 125.7	7.36366	1305.198	173.427
2-Butanol	$C_4H_{10}O$	72.4 to 107.1	7.20131	1157.000	168.279
1-Butene	C_4H_8	−77.5 to −3.7	6.53101	810.261	228.066
Butyric acid	$C_4H_8O_2$	20.0 to 150.0	8.71019	2433.014	255.189
Carbon disulfide	CS_2	3.6 to 79.9	6.94279	1169.110	241.593
Carbon tetrachloride	CCl_4	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	C_6H_5Cl	62.0 to 131.7	6.97808	1431.053	217.550
Chlorobenzene*	C_6H_5Cl	0 to 42	7.10690	1500.0	224.0
Chlorobenzene*	C_6H_5Cl	42 to 230	6.94504	1413.12	216.0
Chloroform	$CHCl_3$	−10.4 to 60.3	6.95465	1170.966	226.232
Chloroform*	$CHCl_3$	−30 to 150	6.90328	1163.03	227.4
Cyclohexane	C_6H_{12}	19.9 to 81.6	6.84941	1206.001	223.148
Cyclohexanol	$C_6H_{12}O$	93.7 to 160.7	6.25530	912.866	109.126
n-Decane	n-$C_{10}H_{22}$	94.5 to 175.1	6.95707	1503.568	194.738
1-Decene	$C_{10}H_{20}$	86.8 to 171.6	6.95433	1497.527	197.056
1,1-Dichloroethane	$C_2H_4Cl_2$	−38.8 to 17.6	6.97702	1174.022	229.060
1,2-Dichloroethane	$C_2H_4Cl_2$	−30.8 to 99.4	7.02530	1271.254	222.927
Dichloromethane	CH_2Cl_2	−40.0 to 40	7.40916	1325.938	252.616
Diethyl ether	$C_4H_{10}O$	−60.8 to 19.9	6.92032	1064.066	228.799
Diethyl ketone	$C_5H_{10}O$	56.5 to 111.3	7.02529	1310.281	214.192
Diethylene glycol	$C_4H_{10}O_2$	130.0 to 243.0	7.63666	1939.359	162.714
Dimethyl ether	C_2H_6O	−78.2 to −24.9	6.97603	889.264	241.957
Dimethylamine	C_2H_7N	−71.8 to 6.9	7.08212	960.242	221.667
N,*N*-Dimethylformamide	C_3H_7NO	30.0 to 90.0	6.92796	1400.869	196.434
1,4-Dioxane	$C_4H_8O_2$	20.0 to 105.0	7.43155	1554.679	240.337
Ethanol	C_2H_6O	19.6 to 93.4	8.11220	1592.864	226.184
Ethanolamine	C_2H_7NO	65.4 to 170.9	7.45680	1577.670	173.368
Ethyl acetate	$C_4H_8O_2$	15.6 to 75.8	7.10179	1244.951	217.881
Ethyl acetate*	$C_4H_8O_2$	−20 to 150	7.09808	1238.710	217.0
Ethyl chloride	C_2H_5Cl	−55.9 to 12.5	6.98647	1030.007	238.612
Ethylbenzene	C_8H_{10}	56.5 to 137.1	6.95650	1423.543	213.091

[a]Based on T. Boublik, V. Fried, and E. Hala, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam, 1973. If marked with an asterisk (*), constants are from *Lange's Handbook of Chemistry*, 9th Edition, Handbook Publishers, Inc., Sandusky, OH, 1956.

(*continued*)

TABLE B.4 (*Continued*)

Compound	Formula	Range (°C)	*A*	*B*	*C*
Ethylene glycol	$C_2H_6O_2$	50.0 to 200.0	8.09083	2088.936	203.454
Ethylene oxide	C_2H_4O	0.3 to 31.8	8.69016	2005.779	334.765
1,2-Ethylenediamine	$C_2H_8N_2$	26.5 to 117.4	7.16871	1336.235	194.366
Formaldehyde	HCHO	−109.4 to −22.3	7.19578	970.595	244.124
Formic acid	CH_2O_2	37.4 to 100.7	7.58178	1699.173	260.714
Glycerol	$C_3H_8O_3$	183.3 to 260.4	6.16501	1036.056	28.097
n-Heptane	*n*-C_7H_{16}	25.9 to 99.3	6.90253	1267.828	216.823
i-Heptane	*i*-C_7H_{16}	18.5 to 90.9	6.87689	1238.122	219.783
1-Heptene	C_7H_{14}	21.6 to 94.5	6.91381	1265.120	220.051
n-Hexane	*n*-C_6H_{14}	13.0 to 69.5	6.88555	1175.817	224.867
i-Hexane	*i*-C_6H_{14}	12.8 to 61.1	6.86839	1151.401	228.477
1-Hexene	C_6H_{12}	15.9 to 64.3	6.86880	1154.646	226.046
Hydrogen Cyanide	HCN	−16.4 to 46.2	7.52823	1329.49	260.418
Methanol	CH_3OH	14.9 to 83.7	8.08097	1582.271	239.726
Methanol*	CH_3OH	−20 to 140	7.87863	1473.11	230.0
Methyl acetate	$C_3H_6O_2$	1.8 to 55.8	7.06524	1157.630	219.726
Methyl bromide	CH_3Br	−70.0 to 3.6	7.09084	1046.066	244.914
Methyl chloride	CH_3Cl	−75.0 to 5.0	7.09349	948.582	249.336
Methyl ethyl ketone	C_4H_8O	42.8 to 88.4	7.06356	1261.339	221.969
Methyl isobutyl ketone	$C_6H_{12}O$	21.7 to 116.2	6.67272	1168.408	191.944
Methyl methacrylate	$C_5H_8O_2$	39.2 to 89.2	8.40919	2050.467	274.369
Methylamine	CH_5N	−83.1 to −6.2	7.33690	1011.532	233.286
Methylcyclohexane	C_7H_{14}	25.6 to 101.8	6.82827	1273.673	221.723
Naphthalene	$C_{10}H_8$	80.3 to 179.5	7.03358	1756.328	204.842
Nitrobenzene	$C_6H_5NO_2$	134.1 to 210.6	7.11562	1746.586	201.783
Nitromethane	CH_3NO_2	55.7 to 136.4	7.28166	1446.937	227.600
n-Nonane	*n*-C_9H_{20}	70.3 to 151.8	6.93764	1430.459	201.808
1-Nonene	C_9H_{18}	66.6 to 147.9	6.95777	1437.862	205.814
n-Octane	*n*-C_8H_{18}	52.9 to 126.6	6.91874	1351.756	209.100
i-Octane	*i*-C_8H_{18}	41.7 to 118.5	6.88814	1319.529	211.625
1-Octene	C_8H_{16}	44.9 to 122.2	6.93637	1355.779	213.022
n-Pentane	*n*-C_5H_{12}	13.3 to 36.8	6.84471	1060.793	231.541
i-Pentane	*i*-C_5H_{12}	16.3 to 28.6	6.73457	992.019	229.564
1-Pentanol	$C_5H_{12}O$	74.7 to 156.0	7.18246	1287.625	161.330
1-Pentene	C_5H_{10}	12.8 to 30.7	6.84268	1043.206	233.344
Phenol	C_6H_6O	107.2 to 181.8	7.13301	1516.790	174.954
1-Propanol	C_3H_8O	60.2 to 104.6	7.74416	1437.686	198.463
2-Propanol	C_3H_8O	52.3 to 89.3	7.74021	1359.517	197.527
Propionic acid	$C_3H_6O_2$	72.4 to 128.3	7.71423	1733.418	217.724
Propylene oxide	C_3H_6O	−24.2 to 34.8	7.01443	1086.369	228.594
Pyridine	C_5H_5N	67.3 to 152.9	7.04115	1373.799	214.979
Styrene	C_8H_8	29.9 to 144.8	7.06623	1507.434	214.985
Toluene	C_7H_8	35.3 to 111.5	6.95805	1346.773	219.693
1,1,1-Trichloroethane	$C_2H_3Cl_3$	−5.4 to 16.9	8.64344	2136.621	302.769
1,1,2-Trichloroethane	$C_2H_3Cl_3$	50.0 to 113.7	6.95185	1314.410	209.197
Trichloroethylene	C_2HCl_3	17.8 to 86.5	6.51827	1018.603	192.731
Vinyl acetate	$C_4H_6O_2$	21.8 to 72.0	7.21010	1296.130	226.655
Water*	H_2O	0 to 60	8.10765	1750.286	235.000
Water*	H_2O	60 to 150	7.96681	1668.210	228.000
m-Xylene	*m*-C_8H_{10}	59.2 to 140.0	7.00646	1460.183	214.827
o-Xylene	*o*-C_8H_{10}	63.5 to 145.4	7.00154	1476.393	213.872
p-Xylene	*p*-C_8H_{10}	58.3 to 139.3	6.98820	1451.792	215.111

TABLE B.5 Properties of Saturated Steam: Temperature Table[a]

		$\hat{V}$(m³/kg)		$\hat{U}$(kJ/kg)		$\hat{H}$(kJ/kg)		
T(°C)	P(bar)	Water	Steam	Water	Steam	Water	Evaporation	Steam
0.01	0.00611	0.001000	206.2	zero	2375.6	+0.0	2501.6	2501.6
2	0.00705	0.001000	179.9	8.4	2378.3	8.4	2496.8	2505.2
4	0.00813	0.001000	157.3	16.8	2381.1	16.8	2492.1	2508.9
6	0.00935	0.001000	137.8	25.2	2383.8	25.2	2487.4	2512.6
8	0.01072	0.001000	121.0	33.6	2386.6	33.6	2482.6	2516.2
10	0.01227	0.001000	106.4	42.0	2389.3	42.0	2477.9	2519.9
12	0.01401	0.001000	93.8	50.4	2392.1	50.4	2473.2	2523.6
14	0.01597	0.001001	82.9	58.8	2394.8	58.8	2468.5	2527.2
16	0.01817	0.001001	73.4	67.1	2397.6	67.1	2463.8	2530.9
18	0.02062	0.001001	65.1	75.5	2400.3	75.5	2459.0	2534.5
20	0.0234	0.001002	57.8	83.9	2403.0	83.9	2454.3	2538.2
22	0.0264	0.001002	51.5	92.2	2405.8	92.2	2449.6	2541.8
24	0.0298	0.001003	45.9	100.6	2408.5	100.6	2444.9	2545.5
25	0.0317	0.001003	43.4	104.8	2409.9	104.8	2442.5	2547.3
26	0.0336	0.001003	41.0	108.9	2411.2	108.9	2440.2	2549.1
28	0.0378	0.001004	36.7	117.3	2414.0	117.3	2435.4	2552.7
30	0.0424	0.001004	32.9	125.7	2416.7	125.7	2430.7	2556.4
32	0.0475	0.001005	29.6	134.0	2419.4	134.0	2425.9	2560.0
34	0.0532	0.001006	26.6	142.4	2422.1	142.4	2421.2	2563.6
36	0.0594	0.001006	24.0	150.7	2424.8	150.7	2416.4	2567.2
38	0.0662	0.001007	21.6	159.1	2427.5	159.1	2411.7	2570.8
40	0.0738	0.001008	19.55	167.4	2430.2	167.5	2406.9	2574.4
42	0.0820	0.001009	17.69	175.8	2432.9	175.8	2402.1	2577.9
44	0.0910	0.001009	16.04	184.2	2435.6	184.2	2397.3	2581.5
46	0.1009	0.001010	14.56	192.5	2438.3	192.5	2392.5	2585.1
48	0.1116	0.001011	13.23	200.9	2440.9	200.9	2387.7	2588.6
50	0.1234	0.001012	12.05	209.2	2443.6	209.3	2382.9	2592.2
52	0.1361	0.001013	10.98	217.7	2446	217.7	2377	2595
54	0.1500	0.001014	10.02	226.0	2449	226.0	2373	2599
56	0.1651	0.001015	9.158	234.4	2451	234.4	2368	2602
58	0.1815	0.001016	8.380	242.8	2454	242.8	2363	2606
60	0.1992	0.001017	7.678	251.1	2456	251.1	2358	2609
62	0.2184	0.001018	7.043	259.5	2459	259.5	2353	2613
64	0.2391	0.001019	6.468	267.9	2461	267.9	2348	2616
66	0.2615	0.001020	5.947	276.2	2464	276.2	2343	2619
68	0.2856	0.001022	5.475	284.6	2467	284.6	2338	2623

[a]From R. W. Haywood, *Thermodynamic Tables in SI (Metric) Units,* Cambridge University Press, London, 1968. $\hat{V}$ = specific volume, $\hat{U}$ = specific internal energy, and $\hat{H}$ = specific enthalpy. *Note:* kJ/kg × 0.4303 = Btu/lb_m.

(*continued*)

TABLE B.5 (*Continued*)

		$\hat{V}$(m³/kg)		$\hat{U}$(kJ/kg)		$\hat{H}$(kJ/kg)		
T(°C)	P(bar)	Water	Steam	Water	Steam	Water	Evaporation	Steam
70	0.3117	0.001023	5.045	293.0	2469	293.0	2333	2626
72	0.3396	0.001024	4.655	301.4	2472	301.4	2329	2630
74	0.3696	0.001025	4.299	309.8	2474	309.8	2323	2633
76	0.4019	0.001026	3.975	318.2	2476	318.2	2318	2636
78	0.4365	0.001028	3.679	326.4	2479	326.4	2313	2639
80	0.4736	0.001029	3.408	334.8	2482	334.9	2308	2643
82	0.5133	0.001030	3.161	343.2	2484	343.3	2303	2646
84	0.5558	0.001032	2.934	351.6	2487	351.7	2298	2650
86	0.6011	0.001033	2.727	360.0	2489	360.1	2293	2653
88	0.6495	0.001034	2.536	368.4	2491	368.5	2288	2656
90	0.7011	0.001036	2.361	376.9	2493	377.0	2282	2659
92	0.7560	0.001037	2.200	385.3	2496	385.4	2277	2662
94	0.8145	0.001039	2.052	393.7	2499	393.8	2272	2666
96	0.8767	0.001040	1.915	402.1	2501	402.2	2267	2669
98	0.9429	0.001042	1.789	410.6	2504	410.7	2262	2673
100	1.0131	0.001044	1.673	419.0	2507	419.1	2257	2676
102	1.0876	0.001045	1.566	427.1	2509	427.5	2251	2679

TABLE B.6 Properties of Saturated Steam: Pressure Table[a]

		$\hat{V}$(m³/kg)		$\hat{U}$(kJ/kg)		$\hat{H}$(kJ/kg)		
P(bar)	T(°C)	Water	Steam	Water	Steam	Water	Evaporation	Steam
0.00611	0.01	0.001000	206.2	zero	2375.6	+0.0	2501.6	2501.6
0.008	3.8	0.001000	159.7	15.8	2380.7	15.8	2492.6	2508.5
0.010	7.0	0.001000	129.2	29.3	2385.2	29.3	2485.0	2514.4
0.012	9.7	0.001000	108.7	40.6	2388.9	40.6	2478.7	2519.3
0.014	12.0	0.001000	93.9	50.3	2392.0	50.3	2473.2	2523.5
0.016	14.0	0.001001	82.8	58.9	2394.8	58.9	2468.4	2527.3
0.018	15.9	0.001001	74.0	66.5	2397.4	66.5	2464.1	2530.6
0.020	17.5	0.001001	67.0	73.5	2399.6	73.5	2460.2	2533.6
0.022	19.0	0.001002	61.2	79.8	2401.7	79.8	2456.6	2536.4
0.024	20.4	0.001002	56.4	85.7	2403.6	85.7	2453.3	2539.0
0.026	21.7	0.001002	52.3	91.1	2405.4	91.1	2450.2	2541.3
0.028	23.0	0.001002	48.7	96.2	2407.1	96.2	2447.3	2543.6
0.030	24.1	0.001003	45.7	101.0	2408.6	101.0	2444.6	2545.6
0.035	26.7	0.001003	39.5	111.8	2412.2	111.8	2438.5	2550.4
0.040	29.0	0.001004	34.8	121.4	2415.3	121.4	2433.1	2554.5
0.045	31.0	0.001005	31.1	130.0	2418.1	130.0	2428.2	2558.2
0.050	32.9	0.001005	28.2	137.8	2420.6	137.8	2423.8	2561.6
0.060	36.2	0.001006	23.74	151.5	2425.1	151.5	2416.0	2567.5
0.070	39.0	0.001007	20.53	163.4	2428.9	163.4	2409.2	2572.6
0.080	41.5	0.001008	18.10	173.9	2432.3	173.9	2403.2	2577.1
0.090	43.8	0.001009	16.20	183.3	2435.3	183.3	2397.9	2581.1
0.10	45.8	0.001010	14.67	191.8	2438.0	191.8	2392.9	2584.8
0.11	47.7	0.001011	13.42	199.7	2440.5	199.7	2388.4	2588.1
0.12	49.4	0.001012	12.36	206.9	2442.8	206.9	2384.3	2591.2
0.13	51.1	0.001013	11.47	213.7	2445.0	213.7	2380.4	2594.0
0.14	52.6	0.001013	10.69	220.0	2447.0	220.0	2376.7	2596.7

0.15	54.0	0.001014	10.02	226.0	2448.9	226.0	2373.2	2599.2
0.16	55.3	0.001015	9.43	231.6	2450.6	231.6	2370.0	2601.6
0.17	56.6	0.001015	8.91	236.9	2452.3	236.9	2366.9	2603.8
0.18	57.8	0.001016	8.45	242.0	2453.9	242.0	2363.9	2605.9
0.19	59.0	0.001017	8.03	246.8	2455.4	246.8	2361.1	2607.9
0.20	60.1	0.001017	7.65	251.5	2456.9	251.5	2358.4	2609.9
0.22	62.2	0.001018	7.00	260.1	2459.6	260.1	2353.3	2613.5
0.24	64.1	0.001019	6.45	268.2	2462.1	268.2	2348.6	2616.8
0.26	65.9	0.001020	5.98	275.6	2464.4	275.7	2344.2	2619.9
0.28	67.5	0.001021	5.58	282.7	2466.5	282.7	2340.0	2622.7
0.30	69.1	0.001022	5.23	289.3	2468.6	289.3	2336.1	2625.4
0.35	72.7	0.001025	4.53	304.3	2473.1	304.3	2327.2	2631.5
0.40	75.9	0.001027	3.99	317.6	2477.1	317.7	2319.2	2636.9
0.45	78.7	0.001028	3.58	329.6	2480.7	329.6	2312.0	2641.7
0.50	81.3	0.001030	3.24	340.5	2484.0	340.6	2305.4	2646.0
0.55	83.7	0.001032	2.96	350.6	2486.9	350.6	2299.3	2649.9
0.60	86.0	0.001033	2.73	359.9	2489.7	359.9	2293.6	2653.6
0.65	88.0	0.001035	2.53	368.5	2492.2	368.6	2288.3	2656.9
0.70	90.0	0.001036	2.36	376.7	2494.5	376.8	2283.3	2660.1
0.75	91.8	0.001037	2.22	384.4	2496.7	384.5	2278.6	2663.0
0.80	93.5	0.001039	2.087	391.6	2498.8	391.7	2274.1	2665.8
0.85	95.2	0.001040	1.972	398.5	2500.8	398.6	2269.8	2668.4
0.90	96.7	0.001041	1.869	405.1	2502.6	405.2	2265.6	2670.9
0.95	98.2	0.001042	1.777	411.4	2504.4	411.5	2261.7	2673.2
1.00	99.6	0.001043	1.694	417.4	2506.1	417.5	2257.9	2675.4
1.01325 (1 atm)	100.0	0.001044	1.673	419.0	2506.5	419.1	2256.9	2676.0

[a]From R. W. Haywood, *Thermodynamic Tables in SI (Metric) Units*, Cambridge University Press, London, 1968. $\hat{V}$ = specific volume, $\hat{U}$ = specific internal energy, and $\hat{H}$ = specific enthalpy. *Note:* kJ/kg × 0.4303 = Btu/lb_m.

(*continued*)

TABLE B.6 (*Continued*)

		$\hat{V}$(m³/kg)		$\hat{U}$(kJ/kg)		$\hat{H}$(kJ/kg)		
P(bar)	T(°C)	Water	Steam	Water	Steam	Water	Evaporation	Steam
1.1	102.3	0.001046	1.549	428.7	2509.2	428.8	2250.8	2679.6
1.2	104.8	0.001048	1.428	439.2	2512.1	439.4	2244.1	2683.4
1.3	107.1	0.001049	1.325	449.1	2514.7	449.2	2237.8	2687.0
1.4	109.3	0.001051	1.236	458.3	2517.2	458.4	2231.9	2690.3
1.5	111.4	0.001053	1.159	467.0	2519.5	467.1	2226.2	2693.4
1.6	113.3	0.001055	1.091	475.2	2521.7	475.4	2220.9	2696.2
1.7	115.2	0.001056	1.031	483.0	2523.7	483.2	2215.7	2699.0
1.8	116.9	0.001058	0.977	490.5	2525.6	490.7	2210.8	2701.5
1.9	118.6	0.001059	0.929	497.6	2527.5	497.8	2206.1	2704.0
2.0	120.2	0.001061	0.885	504.5	2529.2	504.7	2201.6	2706.3
2.2	123.3	0.001064	0.810	517.4	2532.4	517.6	2193.0	2710.6
2.4	126.1	0.001066	0.746	529.4	2535.4	529.6	2184.9	2714.5
2.6	128.7	0.001069	0.693	540.6	2538.1	540.9	2177.3	2718.2
2.8	131.2	0.001071	0.646	551.1	2540.6	551.4	2170.1	2721.5
3.0	133.5	0.001074	0.606	561.1	2543.0	561.4	2163.2	2724.7
3.2	135.8	0.001076	0.570	570.6	2545.2	570.9	2156.7	2727.6
3.4	137.9	0.001078	0.538	579.6	2547.2	579.9	2150.4	2730.3
3.6	139.9	0.001080	0.510	588.1	2549.2	588.5	2144.4	2732.9
3.8	141.8	0.001082	0.485	596.4	2551.0	596.8	2138.6	2735.3
4.0	143.6	0.001084	0.462	604.2	2552.7	604.7	2133.0	2737.6
4.2	145.4	0.001086	0.442	611.8	2554.4	612.3	2127.5	2739.8
4.4	147.1	0.001088	0.423	619.1	2555.9	619.6	2122.3	2741.9
4.6	148.7	0.001089	0.405	626.2	2557.4	626.7	2117.2	2743.9
4.8	150.3	0.001091	0.389	633.0	2558.8	633.5	2112.2	2745.7
5.0	151.8	0.001093	0.375	639.6	2560.2	640.1	2107.4	2747.5
5.5	155.5	0.001097	0.342	655.2	2563.3	655.8	2095.9	2751.7
6.0	158.8	0.001101	0.315	669.8	2566.2	670.4	2085.0	2755.5
6.5	162.0	0.001105	0.292	683.4	2568.7	684.1	2074.7	2758.9
7.0	165.0	0.001108	0.273	696.3	2571.1	697.1	2064.9	2762.0

7.5	167.8	0.001112	0.2554	708.5	2573.3	709.3	2055.5	2764.8
8.0	170.4	0.001115	0.2403	720.0	2575.5	720.9	2046.5	2767.5
8.5	172.9	0.001118	0.2268	731.1	2577.1	732.0	2037.9	2769.9
9.0	175.4	0.001121	0.2148	741.6	2578.8	742.6	2029.5	2772.1
9.5	177.7	0.001124	0.2040	751.8	2580.4	752.8	2021.4	2774.2
10.0	179.9	0.001127	0.1943	761.5	2581.9	762.6	2013.6	2776.2
10.5	182.0	0.001130	0.1855	770.8	2583.3	772.0	2005.9	2778.0
11.0	184.1	0.001133	0.1774	779.9	2584.5	781.1	1998.5	2779.7
11.5	186.0	0.001136	0.1700	788.6	2585.8	789.9	1991.3	2781.3
12.0	188.0	0.001139	0.1632	797.1	2586.9	798.4	1984.3	2782.7
12.5	189.8	0.001141	0.1569	805.3	2588.0	806.7	1977.4	2784.1
13.0	191.6	0.001144	0.1511	813.2	2589.0	814.7	1970.7	2785.4
14	195.0	0.001149	0.1407	828.5	2590.8	830.1	1957.7	2787.8
15	198.3	0.001154	0.1317	842.9	2592.4	844.7	1945.2	2789.9
16	201.4	0.001159	0.1237	856.7	2593.8	858.6	1933.2	2791.7
17	204.3	0.001163	0.1166	869.9	2595.1	871.8	1921.5	2793.4
18	207.1	0.001168	0.1103	882.5	2596.3	884.6	1910.3	2794.8
19	209.8	0.001172	0.1047	894.6	2597.3	896.8	1899.3	2796.1
20	212.4	0.001177	0.0995	906.2	2598.2	908.6	1888.6	2797.2
21	214.9	0.001181	0.0949	917.5	2598.9	920.0	1878.2	2798.2
22	217.2	0.001185	0.0907	928.3	2599.6	931.0	1868.1	2799.1
23	219.6	0.001189	0.0868	938.9	2600.2	941.6	1858.2	2799.8
24	221.8	0.001193	0.0832	949.1	2600.7	951.9	1848.5	2800.4
25	223.9	0.001197	0.0799	959.0	2601.2	962.0	1839.0	2800.9
26	226.0	0.001201	0.0769	968.6	2601.5	971.7	1829.6	2801.4
27	228.1	0.001205	0.0740	978.0	2601.8	981.2	1820.5	2801.7
28	230.0	0.001209	0.0714	987.1	2602.1	990.5	1811.5	2802.0
29	232.0	0.001213	0.0689	996.0	2602.3	999.5	1802.6	2802.2
30	233.8	0.001216	0.0666	1004.7	2602.4	1008.4	1793.9	2802.3
32	237.4	0.001224	0.0624	1021.5	2602.5	1025.4	1776.9	2802.3
34	240.9	0.001231	0.0587	1037.6	2602.5	1041.8	1760.3	2802.1
36	244.2	0.001238	0.0554	1053.1	2602.2	1057.6	1744.2	2801.7
38	247.3	0.001245	0.0524	1068.0	2601.9	1072.7	1728.4	2801.1

(*continued*)

TABLE B.6 (*Continued*)

		$\hat{V}$(m³/kg)		$\hat{U}$(kJ/kg)		$\hat{H}$(kJ/kg)		
P(bar)	T(°C)	Water	Steam	Water	Steam	Water	Evaporation	Steam
40	250.3	0.001252	0.0497	1082.4	2601.3	1087.4	1712.9	2800.3
42	253.2	0.001259	0.0473	1096.3	2600.7	1101.6	1697.8	2799.4
44	256.0	0.001266	0.0451	1109.8	2599.9	1115.4	1682.9	2798.3
46	258.8	0.001272	0.0430	1122.9	2599.1	1128.8	1668.3	2797.1
48	261.4	0.001279	0.0412	1135.6	2598.1	1141.8	1653.9	2795.7
50	263.9	0.001286	0.0394	1148.0	2597.0	1154.5	1639.7	2794.2
52	266.4	0.001292	0.0378	1160.1	2595.9	1166.8	1625.7	2792.6
54	268.8	0.001299	0.0363	1171.9	2594.6	1178.9	1611.9	2790.8
56	271.1	0.001306	0.0349	1183.5	2593.3	1190.8	1598.2	2789.0
58	273.3	0.001312	0.0337	1194.7	2591.9	1202.3	1584.7	2787.0
60	275.6	0.001319	0.0324	1205.8	2590.4	1213.7	1571.3	2785.0
62	277.7	0.001325	0.0313	1216.6	2588.8	1224.8	1558.0	2782.9
64	279.8	0.001332	0.0302	1227.2	2587.2	1235.7	1544.9	2780.6
66	281.8	0.001338	0.0292	1237.6	2585.5	1246.5	1531.9	2778.3
68	283.8	0.001345	0.0283	1247.9	2583.7	1257.0	1518.9	2775.9
70	285.8	0.001351	0.0274	1258.0	2581.8	1267.4	1506.0	2773.5
72	287.7	0.001358	0.0265	1267.9	2579.9	1277.6	1493.3	2770.9
74	289.6	0.001364	0.0257	1277.6	2578.0	1287.7	1480.5	2768.3
76	291.4	0.001371	0.0249	1287.2	2575.9	1297.6	1467.9	2765.5
78	293.2	0.001378	0.0242	1296.7	2573.8	1307.4	1455.3	2762.8
80	295.0	0.001384	0.0235	1306.0	2571.7	1317.1	1442.8	2759.9
82	296.7	0.001391	0.0229	1315.2	2569.5	1326.6	1430.3	2757.0
84	298.4	0.001398	0.0222	1324.3	2567.2	1336.1	1417.9	2754.0
86	300.1	0.001404	0.0216	1333.3	2564.9	1345.4	1405.5	2750.9
88	301.7	0.001411	0.0210	1342.2	2562.6	1354.6	1393.2	2747.8
90	303.3	0.001418	0.02050	1351.0	2560.1	1363.7	1380.9	2744.6
92	304.9	0.001425	0.01996	1359.7	2557.7	1372.8	1368.6	2741.4
94	306.4	0.001432	0.01945	1368.2	2555.2	1381.7	1356.3	2738.0

96	308.0	0.001439	0.01897	1376.7	2552.6	1390.6	1344.1	2734.7
98	309.5	0.001446	0.01849	1385.2	2550.0	1399.3	1331.9	2731.2
100	311.0	0.001453	0.01804	1393.5	2547.3	1408.0	1319.7	2727.7
105	314.6	0.001470	0.01698	1414.1	2540.4	1429.5	1289.2	2718.7
110	318.0	0.001489	0.01601	1434.2	2533.2	1450.6	1258.7	2709.3
115	321.4	0.001507	0.01511	1454.0	2525.7	1471.3	1228.2	2699.5
120	324.6	0.001527	0.01428	1473.4	2517.8	1491.8	1197.4	2689.2
125	327.8	0.001547	0.01351	1492.7	2509.4	1512.0	1166.4	2678.4
130	330.8	0.001567	0.01280	1511.6	2500.6	1532.0	1135.0	2667.0
135	333.8	0.001588	0.01213	1530.4	2491.3	1551.9	1103.1	2655.0
140	336.6	0.001611	0.01150	1549.1	2481.4	1571.6	1070.7	2642.4
145	339.4	0.001634	0.01090	1567.5	2471.0	1591.3	1037.7	2629.1
150	342.1	0.001658	0.01034	1586.1	2459.9	1611.0	1004.0	2615.0
155	344.8	0.001683	0.00981	1604.6	2448.2	1630.7	969.6	2600.3
160	347.3	0.001710	0.00931	1623.2	2436.0	1650.5	934.3	2584.9
165	349.8	0.001739	0.00883	1641.8	2423.1	1670.5	898.3	2568.8
170	352.3	0.001770	0.00837	1661.6	2409.3	1691.7	859.9	2551.6
175	354.6	0.001803	0.00793	1681.8	2394.6	1713.3	820.0	2533.3
180	357.0	0.001840	0.00750	1701.7	2378.9	1734.8	779.1	2513.9
185	359.2	0.001881	0.00708	1721.7	2362.1	1756.5	736.6	2493.1
190	361.4	0.001926	0.00668	1742.1	2343.8	1778.7	692.0	2470.6
195	363.6	0.001977	0.00628	1763.2	2323.6	1801.8	644.2	2446.0
200	365.7	0.00204	0.00588	1785.7	2300.8	1826.5	591.9	2418.4
205	367.8	0.00211	0.00546	1810.7	2274.4	1853.9	532.5	2386.4
210	369.8	0.00220	0.00502	1840.0	2242.1	1886.3	461.3	2347.6
215	371.8	0.00234	0.00451	1878.6	2198.1	1928.9	366.2	2295.2
220	373.7	0.00267	0.00373	1952	2114	2011	185	2196
221.2 (Critical point)	374.15	0.00317	0.00317	2038	2038	2108	0	2108

TABLE B.7 Properties of Superheated Steam[a]

P(bar) ($T_{sat.}$°C)		Sat'd Water	Sat'd Steam	Temperature (°C)→ 50	75	100	150	200	250	300	350
0.0	$\hat{H}$	—	—	2595	2642	2689	2784	2880	2978	3077	3177
(—)	$\hat{U}$	—	—	2446	2481	2517	2589	2662	2736	2812	2890
	$\hat{V}$	—	—	—	—	—	—	—	—	—	—
0.1	$\hat{H}$	191.8	2584.8	2593	2640	2688	2783	2880	2977	3077	3177
(45.8)	$\hat{U}$	191.8	2438.0	2444	2480	2516	2588	2661	2736	2812	2890
	$\hat{V}$	0.00101	14.7	14.8	16.0	17.2	19.5	21.8	24.2	26.5	28.7
0.5	$\hat{H}$	340.6	2646.0	209.3	313.9	2683	2780	2878	2979	3076	3177
(81.3)	$\hat{U}$	340.6	2484.0	209.2	313.9	2512	2586	2660	2735	2811	2889
	$\hat{V}$	0.00103	3.24	0.00101	0.00103	3.41	3.89	4.35	4.83	5.29	5.75
1.0	$\hat{H}$	417.5	2675.4	209.3	314.0	2676	2776	2875	2975	3074	3176
(99.6)	$\hat{U}$	417.5	2506.1	209.2	313.9	2507	2583	2658	2734	2811	2889
	$\hat{V}$	0.00104	1.69	0.00101	0.00103	1.69	1.94	2.17	2.40	2.64	2.87
5.0	$\hat{H}$	640.1	2747.5	209.7	314.3	419.4	632.2	2855	2961	3065	3168
(151.8)	$\hat{U}$	639.6	2560.2	209.2	313.8	418.8	631.6	2643	2724	2803	2883
	$\hat{V}$	0.00109	0.375	0.00101	0.00103	0.00104	0.00109	0.425	0.474	0.522	0.571
10	$\hat{H}$	762.6	2776.2	210.1	314.7	419.7	632.5	2827	2943	3052	3159
(179.9)	$\hat{U}$	761.5	2582	209.1	313.7	418.7	631.4	2621	2710	2794	2876
	$\hat{V}$	0.00113	0.194	0.00101	0.00103	0.00104	0.00109	0.206	0.233	0.258	0.282
20	$\hat{H}$	908.6	2797.2	211.0	315.5	420.5	633.1	852.6	2902	3025	3139
(212.4)	$\hat{U}$	906.2	2598.2	209.0	313.5	418.4	603.9	850.2	2679	2774	2862
	$\hat{V}$	0.00118	0.09950	0.00101	0.00102	0.00104	0.00109	0.00116	0.111	0.125	0.139
40	$\hat{H}$	1087.4	2800.3	212.7	317.1	422.0	634.3	853.4	1085.8	2962	3095
(250.3)	$\hat{U}$	1082.4	2601.3	208.6	313.0	417.8	630.0	848.8	1080.8	2727	2829
	$\hat{V}$	0.00125	0.04975	0.00101	0.00102	0.00104	0.00109	0.00115	0.00125	0.0588	0.0665
60	$\hat{H}$	1213.7	2785.0	214.4	318.7	423.5	635.6	854.2	1085.8	2885	3046
(275.6)	$\hat{U}$	1205.8	2590.4	208.3	312.6	417.3	629.1	847.3	1078.3	2668	2792
	$\hat{V}$	0.00132	0.0325	0.00101	0.00103	0.00104	0.00109	0.00115	0.00125	0.0361	0.0422
80	$\hat{H}$	1317.1	2759.9	216.1	320.3	425.0	636.8	855.1	1085.8	2787	2990
(295.0)	$\hat{U}$	1306.0	2571.7	208.1	312.3	416.7	628.2	845.9	1075.8	2593	2750
	$\hat{V}$	0.00139	0.0235	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.0243	0.0299
100	$\hat{H}$	1408.0	2727.7	217.8	322.9	426.5	638.1	855.9	1085.8	1343.4	2926
(311.0)	$\hat{U}$	1393.5	2547.3	207.8	311.7	416.1	627.3	844.4	1073.4	1329.4	2702
	$\hat{V}$	0.00145	0.0181	0.00101	0.00102	0.00104	0.00109	0.00115	0.00124	0.00140	0.0224
150	$\hat{H}$	1611.0	2615.0	222.1	326.0	430.3	641.3	858.1	1086.2	1338.2	2695
(342.1)	$\hat{U}$	1586.1	2459.9	207.0	310.7	414.7	625.0	841.0	1067.7	1317.6	2523
	$\hat{V}$	0.00166	0.0103	0.00101	0.00102	0.00104	0.00108	0.00114	0.00123	0.00138	0.0115
200	$\hat{H}$	1826.5	2418.4	226.4	330.0	434.0	644.5	860.4	1086.7	1334.3	1647.1
(365.7)	$\hat{U}$	1785.7	2300.8	206.3	309.7	413.2	622.9	837.7	1062.2	1307.1	1613.7
	$\hat{V}$	0.00204	0.005875	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00136	0.00167
221.2(P_c)	$\hat{H}$	2108	2108	228.2	331.7	435.7	645.8	861.4	1087.0	1332.8	1635.5
(374.15)(T_c)	$\hat{U}$	2037.8	2037.8	206.0	309.2	412.8	622.0	836.3	1060.0	1302.9	1600.3
	$\hat{V}$	0.00317	0.00317	0.00100	0.00102	0.00103	0.00108	0.00114	0.00122	0.00135	0.00163
250	$\hat{H}$	—	—	230.7	334.0	437.8	647.7	862.8	1087.5	1331.1	1625.0
(—)	$\hat{U}$	—	—	205.7	308.7	412.1	620.8	834.4	1057.0	1297.5	1585.0
	$\hat{V}$	—	—	0.00100	0.00101	0.00103	0.00108	0.00113	0.00122	0.00135	0.00160
300	$\hat{H}$	—	—	235.0	338.1	441.6	650.9	865.2	1088.4	1328.7	1609.9
(—)	$\hat{U}$	—	—	205.0	307.7	410.8	618.7	831.3	1052.1	1288.7	1563.3
	$\hat{V}$	—	—	0.0009990	0.00101	0.00103	0.00107	0.00113	0.00121	0.00133	0.00155
500	$\hat{H}$	—	—	251.9	354.2	456.8	664.1	875.4	1093.6	1323.7	1576.3
(—)	$\hat{U}$	—	—	202.4	304.0	405.8	611.0	819.7	1034.3	1259.3	1504.1
	$\hat{V}$	—	—	0.0009911	0.00100	0.00102	0.00106	0.00111	0.00119	0.00129	0.00144
1000	$\hat{H}$	—	—	293.9	394.3	495.1	698.0	903.5	1113.0	1328.7	1550.5
(—)	$\hat{U}$	—	—	196.5	295.7	395.1	594.4	795.3	999.0	1207.1	1419.0
	$\hat{V}$	—	—	0.0009737	0.0009852	0.001000	0.00104	0.00108	0.00114	0.00122	0.00131

[a]Adapted from R. W. Haywood, *Thermodynamic Tables in SI (Metric) Units,* Cambridge University Press, London, 1968. Water is a liquid in the enclosed region between 50°C and 350°C. $\hat{H}$ = specific enthalpy (kJ/kg), $\hat{U}$ = specific internal energy (kJ/kg), $\hat{V}$ = specific volume (m^3/kg). *Note:* kJ/kg × 0.4303 = Btu/lb_m.

(*continued*)

TABLE B.7 (*Continued*)

P(bar) ($T_{sat.}$°C)		Temperature (°C)→ 400	450	500	550	600	650	700	750
0.0	$\hat{H}$	3280	3384	3497	3597	3706	3816	3929	4043
(—)	$\hat{U}$	2969	3050	3132	3217	3303	3390	3480	3591
	$\hat{V}$	—	—	—	—	—	—	—	—
0.1	$\hat{H}$	3280	3384	3489	3596	3706	3816	3929	4043
(45.8)	$\hat{U}$	2969	3050	3132	3217	3303	3390	3480	3571
	$\hat{V}$	21.1	33.3	35.7	38.0	40.3	42.6	44.8	47.2
0.5	$\hat{H}$	3279	3383	3489	3596	3705	3816	3929	4043
(81.3)	$\hat{U}$	2969	3049	3132	3216	3302	3390	3480	3571
	$\hat{V}$	6.21	6.67	7.14	7.58	8.06	8.55	9.01	9.43
1.0	$\hat{H}$	3278	3382	3488	3596	3705	3816	3928	4042
(99.6)	$\hat{U}$	2968	3049	3132	3216	3302	3390	3479	3570
	$\hat{V}$	3.11	3.33	3.57	3.80	4.03	4.26	4.48	4.72
5.0	$\hat{H}$	3272	3379	3484	3592	3702	3813	3926	4040
(151.8)	$\hat{U}$	2964	3045	3128	3213	3300	3388	3477	3569
	$\hat{V}$	0.617	0.664	0.711	0.758	0.804	0.850	0.897	0.943
10	$\hat{H}$	3264	3371	3478	3587	3697	3809	3923	4038
(179.9)	$\hat{U}$	2958	3041	3124	3210	3296	3385	3475	3567
	$\hat{V}$	0.307	0.330	0.353	0.377	0.402	0.424	0.448	0.472
20	$\hat{H}$	3249	3358	3467	3578	3689	3802	3916	4032
(212.4)	$\hat{U}$	2946	3031	3115	3202	3290	3379	3470	3562
	$\hat{V}$	0.151	0.163	0.175	0.188	0.200	0.211	0.223	0.235
40	$\hat{H}$	3216	3331	3445	3559	3673	3788	3904	4021
(250.3)	$\hat{U}$	2922	3011	3100	3188	3278	3368	3460	3554
	$\hat{V}$	0.0734	0.0799	0.0864	0.0926	0.0987	0.105	0.111	0.117
60	$\hat{H}$	3180	3303	3422	3539	3657	3774	3892	4011
(275.6)	$\hat{U}$	2896	2991	3083	3174	3265	3357	3451	3545
	$\hat{V}$	0.0474	0.0521	0.0566	0.0609	0.0652	0.0693	0.0735	0.0776
80	$\hat{H}$	3142	3274	3399	3520	3640	3759	3879	4000
(295.0)	$\hat{U}$	2867	2969	3065	3159	3252	3346	3441	3537
	$\hat{V}$	0.0344	0.0382	0.0417	0.0450	0.0483	0.0515	0.0547	0.0578
100	$\hat{H}$	3100	3244	3375	3500	3623	3745	3867	3989
(311.0)	$\hat{U}$	2836	2946	3047	3144	3240	3335	3431	3528
	$\hat{V}$	0.0264	0.0298	0.0328	0.0356	0.0383	0.0410	0.0435	0.0461
150	$\hat{H}$	2975	3160	3311	3448	3580	3708	3835	3962
(342.1)	$\hat{U}$	2744	2883	2999	3105	3207	3307	3407	3507
	$\hat{V}$	0.0157	0.0185	0.0208	0.0229	0.0249	0.0267	0.0286	0.0304
200	$\hat{H}$	2820	3064	3241	3394	3536	3671	3804	3935
(365.7)	$\hat{U}$	2622	2810	2946	3063	3172	3278	3382	3485
	$\hat{V}$	0.009950	0.0127	0.0148	0.0166	0.0182	0.197	0.211	0.0225
221.2(P_c)	$\hat{H}$	2733	3020	3210	3370	3516	3655	3790	3923
(374.15)(T_c)	$\hat{U}$	2553	2776	2922	3045	3157	3265	3371	3476
	$\hat{V}$	0.008157	0.0110	0.0130	0.0147	0.0162	0.0176	0.0190	0.0202
250	$\hat{H}$	2582	2954	3166	3337	3490	3633	3772	3908
(—)	$\hat{U}$	2432	2725	2888	3019	3137	3248	3356	3463
	$\hat{V}$	0.006013	0.009174	0.0111	0.0127	0.0141	0.0143	0.0166	0.0178
300	$\hat{H}$	2162	2826	3085	3277	3443	3595	3740	3880
(—)	$\hat{U}$	2077	2623	2825	2972	3100	3218	3330	3441
	$\hat{V}$	0.002830	0.006734	0.008680	0.0102	0.0114	0.0126	0.0136	0.0147
500	$\hat{H}$	1878	2293	2723	3021	3248	3439	3610	3771
(—)	$\hat{U}$	1791	2169	2529	2765	2946	3091	3224	3350
	$\hat{V}$	0.001726	0.002491	0.003882	0.005112	0.006112	0.007000	0.007722	0.008418
1000	$\hat{H}$	1798	2051	2316	2594	2857	3105	3324	3526
(—)	$\hat{U}$	1653	1888	2127	2369	2591	2795	2971	3131
	$\hat{V}$	0.001446	0.001628	0.001893	0.002246	0.002668	0.003106	0.003536	0.003953

TABLE B.8 Specific Enthalpies of Selected Gases: SI Units

$\hat{H}$(kJ/mol)
Reference state: Gas, P_{ref} = 1 atm, T_{ref} = 25°C

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
0	−0.72	−0.73	−0.73	−0.72	−0.73	−0.92	−0.84
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	2.19	2.24	2.19	2.16	2.19	2.90	2.54
200	5.15	5.31	5.13	5.06	5.16	7.08	6.01
300	8.17	8.47	8.12	7.96	8.17	11.58	9.57
400	11.24	11.72	11.15	10.89	11.25	16.35	13.23
500	14.37	15.03	14.24	13.83	14.38	21.34	17.01
600	17.55	18.41	17.39	16.81	17.57	26.53	20.91
700	20.80	21.86	20.59	19.81	20.82	31.88	24.92
800	24.10	25.35	23.86	22.85	24.13	37.36	29.05
900	27.46	28.89	27.19	25.93	27.49	42.94	33.32
1000	30.86	32.47	30.56	29.04	30.91	48.60	37.69
1100	34.31	36.07	33.99	32.19	34.37	54.33	42.18
1200	37.81	39.70	37.46	35.39	37.87	60.14	46.78
1300	41.34	43.38	40.97	38.62	41.40	65.98	51.47
1400	44.89	47.07	44.51	41.90	44.95	71.89	56.25
1500	48.45	50.77	48.06	45.22	48.51	77.84	61.09

TABLE B.9 Specific Enthalpies of Selected Gases: U.S. Customary Units

$\hat{H}$(Btu/lb-mole)
Reference state: Gas, P_{ref} = 1 atm, T_{ref} = 77°F

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
32	−312	−315	−312	−310	−312	−394	−361
77	0	0	0	0	0	0	0
100	160	162	160	159	160	206	185
200	858	875	857	848	859	1132	996
300	1563	1602	1558	1539	1564	2108	1818
400	2275	2342	2265	2231	2276	3129	2652
500	2993	3094	2976	2925	2994	4192	3499
600	3719	3858	3694	3621	3720	5293	4359
700	4451	4633	4418	4319	4454	6429	5233
800	5192	5418	5150	5021	5195	7599	6122
900	5940	6212	5889	5725	5945	8790	7025
1000	6695	7015	6635	6433	6702	10015	7944
1100	7459	7826	7399	7145	7467	11263	8880
1200	8230	8645	8151	7861	8239	12533	9831
1300	9010	9471	8922	8581	9021	13820	10799
1400	9797	10304	9699	9306	9809	15122	11783
1500	10590	11142	10485	10035	10606	16436	12783
1600	11392	11988	11278	10769	11409	17773	13798
1700	12200	12836	12080	11509	12220	19119	14831
1800	13016	13691	12888	12254	13036	20469	15877
1900	13837	14551	13702	13003	13858	21840	16941
2000	14663	15415	14524	13759	14688	23211	18019

TABLE B.10 Atomic Heat Capacities for Kopp's Rule[a]

	C_{pa}[J/(g-atom·°C)]	
Element	Solids	Liquids
C	7.5	12
H	9.6	18
B	11	20
Si	16	24
O	17	25
F	21	29
P	23	31
S	26	31
All Others	26	33

[a]D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, Prentice-Hall, Englewood Cliffs, NJ, 1974, p. 270.

TABLE B.11 Integral Heats of Solution and Mixing at 25°C[a]

r(mol H_2O/mol solute)	$(\Delta\hat{H}_s)_{HCl(g)}$ kJ/mol HCl	$(\Delta\hat{H}_s)_{NaOH(s)}$ kJ/mol NaOH	$(\Delta\hat{H}_m)_{H_2SO_4}$ kJ/mol H_2SO_4
0.5	—	—	−15.73
1	−26.22	—	−28.07
1.5	—	—	−36.90
2	−48.82	—	−41.92
3	−56.85	−28.87	−48.99
4	−61.20	−34.43	−54.06
5	−64.05	−37.74	−58.03
10	−69.49	−42.51	−67.03
20	−71.78	−42.84	—
25	—	—	−72.30
30	−72.59	−42.72	—
40	−73.00	−42.59	—
50	−73.26	−42.51	−73.34
100	−73.85	−42.34	−73.97
200	−74.20	−42.26	—
500	−74.52	−42.38	−76.73
1 000	−74.68	−42.47	−78.57
2 000	−74.82	−42.55	—
5 000	−74.93	−42.68	−84.43
10 000	−74.99	−42.72	−87.07
50 000	−75.08	−42.80	—
100 000	−75.10	—	−93.64
500 000	—	—	−95.31
∞	−75.14	−42.89	−96.19

[a]Adapted from J. C. Whitwell and R. K. Toner, *Conservation of Mass and Energy*, pp. 344–346. Copyright © 1969 by McGraw-Hill, Inc. Used with permission of McGraw-Hill.

Answers to Test Yourselves

p. 7

1. A ratio of equivalent values of a quantity expressed in different units.
2. $(60\text{ s})/(1\text{ min})$
3. $(1\text{ min}^2)/(3600\text{ s}^2)$
4. $(1\text{ m}^3)/(10^6\text{ cm}^3)$

p. 9

1. **(a)** $(1000\text{ mm})/(1\text{ m})$; **(b)** $(10^{-9}\text{ s})/(1\text{ ns})$; **(c)** $(1\text{ m}^2)/(10^4\text{ cm}^2)$; **(d)** $(1\text{ m}^3)/(35.3145\text{ ft}^3)$; **(e)** $(9.486 \times 10^{-4}\text{ Btu/s})/(1.341 \times 10^{-3}\text{ hp})$
2. m/s; cm/s; ft/s

p. 11

1. 2 N; $(2/32.174)\text{ lb}_\text{f}$
2. No
3. 1 kg; same; less
4. 2 lb_m; same; less

p. 13

1. **(a)** 1.22×10^4 (3 s.f.); **(b)** 1.22000×10^4 (6 s.f.); **(c)** 3.040×10^{-3} (4 s.f.)
2. **(a)** 134,000 (3 s.f.); **(b)** 0.01340 (4 s.f.); **(c)** 4200 (3 s.f.)
3. **(a)** 3 s.f.; **(b)** 2 s.f.; **(c)** 3 s.f., 11.2; **(d)** 2 s.f., 12
4. **(a)** 1460; **(b)** 13.4; **(c)** 1.76×10^{-7}
5. **(a)** 4.25–4.35; **(b)** 4.295–4.305; **(c)** $2.7775 \times 10^{-3} - 2.7785 \times 10^{-3}$; **(d)** 2450–2550; **(e)** 2499.5–2500.5

p. 16

1. Breakdowns, routine or unplanned shutdowns, or installing new equipment in the second week. (Many other possibilities exist.)
2. 35.5 or 35 batches/week.
3. 40 batches/week. The second week was clearly abnormal and shouldn't influence the prediction.

p. 18

(a) $\overline{V} = 237.4\text{ cm}^3/\text{s}$, range $= 21\text{ cm}^3/\text{s}$, $s_V^2 = 66.3\text{ cm}^6/\text{s}^2$, $s_V = 8.1\text{ cm}^3/\text{s}$
(b) $\dot{V} = 237.4\text{ cm}^3/\text{s} \pm 16.2\text{ cm}^3/\text{s}$

p. 21

1. All additive terms have the same dimensions. No. Yes.
2. $\text{m}^{-2} \cdot \text{s}^{-2}$
3. A multiplicative combination of factors with no net units; st^2/r or r/st^2.
4. $a(\text{lb}_\text{f})$; Q is dimensionless.

p. 22

1. Substitute in Equation 2.7-1.
2. Correct; too high; too low; too low.

p. 26

1. $y = a(x^2 - 2)$
2. **(b)** Plot $1/y$ versus $(x-3)^2$: a = slope, b = intercept.
(c) Plot y^3 versus x^2; a = slope, $b = -$intercept.
(d) Plot $\sqrt{x/\sin y}$ versus x: a = slope, b = intercept.
(e) Plot $\ln y$ versus x: $b = \ln(y_2/y_1)/(x_2 - x_1)$, $\ln a = \ln y_1 - bx_1$, $a = e^{\ln a}$.
(f) Plot $\ln y$ versus $\ln x$: $b = \ln(y_2/y_1)/\ln(x_2/x_1)$, $\ln a = \ln y_1 - b \ln x_1$, $a = e^{\ln a}$.

p. 29

1. **(a)** $P = at + b$; **(b)** $P = ae^{bt}$; **(c)** $P = at^b$; **(d)** $y^2 = 3 + a \exp(b/x^2)$; **(e)** $1/F = a(t^2 - 4)^b$.
2. **(a)** P versus t on semilog paper; **(b)** P versus t on log paper; **(c)** P^2 versus t^3 on semilog paper; **(d)** $1/P$ (or P) versus $(t-4)$ on log paper.

p. 47

1. Dimensionless.
2. 0.50 g/cm^3; $2.0\text{ cm}^3/\text{g}$; $31\text{ lb}_\text{m}/\text{ft}^3$; 1.5 g; 36 cm^3
3. Yes.
4. No—possibly different reference densities used for each.
5. $\rho_{H_2O(s)} < \rho_{H_2O(l)}$; $\rho_{NBA(s)} > \rho_{NBA(l)}$
6. When T rises, the mercury in the thermometer expands. At higher temperatures the same mass thus occupies a greater volume, meaning that the density of mercury $(= m/V)$ *decreases*.

p. 49

1. $10.0\text{ cm}^3/\text{s}$
2. 159.5 g/min
3. Same; same; greater at outlet.

p. 50

1. 100 mL/min; 100 g/min
2. Flowmeters—see Figure 3.2-1.
3. Too low (the gas is much less dense, so it must flow at a much higher rate than the liquid to raise the float to the same position).

p. 52

1. **(a)** 6.02×10^{23} molecules; **(b)** M grams

2. The molecular weight of the species expressed in tons.
3. **(a)** 1 lb-mole, 2 lb_m
   (b) 2 lb-moles, 2 lb_m
4. 2000
5. 50×10^3 mol/h
6. 1.4×10^{-4} mol

p. 55

1. **(a)** 80/81; **(b)** 0.5
2. 0.25 lb_m A/lb_m; 0.75 lb_m B/lb_m; 0.333 mole A/mole; 0.667 mole B/mole; 100 lb_m A/min; 100 lb-moles B/min; 400 lb_m/min; 150 lb-moles/min

p. 56

1. n/V (mol/L)
2. nM/V (g/L)
3. $(20/C_A)$ (L)
4. $(120\, c_A)$ g/h

p. 57

1. 68×10^{-6} kg creatinine/kg blood (or g/g or lb_m/lb_m)
2. 68 mg creatinine
3. 0.0721 g creatinine/L blood (blood density = 1060 kg/m^3)

p. 59

1. See Figures 3.4-1 and 3.4-2 and Equation 3.4-2.
2. The fluid pressure is higher at the bottom than at the top (hydrostatic head effect). No. Maybe. Yes. (The answers depend on how large the tank is.)
3. No. Convert 1300 mm Hg to (say) dynes/cm^2, then multiply by 4 cm^2 to calculate F(dynes).
4. 79 mm Hg

p. 60

1. No
2. Pressure relative to a vacuum; pressure relative to atmospheric pressure.
3. 735 mm Hg (absolute); 20 mm Hg of vacuum.
4. 4 inches Hg; 33.9 inches Hg

p. 63

1. See Figure 3.4-3; 0–7000 atm; gauge.
2. See Figure 3.4-4.
3. **(a)** True; **(b)** true; **(c)** false
4. −14 mm Hg

p. 65

1. Immerse in ice–water mixture, mark mercury level as 0°. Immerse in boiling water, mark level as 100°. Divide 0 to 100 interval into 100 equal subintervals, label appropriately.
2. 1°C
3. 1°C

p. 92

1. Semibatch, transient
2. Batch, transient
3. Semibatch, transient
4. **(a)** Continuous, transient;
   (b) continuous, steady state

p. 97

3. Steady-state, either no reactions or no net mole change on reaction (e.g., A → B but not A → 2B or A + B → C).
4. Steady-state, A is nonreactive.
5. Steady-state, no density change from inlet to outlet. (Good approximation for liquids and solids, effectively requires no reactions and constant temperature and pressure for gases.)

p. 101

2. $\dot{m}_T = 250(1 - x)/60$
3. $n = (75)(1.595)/(154)$
4. $\dot{m} = 50 + \dot{m}_{dg}$; $\dot{m}_{co} = 0.25\dot{m}_{dg}$; $y = 0.75\dot{m}_{dg}/(50 + \dot{m}_{dg})$

p. 104

1. $(\text{atoms})_{in} = (\text{atoms})_{out}$ for each atomic species; multiply all stream amounts by a constant factor; an assumed amount of an input or output stream.
2. **(a)** Flow rates are 1000, 20,000, and 21,000 (all kmol/h), mole fractions are unchanged.
   (b) Flow rates are 200, 100, and 100 (all lb_m/min), mass fractions are unchanged.

p. 107

1. H_2: $(5\,lb_m)_{in} = (1\,lb_m + 4\,lb_m)_{out}$; O_2: $(5\,lb_m)_{in} = (4\,lb_m + 1\,lb_m)_{out}$; total mass: $(10\,lb_m)_{in} = (10\,lb_m)_{out}$.
2. Balance on B, solve for $\dot{m}_1$; balance on C, solve for x; total mass balance, solve for $\dot{m}_2$.

p. 130

1. Yes
2. 4
3. (4 moles H_2O produced)/(6 moles O_2 consumed)
4. (400)(6)/(4) = 600
5. 200 mol/min

p. 134

1. C_2H_4
2. 100%
3. 50 kmol O_2; 100 kmol C_2H_4O; 50 kmol
4. 50 kmol C_2H_4; 75 kmol O_2; 50 kmol C_2H_4O; 25 kmol
5. 0.80; 0.40; 40 kmol

p. 140

1. 0.90
2. 80%
3. 16 mol B/mol C
4. 80 mol, 10 mol

p. 143

1. Three independent molecular species (C_2H_4, C_4H_8, N_2). Two independent atomic species (N and either C or H).

2. **(a)** $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
(b) $CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$
(c) $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$
(d) $C_2H_6 + \frac{5}{2}O_2 \rightarrow 2CO + 3H_2O$
Since (b) can be obtained as (a) $- \frac{1}{2}$[(c) − (d)] (*verify*), the four equations are not independent.

p. 150

1. 60 mol; 0.60
2. 120 mol; 0.48
3. 40 mol CH_4 = 100 mol $CH_4 - \xi \Rightarrow \xi = 60$ mol
130 mol O_2 = 250 mol $O_2 - 2\xi \Rightarrow \xi = 60$ mol
60 mol CO_2 = 0 mol $O_2 + \xi \Rightarrow \xi = 60$ mol
4. Four molecular species balances (CH_4, O_2, CO_2, H_2O). Three atomic species balances (C, H, O).
5. **(b)** I = O. (250)(2) mol O in = [(130)(2) + (60)(2) + (120)(1)] mol O out
(c) I = O + C. 250 mol O_2 in = 130 mol O_2 out + 120 mol O_2 consumed
(d) G = O. 120 mol H_2O generated = 120 mol H_2O out
(e) I = O. (100)(4) mol H in = [(40)(4) + (120)(2)] mol H out

p. 151

1. Overall = 100/110 = 0.909 mol A consumed/mol A fed; single pass = 100/200 = 0.500 mol A consumed/mol A fed.

p. 154

1. Overall conversion = 0.833 (83.3%), single-pass conversion = 0.25 (25%).
2. Customers want B, not a mixture that contains mostly A. Makes no sense to pay for 200 mol of A (fresh feed) and then discard 140 mol of it.
3. C would keep building up in the system. Take off a purge stream from the recycle.
4. The cost of the reactor that would be required to achieve an 83.3% conversion in a single pass could be much greater than the cost of the separation and recycle equipment.

p. 163

1. 21% O_2, 79% N_2; 79/21 = 3.76 moles N_2/mole O_2
2. 25% H_2, 25% O_2, 50% H_2O; 50% H_2, 50% O_2
3. 20; 0.95; 5/95 = 0.0526

p. 164

1. 200 mol O_2/h
2. 200 mol O_2/h
3. (4.76 × 200) mol air/h
4. (2 × 4.76 × 200) mol air/h
5. 50%

p. 219

1. 255 cm^3/s. If T is raised, mass flow rate remains constant but volumetric flow rate increases slightly. Look up the density of liquid water at 75°C and divide it into 255 g/s.
2. $P_h = \rho g h$, and ρ_{Hg} varies with temperature. The difference would be extremely slight.
3. $V_{tot} = \frac{m_1}{\rho_1} + \frac{m_2}{\rho_2} + \cdots + \frac{m_n}{\rho_n}$;
$\frac{1}{\rho} = \frac{V_{tot}}{m_{tot}} = \frac{m_1}{m_{tot}\rho_1} + \frac{m_2}{m_{tot}\rho_2} + \cdots = \frac{x_1}{\rho_1} + \frac{x_2}{\rho_2} + \cdots$

p. 222

1. A relation between absolute pressure, specific volume, and absolute temperature of a substance. $P\hat{V} = RT$. High T, low P.
2. (c), (e). The mass and mass density of CO_2 are each greater by a factor $(MW_{CO_2}/MW_{H_2}) = 22$.
3. (a) and (c).

$$\dot{V} = \frac{\dot{n}RT}{P} = \frac{\dot{m}}{MW}\frac{RT}{P}$$

Let E denote ethylene and B denote butene. $MW_B = 2MW_E \Rightarrow \dot{V}_E = 2\dot{V}_B$.
$\hat{V} = RT/P$, which is the same for B and E.
Mass density: $\rho = \dot{m}/\dot{V} = (MW)P/RT \Rightarrow \rho_B = 2\rho_E$
4. RT/P = [0.08206 L·atm/(mol·K)](200 K)/(20 atm) = 0.8206 L/mol < 5 L/mol. From Equation 5.2-3, the error is likely to be greater than 1%.

p. 225

1. See Table 5.2-1.
2. $V_{new} = V_{old}/2$; $V_{new} = 2V_{old}$
3. Decreases (n is unchanged, V increases); nothing
4. (a)

p. 226

1. (b), (d)
2. 5 bar; 50 m^3; p_{H_2} increases, v_{H_2} is unchanged.
3. Greater than

p. 229

1. Vapor
2. **(a)** $P_a < P_b$; **(b)** ρ_{va}?ρ_{vb}; **(c)** $\rho_{la} > \rho_{lb}$
3. Gas. Supercritical fluid.

p. 235

1. The equation to determine $\hat{V}$ for given values of T and P is a cubic equation.
2. Critical temperature and pressure (Table B.1), Pitzer acentric factor (Table 5.3-1).
3. (b), (a), (c)

p. 240

1. No; $T_r = (-190 + 273.2)/(T_c + 8)$, look up z on charts, calculate $V = znRT/P$.
2. Need a different chart for each species.
3. The law of corresponding states says that the values of certain physical properties of a gas depend on the proximity of the gas to its critical state. This suggests that a plot of z versus T_r and P_r should be approximately the same for all substances (the generalized compressibility chart).

p. 241

See Example 5.4-2. Nonpolar compounds with similar critical properties.

p. 274

1. Distillation. The naphthas come off from the top of the column, the lubricating oils from the bottom, and the heating oils from the middle.
2. Evaporation, filtration, centrifugation
3. Evaporation, reverse osmosis (membrane filtration at high pressure)
4. Condensation, absorption;
5. Adsorption.

p. 279

1. −5°C, 3 mm Hg
2. −56.6°C, 5.112 atm
3. All CO_2 solidifies at 1 atm, solid melts at 9.9 atm, and −56°C, liquid boils at 9.9 atm and −40°C.
4. 1 atm; 9.9 atm
5. −78.5°C; −56°C, −40°C;
6. No

p. 282

1. **(a)** 1304.063 mm Hg; **(b)** 1304.063 mm Hg
2. (i) look up T_b for benzene in Table B.1; (ii) using the Antoine equation for benzene, solve for T_b given $p^* = 760$ mm Hg; (iii) use the function AntoineT for benzene in APEx.
3. Plot p^* versus $1/T_{absolute}$ on semilog paper, draw line through points, and extrapolate to $1/T_4$.

p. 283

1. Eq. 6.2-1
2. **(a)** 2; **(b)** 2; **(c)** 4; **(d)** 3

p. 287

1. Yes; yes.
2. 200 mm Hg; 600 mm Hg; 200/960; look up or calculate the temperature at which $p^*_{acetone} = 960$ mm Hg.
3. **(a)** The temperature to which a gas must be cooled before any constituent condenses; superheated, saturated.
   (b) $y_{H_2O} = p^*_{H_2O}(T_0)/P_0$ (i) nothing; (ii) condense; (iii) condense; (iv) nothing
   (c) $p^*_{H_2O}(T_{dp}) = y_{H_2O}P_0$. Look up the temperature at which the vapor pressure is $p^*_{H_2O}$.
   (d) $T_{dp} = T_0 - T_{sh}$; $y_{H_2O} = p^*_{H_2O}(T_{dp})/P_0$.

p. 289

1. 82°C
2. 50%
3. $s_m = 0.111$, $s_p = 44.4\%$

p. 293

1. Raoult's law: $p_A = x_A p^*_A$, where x_A is the mole fraction of A in the liquid phase; most likely to be valid as $x_A \to 1.0$.
2. Henry's law: $p_A = x_A H_A$; most likely to be valid when $x_A \to 0$.
3. A solution for which either Raoult's law or Henry's law is obeyed for all species at all solution compositions.
4. Henry's law for x_{CO_2} and p_{CO_2}, Raoult's law for x_{H_2O} and p_{H_2O}. Look up Henry's law constant for CO_2 (*Perry's Chemical Engineers' Handbook*, 8th Edition, p. 2-130 to 2-133) and vapor pressure of H_2O (Table B.3 of this book).
5. When the can is opened, P immediately decreases to atmospheric pressure. At the lower pressure, CO_2 is less soluble in the liquid, and so bubbles of CO_2 emerge. As the concentration of dissolved CO_2 (x_{CO_2}) approaches its equilibrium value, the bubbling slows down. Over a longer time period, the can warms up and the mole fraction of CO_2 in the gas above the liquid decreases as the gas mixes with air. Both of these phenomena decrease the solubility of CO_2 even more, and bubbles continue to emerge. Eventually y_{CO_2} is close to zero, almost no dissolved CO_2 remains in the liquid, and the soda goes flat.

p. 299

1. The temperature at which the first bubble of vapor forms if the liquid is heated at the given pressure. The temperature at which the first drop of liquid forms if the vapor mixture is cooled at the given pressure.
2. 92°C; 0.70 mol benzene/mol (from Figure 6.4-1*a*)
3. 99°C; 0.30 mol benzene/mol (from Figure 6.4-1*a*); decreases
4. Increase (see Equation 6.4-4); increase (see Equation 6.4-6)
5. The hydrostatic head of the liquid must be added to the pressure at the liquid surface. Convert 5 ft of water to atm, add it to 1 atm, and look up the boiling point of water at the corrected pressure.
6. The nonlinear equations cannot be solved explicitly for I.

p. 303

1. 380 g. The added salt will not remain undissolved.
2. 55°C. Increasing quantities of KNO_3 crystals precipitate (come out of solution).
3. See Table 6.5-1. Magnesium sulfate tetrahydrate.
4. 120.4/138.4 = 0.870
5. Above 40°C the crystals that precipitate are hydrated salts.

p. 306

1. A solution property that depends only on concentration, and not what the solute and solvent are. Vapor pressure, boiling point, and freezing point.
2. 850 mm Hg. Solute is nonvolatile, nondissociative, and nonreactive with the solvent; Raoult's law holds.
3. Greater. $p^* = (1000 \text{ mm Hg})/0.85 = 1176$ mm Hg.
4. It lowers the freezing point of water, so it keeps ice from forming at temperatures where it would otherwise form.
5. Antifreeze lowers the freezing point and raises the boiling point of water, so the radiator is less likely to freeze in winter and to boil in summer.

p. 308

1. Given A and S, two nearly immiscible liquids, and B, a solute distributed between the phases of an A-S mixture, the distribution coefficient of component B is the ratio of the mass fraction of B in the S phase to that in the A phase. Extraction is transference of a solute from one liquid solvent to another.
2. Less soluble; $m_{VA} \gg m_W$

p. 310

1. A tie line connects compositions of two phases in equilibrium.
2. H_2O-rich phase—95.0% H_2O, 2.5% acetone, 2.5% MIBK; MIBK-rich phase—92.5% MIBK, 2.5% H_2O, 5.0% acetone.

Mass ratio of MIBK phase to H_2O

$$\text{phase} = \frac{0.950 - 0.450}{0.450 - 0.025} = 1.18.$$

p. 314

1. In absorption a gas species dissolves in a liquid; in adsorption a gas or liquid species adheres to the surface of a solid.
2. An adsorbate is a species adhering to the surface of a solid adsorbent.
3. Concentration equals partial pressure times a constant (and vice versa).
4. Toxic species in the air are adsorbed on the surface of the carbon. Nonactivated carbon has much less surface area so the mask would become saturated in much less time.

p. 358

1. Kinetic, potential, internal; heat, work
2. Heat is only defined in terms of energy being transferred.
3. $E_i + Q + W = E_f$

p. 360

1. The mass flow rates are the same; $\rho_{outlet} < \rho_{inlet}$; $V_{outlet} > V_{inlet}$.
2. $\Delta E_p > 0$, $\Delta E_k > 0$

p. 361

1. Closed system: no mass crosses system boundaries. Open system: mass crosses system boundaries. Adiabatic system: no heat transferred to or from system.
2. $Q = 250\,\text{J}$
   $W = -250\,\text{J}$
3. $\Delta U = -50\,\text{kcal}$
4. If the substance is a liquid or a solid, or a gas under nearly ideal conditions, it is reasonable to neglect the dependence of U on pressure.

p. 363

1. $\dot{V}_{in} = \dot{V}_{out}$
2. $P_{in} > P_{out}$

p. 364

1. 6000 cal
2. 1000 cal/min
3. The specific volume and pressure: $\hat{H} = \hat{U} + P\hat{V}$

p. 366

1. $\dot{W}_s = 0$
2. $\dot{Q} = 0$
3. $\Delta\dot{E}_k = 0$
4. $\Delta\dot{E}_p = 0$

p. 369

1. A property whose change of value in any process depends only on its initial and final states and not on the path between them.
2. **(a)** 0;
   (b) 5000 J/kg;
   (c) $\Delta\hat{H} = \hat{H}_A(\text{v}, 0°\text{C}, 1\text{ atm}) - \hat{H}_A(\text{v}, 30°\text{C}, 1\text{ atm})$
   $= (5000\,\text{J/kg} - 7500\,\text{J/kg}) = -2500\,\text{J/kg}$
   (d) No—$\hat{H}$ is a state property.

p. 379

1. Incompressible fluid, negligible heat transfer, and no internal energy changes due to anything but friction.
2. Above, plus no friction or shaft work.

p. 404

$\hat{H} = -2751\,\text{kJ/kg}$. $\hat{U} = -2489\,\text{kJ/kg}$.

p. 406

2. Lower P isothermally to 1 atm, cool at 1 atm to 80.7°C, condense at 80.7°C and 1 atm, cool liquid at 1 atm to 25°C, raise pressure to 5 atm.
3. Keeping pressure constant at 1 atm, cool water to 25°C, dissolve NaOH in water at 25°C, raise solution to 50°C.
4. Keeping pressure constant at 1 atm, cool O_2 to 25°C, mix O_2 and CH_4 at 25°C, carry out reaction at 25°C, raise product gas to 300°C.

p. 412

1. **(a)** ii; **(b)** i; **(c)** iii
2. Determine z for C_2H_6 at each of the system conditions. If z is close to 1 for both states, it may be reasonable to neglect $\Delta\hat{H}$.

p. 414

1. $C_v = (\partial\hat{U}/\partial T)_v$,
   $C_p = (\partial\hat{H}/\partial T)_P$
2. **(a)** exact;
   (b) inaccurate;
   (c) good approximation
3. $\Delta H = (5\,\text{g})[0.5\,\text{cal/(g}\cdot°\text{C)}](20°\text{C}) = 50\,\text{cal}$

p. 418

1. 28.5 J/(mol·°C)
2. 5 cal/(mol·°C); 7 cal/(mol·°C)
3. **(a)** 22.44 kJ/mol;
   (b) −25.78 kJ/mol;
   (c) -2.22×10^5 Btu/h (Neglect pressure effects.)

p. 420

1. $CaCO_3(s)$: $C_p = 26 + 7.5 + 3(17) = 84.5\,\text{J/(mol}\cdot°\text{C)}$
2. $\Delta H = \{(2\,\text{kg})[2.5\,\text{kJ/(kg}\cdot°\text{C)}]$
   $+ (1\,\text{kg})(1.8\,\text{kJ/(kg}\cdot°\text{C)})\}(10°\text{C}) = 68\,\text{kJ}$
   $\Delta\hat{H} = 68\,\text{kJ}/3\,\text{kg} = 23\,\text{kJ/kg}$
3. $\Delta\hat{H} = 25\,\text{cal/g}$
4. $(C_p)_{mixture} = [(0.50)(1.00) + (0.50)(0.54)]\,\text{cal/g} = 0.77\,\text{cal/g}$

p. 428

1. Yes; no
2. **(a)** 0; **(b)** 900 J/mol
   (c) Cool the vapor to 75°C; condense at 75°C; cool the liquid to 25°C.
3. $\Delta\hat{U}_f \approx 5500\,\text{cal/mol}$
   $\Delta U_v = \Delta\hat{H}_v - |RT = 26{,}710\,\text{cal/mol}$

p. 430

1. Equation 8.4-3
2. Equation 8.4-4
3. From Equation 8.4-6, slope of line is $-\Delta\hat{H}_v/R$.
4. From Equation 8.4-7, slope of tangent to curve at $p^* = 1$ atm is $-\Delta\hat{H}_v/R$.
5. Equation 8.4-8
6. $\Delta\hat{H}_v(T_2) = \int_{T_2}^{T_1} C_{pl}dT + \Delta\hat{H}_v(T_1) + \int_{T_1}^{T_2} C_{pv}dT$

p. 439

Air at 25°C, $h_r = 20\% \Longrightarrow h_a = 0.0040$ kg H_2O/kg dry air; $T_{wb} = 12.5$°C; $T_{dp} = 0.5$°C; $\hat{V}_H = 0.85$ m^3/kg dry air, $\hat{H} = (35.00 - 0.27)$ kJ/kg dry air $= 34.73$ kJ/kg dry air

p. 443

1. **(a)** $(C_p)_{gas}$, $(C_p)_{liquid}$, and $(\Delta\hat{H}_v)_{liquid}$ are independent of temperature, and the enthalpy change of unevaporated liquid is small compared to the heat of vaporization and the enthalpy of the gas.
   (b) Yes; **(c)** no
2. $T_{as} = 11$°C; $h_a = 0.0069$ kg H_2O/kg dry air; $h_r = 70\%$; $\hat{H} = (31.60 - 0.06)$ kJ/kg dry air $= 31.54$ kJ/kg dry air

p. 445

1. **(a)** $\hat{H} = -40$ kJ/mol A; **(b)** $\hat{H} = 20$ kJ/mol A
2. $Q = \Delta H = (5)(-40)$ kJ $= -200$ kJ (evolved)
3. $Q = 5(-60 + 40)$ kJ $= -100$ kJ (evolved)

p. 450

1. -97 Btu/lb$_m$ solution
2. 77°F (the reference temperature for H_2SO_4)
3. 190°F. 65 wt% H_2SO_4. (Highest temperature on a line between the feed points.)
4. **(a)** -60 Btu/lb$_m$ solution. **(b)** 30 Btu/lb$_m$ solution. The heat of solution at 77°F (or the energy required to heat the solution from 77°F to its adiabatic mixing temperature of about 195°F).

p. 454

1. 130°F, 0.15
2. 600 Btu/lb$_m$
3. Vapor fraction $\approx (0.50 - 0.18)/(0.88 - 0.18) = 0.46$

p. 493

2. The second sentence is wrong and the first sentence is correct, but only if the reactants and products are at the same temperature. The energy released by the breaking of reactant bonds and forming of product bonds must be transferred from the reactor to keep the products at the same temperature; otherwise it remains in the reactor and raises the product temperature. If the reactor is adiabatic, the products at the higher temperature would be at the *same* energy level as the reactants at the lower temperature.

p. 499

1. $H_{products} - H_{reactants}$ when stoichiometric quantities of reactants are fed, the reaction proceeds to completion, and reactants and products are at the same temperature and pressure. As above, with reactants and products at 25°C and 1 atm.
2. **(a)** -20 kJ/mol A reacted; **(b)** exothermic; **(c)** withdrawn; **(d)** higher
3. The latent heat of vaporization of C_6H_{14} at 25°C and 1 atm
4. $\Delta U_r(T) = \Delta H_r(T) + 2RT$
5. $\Delta H_r = \sum_{\text{products}} |v_i|\hat{H}_i - \sum_{\text{reactants}} |v_i|\hat{H}_i$

   In general, $\hat{H}_i = \hat{U}_i + P\hat{V}_i$; for liquids and solids, $\hat{H}_i \approx \hat{U}_i$; and for ideal gases, $P\hat{V}_i = RT$, so that $\hat{H}_i = \hat{U}_i + RT$. To obtain the desired result, substitute for $\hat{H}_i$ in the expression for ΔH_r, and recognize that

$$\Delta U_r = \sum_{\text{products}} |v_i|\hat{U}_i - \sum_{\text{reactants}} |v_i|\hat{U}_i$$

p. 501

1. See last paragraph of Section 9.2.
2. Multiply Equation 2 by -2 and add the result to Equation 1

$$2A + B - 2A - 2D \rightarrow 2C - 2C - 6E$$
$$\Downarrow$$
$$B + 6E \rightarrow 2D,\ \Delta H_r = \Delta H_{r1} - 2\Delta H_{r2} = 3000 \text{ kJ}$$

p. 502

1. The formation reaction of CO is $C + \frac{1}{2}O_2 \rightarrow CO$, so the heat of formation is $-\frac{1}{2}$ times the heat of the given reaction, or -110.5 kJ/mol. (This checks with the value in Table B.1.)
2. The heat of vaporization of propane at 25°C.
3. $\Delta H_r^\circ = (\Delta\hat{H}_f^\circ)_{CO_2} + 2(\Delta\hat{H}_f^\circ)_{H_2O(v)} - (\Delta\hat{H}_f^\circ)_{CH_4}$

p. 519

1. **(a)** $\Delta\hat{H}_f^\circ(\text{soln}, n = 50) = (\Delta H_f)_A - 100 - 10$
   $= -110$ kJ/mol A
   (b) $\Delta\hat{H}_f^\circ(\text{soln}, n = \infty) = -115$ kJ/mol A
2. **(a)** $\hat{H}(25°C) = -110$ kJ/mol A
   (b) $H(25°C) = -550$ kJ

p. 521

1. $LHV = 2658$ kJ/mol
   $HHV = 2658$ kJ/mol $+ 5(44.013$ kJ/mol$)$
   $= 2878$ kJ/mol
2. $HHV = (0.40)(143$ kJ/g$) + (0.60)(55$ kJ/g$)$
   $= 90.2$ kJ/g
3. For coal:

$$(\$150/\text{ton})(1 \text{ lb}_m/15{,}000 \text{ Btu})(1 \text{ ton}/2000 \text{ lb}_m) = 5.0 \times 10^{-6} \$/\text{Btu}$$

   For natural gas:

$$x(\$/\text{ton})(1 \text{ ton}/2000 \text{ lb}_m)(1 \text{ lb}_m/23{,}000 \text{ Btu}) = 5.0 \times 10^{-6} \$/\text{Btu}$$
$$\Downarrow$$
$$x = \$230/\text{ton}$$

p. 524

1. The product temperature when the fuel is burned completely in an adiabatic reactor.
2. Heat loss through reactor walls, incomplete reaction.
3. With an air feed, the heat released from combustion of a fixed amount (say, 1 mol) of fuel goes into heating the nitrogen in the air as well as the reaction products and excess oxygen, whereas only the latter must be heated for a pure O_2 feed. If a fixed quantity of heat is added to a greater amount of material, the resulting temperature rise must be less.

p. 527

1. **(a)** Ignition—abrupt increase in the rate of an oxidation reaction.
   (b) Ignition temperature—the temperature at which ignition occurs when a combustible mixture is heated slowly.
   (c) Ignition lag—time between a mixture reaching its ignition temperature and the occurrence of ignition.
   (d) Flammability limits—composition limits outside of which ignition or explosion cannot occur.
   (e) Flash point of a liquid—temperature at which a liquid gives off enough vapor to form an ignitable mixture with the air above the liquid surface.
2. **(a)** An explosion or ignition; no reaction would occur.
   (b) Yes; the reaction would cease.
   (c) There is a region between the emerging jet (pure methane) and the bulk of the room air (almost no methane) within which the methane fraction falls between the flammability limits. The flame persists in this region.

p. 529

1. A flame is a combustion zone in which various species undergo transitions from states of high energy to states of lower energy. The energy lost in the transitions is given off as visible light.
2. In low-temperature flames, which occur when the fuel and oxygen are not well mixed, carbon particles are formed and remain unburned, but the heat in the reaction zone raises them to a temperature at which they glow incandescently. The result is a yellow flame. At higher combustion temperatures, various intermediate species are formed and excited to high-energy states, and emit blue light as they return to lower states. The result is a blue flame.
3. In a detonation, a pressure front (shock wave) forms and propagates at supersonic speed, rapidly compressing and igniting the flammable mixture and giving the appearance of an instantaneous combustion. In the vicinity of the detonation, the force of the shock wave can demolish a building or propel a bullet. The noise is the vibration of the eardrums caused by the shock wave.
4. The rate of the reaction depends strongly on temperature; at room temperature it is immeasurably low.

p. 575

1. **(a)** Accumulation, input, output (although the mass balance will yield the result that accumulation = 0);
   (b) all but generation;
   (c) accumulation, output, consumption
2. $dm/dt = 10\,\text{kg/h} - 10\,\text{kg/h} = 0\,\text{kg/h}$

p. 578

1. $$dy = (2-t)dt \implies \int_1^y dy = \int_0^t (2-t)\,dt$$
   $$\implies y = 1 + 2t - \frac{t^2}{2}$$
2. $$\frac{dy}{2-y} = dt \implies \int_1^y \frac{dy}{2-y} = \int_0^t dt$$
   $$\implies -\ln(2-y)\Big|_1^y = t$$
   $$\implies \ln\left(\frac{1}{2-y}\right) = t$$
   $$\implies \left(\frac{1}{2-y}\right) = e^t$$
   $$\implies y = 2 - e^{-t}$$
3. $$\frac{dy}{2-y} = (2-t)dt \implies \int_1^y \frac{dy}{2-y} = \int_0^t (2-t)\,dt$$
   $$\implies -\ln(2-y)\Big|_1^y = 2t - \frac{t^2}{2}$$
   $$\implies \ln\left(\frac{1}{2-y}\right) = 2t - \frac{t^2}{2}$$
   $$\implies \left(\frac{1}{2-y}\right) = \exp\left(2t - \frac{t^2}{2}\right)$$
   $$\implies y = 2 - \exp\left(-2t + \frac{t^2}{2}\right)$$

p. 587

1. Neglect changes in $\dot{E}_k$ and $\dot{E}_p$; no mass accumulation; $\hat{U}$ and $\hat{H}$ independent of P; no phase changes or chemical reactions; no spatial variations in T; constant C_v and C_p.
2. When the expression for U_{sys} is differentiated to yield Equation 10.3-9, if C_v varies with temperature (and hence with time) another term of the form $M(T_{sys} - T_r)(dC_v/dt)$ would have to be added.

p. 609

1. -1, $+2$
2. The line for which the sum of the squares of the residuals is a minimum.
3. Yes. (Corollary—no.)
4. Positive and negative deviations from the line would cancel out, possibly making a terrible fit look good.

p. 611

1. Linear
2. Nonlinear
3. Nonlinear
4. **(a)** Linear; **(b)** nonlinear
5. **(a)** Linear (multiply equation by z); **(b)** nonlinear; **(c)** linear

p. 612

1. A straight line on a plot of f versus x can only intersect the x axis at one point.

2. One root. (The intersection of a 45° line through the origin with a curve that begins at 1 when $x = 0$ and decreases, approaching 0 as x approaches infinity.)

p. 613

1. **(a)** $x = 4$ and $x = 0$; **(b)** $x_p = 15/4$; $x_n = 5$. Converge to $x = 4$.

2. The equation for a line on an f versus x plot through (x_n, f_n) and (x_p, f_p) is $f = f_n + [(f_p - f_n)/(x_p - x_n)](x - x_n)$. The intercept of this line on the x axis, which we will call x_{new}, is obtained by setting $f = 0$ and solving the resulting equation for x. The result is Equation A.2-1.

p. 616

1. Yes. No. You can solve for the roots directly.

2. The value of $f'(x_0)$ would be 0, and the correction term f/f' would blow up.

p. 617

1. **(a)** Modified successive substitution; **(b)** successive substitution; **(c)** acceleration

2. 13.6

p. 618

1. 2.60

2. A line on an f versus x plot through (2, 2.3) and (2.3, 2.45) intersects the 45° line at $x = 2.60$.

p. 626

1. 80

2. 84

3. 80. The function is cubic, so Simpson's rule is exact.

Answers to Selected Problems

CHAPTER 2

Problem	Selected Answers
2	**(c)** 7200 hp
4	7×10^{16} steps
6	4×10^{11} reports
8	**(a)** 3.15×10^{15} J/yr
10	6.6×10^{6} lb_f
12	1.2×10^{8} m^3
14	**(b)** 1.49 g/cm^3
16	**(b)** 124 kg
18	**(b)** $W = 3$ doozies on the moon
20	**(a)** 27, 23
22	**(a)** $s = 0.3$°C
26	1.5×10^{3}
28	**(a)** 0.888 m/s
30	**(b)** 1.13 g/cm^3
32	**(a)** 3.00 mol/L
34	**(c)** $C = 1250$
36	**(c)** $C_C = 502.25$ mol/L
38	**(c)** $y = 2/x$
40	**(b)** 110 kg H_2O/h
42	**(a)** $T = 9677.6\phi^{-1.19}$
44	**(c)** $V(m^3) = 1.00 \times 10^{-3}\exp(1.5 \times 10^{-7}t^2)$
46	**(b)** $G = 1.806 \times 10^{-3}$
48	**(b)** $y = 1.0065x$
50	**(c)** $C = 12.2$ g/L
52	**(c)** $k = 0.0063\ s^{-1}$

CHAPTER 3

Problem	Selected Answers
2	**(b)** 360 lb_m/ft^3
4	$P_{France} = \$154$
6	1.17
8	**(a)** 445 L
10	242 g
12	**(a)** the pond level falls
14	**(a)** 2.05 kg/L
16	**(c)** 0.29
18	**(a)** $x = 0.9956\ f - 0.0296$
20	**(f)** 1.44×10^{6} g C
22	**(b)** 13,617 lb_m/h
24	**(a)** $SG_{mud} = 2.05$
26	**(c)** 99.3%
28	She was wrong.

Problem	Selected Answers
30	$\dot{n}_C = 109$ lb-mol C/min
32	20,200 mol air/h
34	0.917 g/cm^3
38	**(c)** 93 s
40	**(b)** 76%
42	**(a)** 0.996
44	**(c)** 30.4 N/cm^2
48	$F = 2250$ lb_f
50	**(a)** 576 ft/s^2
52	**(a)** $(P_g)_{tap} = 245$ kPa
54	**(b)** $h = 7.58$ in
56	**(a)** (i) $R = 23.8$ cm
58	8.1 mm Hg
60	**(b)** 23 mm H_2O
62	**(c)** 1.80 mol/s
64	**(a)** 208°F
66	**(b)** $R = 49.3$
68	**(c)** $P_2 = 911.9$ mm Hg

CHAPTER 4

Problem	Selected Answers
2	**(c)** 0.015 L/s
4	**(c)** $y_B = 0.612$ mol B/mol
6	**(b)** $\dot{n}_v = 2.9$ kmol/h
8	**(a)** 3 independent balances
10	**(c)** 44 g/min
12	**(c)** 0.04 egg broken/egg
14	**(c)** $m_1 = 0.49$ lb_m strawberries
16	**(b)** $\dot{V}_E = 54{,}375$ L/d
18	**(b)** 0.176 mol CH_3OH/mol
20	**(b)** $n_{1CS2} = 19$ kmol/h
24	**(c)** $R = 65.5$
26	**(a)** 0.323 (kg H_2SO_4/kg solution)
28	**(e)** Max $x_w = 0.00177$
30	**(b)** 13.5 g of fabric
32	**(b)** $m_5 = 28.6$ kg product
34	**(b)** $D = 1.08$ m
36	**(c)** $x_4 = 0.245$ kg SO_2 absorbed/kg
38	Max. balances = 3 Overall
40	**(b)** Overall benzene recovery: 97%
42	**(c)** $x_B = 0.100$ mol B/mol
44	**(b)** $x_6 = 0.0154$ kg Cr/kg

Problem	Selected Answers
46	**(d)** bacteria ratio: 4.4
48	**(b)** yield = 0.118 kg oil/kg beans fed
50	**(a)** 3.17 lb_m Whizzo
52	**(b)** 33.3% excess C_2H_2
54	**(a)** 1 DOF
56	HBr is the limiting reactant.
58	**(b)** 3.67×10^3 kg CO_2/h
60	3.25 kmol/s
62	**(b)** 9 mol NH_3/day
64	**(b)** 0.688
66	**(e)** 0.324 mol A reacted/mol A fed
68	**(c)** Fractional yield = 0.877
70	147 acres of land
72	0.0129 kg air/kg coal
74	**(c)** $\xi_1 = 0.0593$
76	**(a)** single-pass conversion of CO: 25.07%
78	**(c)** $n_{O2} = 37.8$ lb-mol O_2/h
80	**(a)** Overall CO conversion: 76%
82	Product: 173.5 kmol C_8H_{18}/h
84	**(b)** 68.41 kmol air/h
86	1365 mol air/h
90	**(a)** 16.5% excess O_2
92	**(c)** 18.6% excess air
94	**(b)** 46% excess air
96	10.7% CO_2
98	3.72×10^5 mol air
100	**(a)** 0.62 mol C/mol H

CHAPTER 5

Problem	Selected Answers
2	**(c)** 76.98 mL
4	111.3 m^3/h air
6	**(c)** **(i)** 1415 kg/m^3
8	0.0064 m^3/mol
10	**(a)** 249 kg N_2
12	**(b)** 24 inches of H_2O
14	165 m/s
16	3.9 g/mol
18	**(b)** 7.9
20	**(c)** 2.3% error
22	0.87
24	1.52
28	**(a)** 2440 ft^3/hr
30	**(a)** $y_B = 0.749$ at 1 P.M.
32	**(c)** 12.3 m/s^2
34	**(d)** 1.15 kg/m^3
36	**(b)** 1.078 mL exhaled/mL inhaled
38	**(a)** 0.525 L H_2O lost/day
40	111.3 m^3/h air
42	**(b)** 0.55 L/min
44	4.0×10^4 m^3(STP)/h
48	**(b)** 50% NO conversion
50	**(c)** 9.2×10^5 angstroms
52	**(a)** $0 \le x \le 1$
54	**(a)** 27.3 atm
56	**(b)** 196 kg Ac/h
58	Specification is wrong.
60	**(c)** 0.03832 atm
62	**(b)** Wet basis: 720 ppm SO_2
64	**(a)** 0.762 L
66	**(a)** $x = 390$ m^3 air/100 kg ore required
68	**(c)** $b = 7367$ K
70	**(a)** $\dot{V}_{rec} = 1860$ SCMH
72	**(d)** 3.65×10^4 kg/h
74	**(b)** $\dot{V}_{actual} = 354$ m^3/h
76	**(a)** $n = 5.28 \times 10^6$ lb-mol gas
78	**(a)** $c_3 = 50.0$ atm
80	$T_{ideal} = 435.0$ K
82	**(b)** m_{CO_2}(added) = 3.63 kg
86	**(b)** 83.1 kg/m^3
88	0.246 m^3/h
92	**(c)** Need at least five stages
94	**(b)** 34,900 gal
96	0.041 m^3
98	126 ft^3/min
100	10.6 cm
102	37.3 atm
104	**(a)** 7.44 bar

CHAPTER 6

Problem	Selected Answers
2	**(a)** 269 mm Hg
4	**(b)** slope = −7076 kJ/mol
6	**(a)** 599 mm Hg
8	**(a)** 2 intensive variables
10	**(a)** 38.1°C
12	$h_p = 61\%$
14	**(c)** 2.00 atm
16	**(a)** 383 mm Hg
18	0.0166 kg steam/min
20	**(c)** 49%
22	**(a)** 1.31 lb_m toluene
24	**(a)** 14.5 SCMM
26	26.3 mL H_2O exhaled
28	0.265 kg/hr
30	15.3°C
32	**(d)** 4836 mm Hg

Problem	Selected Answers
34	**(b)** 1.56×10^4 m^3/min
36	**(b)** 90%
38	30.2% excess air
40	49% C_3H_8
42	**(a)** 0.222 mol gas/mol liq fed
44	**(a)** 18.4%
46	**(a)** Raoult's - water, Henry's - N_2
48	378.5 atm
50	**(c)** 5.8 ml M/ml SW
52	**(e)** 1.3%
54	**(c)** 0.958 mol dry air/mol
56	0.0406 mol B/mol
58	**(a)** $P = 7300$ mm Hg at first vapor bubble
60	**(a)** $T_{bp} = 80.5$°C
62	**(c)** 3.62 mol C_4H_{10}/s
64	**(b)** 0.96 kmol B/kmol
66	**(a)** Temperature will decrease
68	**(a)** 13% B
70	**(b)** $x_B = 0.323$, $y_B = 0.615$
72	**(b)** $x_A = 0.47$ mol A/mol
74	116.3°C
76	**(c)** 0.73 torr
78	**(a)** 4.5 ft^3 W/day
80	32.3%
82	**(b)** 114 g A(s)
84	0.429 lb_m crystals/lb_m solution
86	1.51×10^6 L/hr
88	**(b)** 62.2%
90	**(b)** 4.475×10^4 lb_m H_2O/h
92	$T_m = 1.9$°C
94	6.38 kJ/mol
96	5.45 kg xylene
98	**(a)** 1.30×10^4 kg H
100	**(b)** 0.394 kg P/kg
102	4200 g in MIBK-rich phase
104	**(b)** 1.82
106	**(a)** 33.1 g silica gel
108	**(b)** 68 min

CHAPTER 7

Problem	Selected Answers
2	**(a)** 715 Btu
4	**(c)** 431 MW
6	**(a)** 113 J/s
8	**(a)** 23.5 ft/s
10	3.43×10^6 kW·hr/wk
12	**(b)** −765 J
14	**(b)** 2338.72 J/mol
16	**(b)** 9.0×10^3 cal
18	**(a)** 480 K
20	**(b)** $\Delta\dot{H} = \dot{Q}$
22	246 L/s
24	477 m/s
26	**(b)** 1.04 kW
28	**(a)** 711.5 kg/h
30	10.1 GW (LFGTE)
32	**(a)** 5.47×10^3 kW
34	**(a)** 300 kJ/h
36	**(a)** 140 kg/h
38	**(a)** 13 s/discharge
40	**(c)** 39.8 bar
42	**(c)** 337°C
44	**(a)** 587 kJ/h
46	**(a)** 1.82×10^4 cal
48	**(b)** 20 g
50	38 g ice
52	**(a)** 0.53 g
54	37.5 g
56	**(b)** 2.54 cm
58	**(b)** 37 L/s
60	**(a)** 290 ft
62	**(a)** 289.7 m
64	**(a)** 3.23 m

CHAPTER 8

Problem	Selected Answers
2	**(b)** 6750 J/mol
4	**(a)** 0.1618 kJ/mol·C
6	**(b)** −594 kJ/kg
8	$6.890 + 0.001436T$
10	**(a)** 169°F
12	**(b)** 0.223 kJ/mol·K
14	**(c)** Total cost = $4.72
16	**(a)** −2156 kW
20	2062 Btu/hr
22	3378 kJ
24	433 kJ/kg
26	**(a)** 1.447×10^6 Btu/h
28	66 lb_m ice consumed
30	**(b)** 117 kJ
32	**(b)** 52.6 kW
34	**(b)** 79.7%
36	1.39×10^6 J/day
38	**(b)** −294 kW
40	**(b)** 341 kW
42	**(b)** −1730 cal/g

Problem	Selected Answers
44	**(a)** 50.10 kJ/mol
46	**(b)** $h_r = 2.8\%$
48	**(a)** 45.0 min
50	**(c)** 100 s
52	100 kJ/mol
54	**(a)** 49.3°C
56	**(f)** −12.6 kW
58	**(a)** 96.5%
60	**(b)** 257 kW
62	**(a)** 2.42×10^4 kW
64	**(d)** 552°C when $T_f = 36$°C
66	**(b)** 25.5% of river flow diverted to plant
68	**(d)** 4070 kg steam/h
70	**(a)** 4417 kg fresh water/hr
72	**(a)** (i) $SG_{liq} = 0.600$
74	**(c)** 21.6°C
76	**(c)** 2280 kg/h
78	**(c)** 935 kW
80	**(b)** 4667 mm Hg
82	**(b)** 78°F
84	65%
86	**(a)** 10 kg water/min
88	**(b)** 68%
90	**(a)** 0.0059 kg water/kg DA
92	**(b)** 67 m^3
94	**(a)** 0.0083 kg water/kg DA
96	**(b)** 986 kJ transferred from reactor
98	60.9 kJ/mol H_2SO_4
100	**(b)** −471 kJ/L
102	**(a)** −52°C
104	**(a)** 6.49 kmol/h
106	**(b)** 112°C
108	**(b)** −2°C
110	**(a)** 1140 mL water
112	**(a)** 88.3 Btu/lb_m
114	Vapor has 140 g NH_3, 35g H_2O

CHAPTER 9

Problem	Selected Answers
2	**(d)** 57 kJ/mol
4	**(b)** 52.0 kJ
6	**(a)** −17,700 Btu
8	**(b)** −35 kW
10	**(b)** −4.3%
12	**(c)** $Q = -3.68$ kJ
14	**(d)** 4.98×10^6 Btu/ton Fe
16	**(a)** 75% decomposed
18	**(b)** 1.62 kg/hr
20	**(c)** 11.86 kJ
22	**(b)** $g = 1.26787$
24	**(a)** 1.3 kJ
26	**(c)** 5.15 gal H_2O/min
28	**(a)** 2.7×10^6 kJ
30	**(a)** 1724 kPa
32	**(b)** 6.67 lb-moles/hr
34	**(d)** 1892 kg steam/hr
36	**(b)** 10,200 kJ transferred to reactor
38	**(a)** 80.1% conversion
40	0.652 mol CO converted/mol fed
44	**(b)** Endothermic
46	-4.42×10^6 kJ
48	**(b)** −14.2 kJ
50	**(a)** −859.81 kJ/mol
52	**(b)** 43°C
54	−86,995 kJ/h
56	**(b)** (i) 240.0 kmol O_2 fed
58	**(b)** 1.01×10^{-6} kg SO_2/kJ
60	**(b)** 986 kJ transferred from reactor
62	**(a)** −23,300 Btu/lb_m
64	**(a)** -5.85×10^4 kW
66	**(b)** 50% excess air
68	**(c)** −655 kW
70	**(c)** 37.3%
72	**(c)** 150°C
74	**(b)** 2317 K
76	**(a)** 4414°C
78	**(b)** 34.5 atm
80	71.41% CO conversion
82	**(d)** 176 kW

CHAPTER 10

Problem	Selected Answers
2	**(c)** 47.1 min
4	**(d)** 0.30 lb-mole O_2
6	**(a)** 11.5 h
8	**(a)** 200 L
10	**(b)** concave up
12	**(c)** 2.83 hr
14	**(a)** 200 kg
16	**(b)** 17.2 hr
18	**(a)** 0.1038 lb-mole
20	**(d)** 25 hr
22	**(c)** $k_2 = 0.115$ L/mol
24	**(c)** 2.7 h
26	**(b)** 2.53 g/s
28	**(b)** 25°C
30	**(a)** 5.1 min
32	**(a)** 33.3 kW
34	**(a)** $C_{S1} = 3$ g/L
36	**(a)** $a = 1 + b$

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